The Era of Carbon Allotropes

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Chemical functionalization of new carbon allotropes is of fundamental interest and opens the door to unprecedented materials applications. In principle, the physical and chemical properties of fullerenes, carbon nanotubes (CNTs) and graphene are related to each other, although their levels of development vary considerably. In order to efficiently explore the reactivity of the less developed CNTs and especially that of graphene it is our goal to provide a unifying approach for the chemistry of all three new carbon allotropes. The fullerenes present the first family of synthetic carbon allotropes. Since their availability in macroscopic quantities numerous investigations with respect to their physical characterization and chemical functionalization have been carried out. CNTs - the second new family of C-allotropes - exhibit at least the same potential for unprecedented applications. Their chemistry, however, is much less developed. Although many protocols for covalent and non-covalent CNT functionalization have been published there are still many fundamental problems to be solved. This includes *inter alia* the highly selective functionalization of metallic- or semiconducting SWNTs, the high throughput isolation of SWNTs with single helicity, the development of general concepts allowing for tunable doping of individualized tubes with single helicity or least defined transport characteristics (metallic – semiconductive). Finally, the youngest representative in the list of new C-allotropes is graphene and the exploration of its chemistry has just begun to start. So far only investigation on the functionalization of defect rich graphene oxide (GO) but not intact graphene itself have been published. Compared to the various flavours of CNTs (broad variation of helicities, single walled, multi walled) graphene is a much more uniform material. This will facilitate the development of its chemistry considerably. We will present a series of new results of covalent and non-covalent functionalizations of fullerenes, carbon nanotubes and graphene.

Fundamentals of EM Techniques - New Possibilities with Aberration Corrected Electron Microscopy

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The microscope is one of the oldest tools used by scientists to extend the reach of their senses. Self evidently the world around us, both natural and synthetic, is made up of atoms, a microscope capable of showing us which atoms are where, arguably, gives a complete characterisation of that world. The electron microscope was, until the middle of the 1990's, hampered by the poor quality of charged particle lenses. 15 years of spherical (and latterly chromatic) aberration correction has since given a crucial factor-of-two improvement in resolution so that routine atom by atom characterisation of materials is now possible. In particular, the study of carbon based materials such as nano-tubes and graphene has been at the forefront of applications of this new technology. In this tutorial an overview of the capabilities of aberration correction will be given together with applications with an emphasis on *scanning* transmission electron microscopy (STEM).

Computational Modelling of Carbon Nanostructures from First Principles: How to Use Computers to Understand and Design Nanomaterials

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Carbon is a wonder element which underpins life on our planet, represents currently the vast majority of our energy resources, and is arguably the building block of nanotechnology. The past decades have witnessed an explosion of interest in carbon nanomaterials, largely driven by exceptional experimental advances in nanoscale synthesis and characterization. As a result today we know how to produce, control, and modify a variety of carbon allotropes of any dimensionality, from zero-dimensional diamondoids to three-dimensional amorphous carbon. As more complex materials are being discovered and developed, computational materials modelling at the atomic scale is acquiring an increasingly important role in rationalizing experimental observations and exploring new properties and functions. In this tutorial we will provide an outlook of state-of-the-art computational modelling techniques, with a particular emphasis on first-principles quantum-mechanical methods and their application to carbon nanomaterials research. The tutorial is organized in three parts: Background, Understanding, and Design. In the Background part we will present a primer in modelling techniques based on density-functional theory, trying to emphasize the strengths and the limitations of these methods. In the Understanding part we will discuss a few success stories where computational modelling of experimental spectroscopies such as Raman or ARPES has been key to unravelling the electronic and the optical properties of novel carbon materials such as graphene. In the Design part of the tutorial we will describe how first-principles materials modelling is currently expanding towards the simulation of novel hypothetical materials yet to be synthesized. In this context we will discuss materials where modelling was ahead of experimental research, such as for instance graphane, the fully-hydrogenated version of graphene. We will conclude the tutorial by briefly reviewing some of our recent computational work aimed at answering the following fascinating question: can we design and synthesize superconducting carbon nanomaterials having technologically relevant transition temperatures?

Technology Roadmap of Carbon Nanomaterials

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Since the discovery of carbon nanotubes (CNTs) in 1991, tremendous efforts have been made to commercialize CNT technologies, but only a few applications have been realized so far after ~20 years. Recently the graphene materials have inherited the fame of CNTs, but there is still a long way to go toward the practical applications. However, it is too early to be disappointed because it usually takes 20 years or more for any new materials to make a commercial impact. In fact, it took more than 15 years for carbon fibers to be widely used in commercial aircrafts. However, we shouldn't be too optimistic, and the researchers have to take a responsibility of investigating the bright and the dark sides of the carbon nanomaterials carefully and realistically. In addition, a technology roadmap or a guideline needs to be provided to the public people who are interested in carbon nanomaterials. Thus, in this tutorial, I would like to discuss the following issues: i) Recent trends in carbon nanomaterials researches and developments, ii) Comparison with other competing materials, iii) Short/mid/long-term roadmaps for carbon nanomaterials industry, and iv) carbon nanomaterials-related health and environmental issues.

The atomistics of nanotubes and graphene growth - Can we win in carbon Tetris?

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Physical principles augmented by ever-advancing computation technology have become an essential tool for exploring materials and processes. I will first discuss how the concept of dislocations, well-established in physics of crystals, helped solving several puzzles in nanomechanics of carbon filaments, and—if further adopted—the theory of their *catalytic growth*, including the accompanying observed rotation. Nucleation of tubes, treated as an outcome of fluctuations in the carbon-metal “primordial soup”, is largely determined by the energy of the carbon-metal interface, similar to the edge of graphene. I will try to relate the chemical conditions at such edge contact with the chances of emerging tube chirality. Further, the analysis of atoms precipitation at the edge of growing sp^2-network—a nanotube or graphene—reveals the competition of correct and faulty docking of the C, C_2, or C_3 units, when the goal to go on without defects resembles strikingly the game of *Tetris*, played at the nanoscale by the Avogadro number of contestants—the individual tubes.

Understanding The Correlation Between The Catalyst Particles and C-SWNT Diameter: A First Step Towards The Chirality Control

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Controlling the nanotube structure during the CVD growth remains a hot challenge. Here, by studying in a systematic way, using ex situ transmission electron microscopy, the structure of the tubes and the particles from which they grow and of their link, we inspect how the nanotube diameter is driven by the particle. We used a specific HFCVD synthesis protocol described in [1] for, first, making possible the direct observation of both the tubes and their seed particles at any stage of the growth without any post synthesis manipulation and, second, for avoiding any particle size evolution during the synthesis. We performed a statistical study on tens to hundreds nano-objects as a function of the synthesis time. At the early stages of the synthesis, two nucleation modes are identified, depending on whether the tube nucleates tangentially or perpendicularly to the surface of the nanoparticle. In the first case called tangential, the tube diameter is directly linked to that of the particle, which is not the case of the second one called perpendicular [2]. These modes account for the different particle-tube configurations and the apparent discrepancy on the tube-particle diameter ratios found in the literature.
With our synthesis conditions, both modes are active on equal footing at short synthesis time, independently of the particle size. Then, a double selectivity occurs on both the particle size and the nucleation mode so that only nuclei tangentially linked to particles with defined diameter give rise to long tubes. Selectivity on the particle size can be explained by a tuning effect of the carbon feeding rate, which is too large for the smallest particles and too low for the largest ones. Tight-binding calculations using the approach developed in [3] have been performed to understand the origin of the nucleation mode selectivity. Results indicate that the tangential mode is the most stable from a thermodynamical point of view [2]. On this basis, we propose that the perpendicular mode is driven by kinetics effects, dominant in the early stages or for high growth rates and that steady state conditions with low growth rates should be looked for experimentally for favoring the tangential mode and achieving a direct control of the nanotube diameter by the particle size. This represents an essential step towards a better control of the structure during the synthesis.

[1] M.-F. Fiawoo et al, *Surf. Science* **603**, 1115 (2009)
[2] M.-F. Fiawoo et al, submitted to *Phys. Rev. Lett.* (2011)
[3] H. Amara et al, *Phys. Rev. Lett.* **100**, 056105 (2008); H. Amara et al, *Phys. Rev. B* **79**, 014109 (2009).

Advances in SWNT Forests: Growth, Characterization, Applications, and a Pilot Plant

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Vertically aligned single-walled carbon nanotubes (SWNT) forests represent an important field in nanotube research. Water-assisted CVD now known as the “super-growth” [1] technique stands as one representative method to grow SWNT forests in a short time. Here, I will present the current status of our and others researches carried out to understand and to control SWNT forest growth, to realize economical and industrial scale mass productions, and to develop new applications. We have found that any combination of growth enhancers and carbon sources following a basic rule can provide highly efficient growth [2]. This feature has provided an interesting opportunity to tailor the nanotube structure [3] and dispersibility in solutions. A chemical map would be presented that ties growth parameters, such as growth yield, purity, and growth lifetime, to the chemical reaction paths of the carbon source and growth enhancers. In addition, I would describe the launch and impact of the first pilot plant of SWNT forest (spec. 100g/hour) that can continuously grow SWNT forests on 50 cm square substrates fed to a furnace [ref patent] by a belt-conveyer.

The SWNTs within the forests possess exceptional properties of high purity, high surface area, long length, and alignment. These properties has opened up new opportunities for CNTs, exemplified by CNT black body absorbers [4], light mechanical beams [5], stretchable conductors [6], high power and density super-capacitors [7], biofuel cells [8],temperature invariant viscoelastic CNT materials [9], and strain sensors [10] for human motion detection. With the launch of the pilot plant of SWNT forest, some of these applications are expected to be realized in real commercial products soon. My perspectives regarding industrialization of SWNTs forests would be presented.

[1] *Science*, **306**, 1362 (2004).
[2] *Nano Lett.*, **8**, 4288 (2008), *Advanced Materials*, 4811 (2009), *Nano Letters*, **9** (2), 769-773 (2009)
[3] *JACS.* **131**, 15992 (2009)
[4] PNAS, **106** (15), 6044-6047 (2009)
[5] *Physical Review Letters*, **102**, 175505 (2009)
[6] *Science*, **321**, 1468(2008), *Nature Materials*, **8** (6), 494-499 (2009),
[7] *Advanced Materials* **22**, E235-E241 (2010), *JACS* **132**, 18017-18019 (2010)
[8] *JACS* **133**, 5129–5134 (2011),
[9] *Science*, **330** (6009), 1364-1368 (2010), [10] Nature Nanotechnology DOI: 10.1038/NNANO.2011.36

Nanotube Synthesis: Nature Of Catalyst Nanoparticles And Nanotube Alignment Revealed By In-Situ Time-Resolved X-Ray Diffraction

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Catalytic chemical vapour deposition (CCVD) has become a method of choice to manufacture carbon nanotubes (CNT), with in particular the synthesis of aligned Multi-Walled (MW) CNT forests. But a comprehensive understanding of the mechanisms for CNT nucleation, growth and alignment is still missing. To study these mechanisms, in-situ time-resolved experiments are required. We have developed specific reactor and furnace allowing us to perform, for the first time, in-situ and time resolved X-Ray Diffraction (XRD) analysis using synchrotron radiation. Such time resolved experiments (resolution~1s) have been made possible thanks to the development of a new generation of bi-dimensional X-ray detectors. The conception and realisation of specific furnace and reactor to perform aligned MWCNT synthesis in the same conditions as in laboratory, with furnace windows compatible with diffraction measurements, were also a technological challenge. After each in-situ XRD study, ex-situ Scanning and Transmission Electron Microscopy observations were performed to check the quality of the MWCNT obtained in this new setup, yielding similar samples to those obtained in a standard furnace. XRD patterns were recorded as a function of time, during nucleation and growth. These pioneer experiments [2] give access to new information concerning (i) the nature of the catalyst nanoparticles and (ii) the evolution of CNT alignment during the growth. Catalyst particles are shown to be crystalline cementite nanoparticles. Such a result has already been reported in ref. [3,4] but with two major differences with respect to those presented here: CVD methods are different (in particular growth temperatures are smaller, input of metallic precursors are different) and results were obtained at a local scale, compared to XRD ones which correspond to a statistical analysis. The occurrence of cementite as catalyst in our CVD process will be discussed based on thermodynamical arguments. An orientation order parameter can be defined from XRD data and its evolution is followed, quantitatively, as a function of time, during nanotube growth. CNT alignment is a key parameter for some applications of nanotubes in composites or membranes but the mechanism for their alignment is still under discussion (role of van der Waals forces, steric hindrance phenomena, etc). Our quantitative results should give some keys towards a better understanding and thus further improvement of CNT alignment.

[1] M. Pinault, V. Pichot, H. Khodja, P. Launois, C. Reynaud and M. Mayne-L'Hermite, *Nano Lett.* **5**, 2394 (2005)
[2] P. Landois, S. Rouzière, M. Pinault, D. Porterat, C. Mocuta, E. Elkaim, M. Mayne-L'Hermite and P. Launois, Proceedings of IWEPNM 2011, in preparation
[3] S. Hofmann et al., *NanoLett.* **7**, 602 (2007)
[4] H. Yoshida et al., *NanoLett.* **8**, 2082 (2008)

Sub-Second Growth of Carbon Nanotube Arrays on Glasses and Their Field Emission Properties

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Direct growth of carbon nanotubes (CNTs) on device substrates by chemical vapour deposition (CVD) is advantageous in controlling their position and structure. The main drawback of this route is difficulty of application to arbitrary substrates due to high CVD temperatures. Extensive efforts have been devoted to CNT growth at low temperatures tolerable for glass substrates but such approach suffers from exponential decrease in the rate of CNT growth and thus the throughput. An opposite approach, i.e. growth of CNTs at high temperatures in short times tolerable for glass substrates [1], is taken here.
CNTs are implemented selectively on the line-patterned Fe(catalyst)/Al_2O_3(buffer)/ metal electrodes by pulse current heating (PCH) CVD under C_2H_2(feedstock)/Ar(balance) gas atmosphere. The glass tolerable growth was enabled by combination of a high reaction temperature ~1000 °C and a short heating time of 0.5 – 1 s. Effects of the nominal thickness of a catalyst metal (Fe) and multiple pre-PCH of the catalytic layer under H_2 atmosphere were investigated by using combinatorial CNT libraries [2,3]. The combinatorial masked deposition method, in which a slit placed above a substrate dilutes a sputtered metal flux, can reproduce various combinations of thicknesses of catalyst and buffer layers on a single substrate. CVD on such a catalyst library then provides a library of CNTs with structures from single-walled (SW) to multi-walled and morphologies from entangled networks to vertically aligned forests. The multiple pre-PCH process generated catalyst nanoparticles on the line-patterned electrodes. It was revealed that selective growth of thin diameter CNTs including SWCNTs is highly promoted on the electrodes with the nominal Fe thickness of 1 nm in subsequent PCH-CVD (growth rate: ~ 5μm/s). A preferable condition to form CNT field emitters could be extracted by the combinatorial evaluation of field emission for the CNT library [4]. CNT arrays consisting of thin diameter CNTs (containing SWCNTs, 5 μm-tall) formed on the line-patterns (0.5 μm in width, 10 μm in pitch) showed excellent properties to be used as electron sources in lighting devices. Additional selectivity of implementation was revealed by PCH-CVD on a conventional alkali-free glass substrate by introducing periodic necks in the line-patterns, which are selectively heated up to an aimed reaction temperature during PCH-CVD. Instant and easy growth of patterned CNT arrays on glasses using neither vacuum pumps nor substrate heaters will provide various applications of CNTs.

[1] S. Noda, K. Sekiguchi, K. Furuichi, Y. Shiratori, and H. Sugime, Tenth international conference on the science and application of nanotubes (Nanotube 2009), Beijing, China, June 22, A-3, (2009).
[2] H. Sugime and S. Noda, *Carbon*, **48**, 2203-2211, (2010).
[3] K. Hasegawa and S. Noda, *ACS Nano,* **5**, 975-984, (2011).
[4] Y. Shiratori and S. Noda, *J. Phys. Chem. C,* **114**, 12938-12947, (2010).

In-situ TEM Observation of the Gasification and Growth of Carbon Nanotubes through Iron Catalysts

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We report the in-situ transmission electron microscope (TEM) observation of the gasification and growth of carbon nanotubes (CNTs) through catalysts [1]. It is found that iron catalysts can consume back the CNTs when pumping out the reaction gas at the growth temperature, and reinitiate the growth while introducing the precursor gas again. The switching between gasification and growth of CNTs can be repeated many times for the same catalyst. To understand the phenomenon, thermogravimetric analysis (TGA) coupled with mass spectroscopy was then used to study the mechanism involved. It turns out that the residue water molecules in the growth chamber of TEM reacts with and takes away carbon atoms of CNTs as carbon monoxide vapour through the catalysts, when the precursor gas is pumped out. On the basis of a VLS mechanism we suggested for the growth of CNT [2], the gasification of CNTs can be well understood via a SLLV (Solid-Liquid-like-Vapor) mechanism. Elucidating this reaction contributes to a better understanding of the water- assisted and oxygen-assisted synthesis of CNT arrays, and provides useful clues on how to extend the lifetime and improve the catalytic activity of the catalysts.

[1] X. F. Feng, S. W. Chee, R. Sharma, K. Liu, X. Xie, Q. Q. Li, S. S. Fan, K. L. Jiang, *Nano Research*, in press, (2011).
[2] K. L. Jiang, C. Feng, K. Liu, S. S. Fan, *Journal of Nanoscience and Nanotechnology*, **7**, 1494-1504, (2007).

Continuous Spinning Of Fibres Of Metallic Single Wall Carbon Nanotubes

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The structure control of carbon nanotubes (CNTs) remains a central issue in rapidly developing field. Of the various morphological parameters of nanotubes, namely, diameter, number of walls, length, and chirality, it is the control of chirality which presents significant challenges as well as opportunities. Synthesis of carbon nanotubes by chemical vapour deposition (CVD) process and its direct assembly into macroscopic entities such as fibres and films is attractive and desirable for a wide range of applications. CVD typically involves the decomposition of gaseous or volatile carbon compounds in the presence of transition metal nanocatalyst (either formed in situ or prior to the reaction) and formation of carbon nanotubes under reaction temperatures often exceeding 1000 °C. However controlled nucleation and growth of nanotubes at high temperatures has been an immense challenge.

We have been studying the CVD process conditions and the effect of heteroatoms on the growth stability of carbon nanotubes in the floating catalyst system. The reaction parameters have a profound effect on the morphology of the synthesised nanotubes. The addition of growth promoter and selection of specific synthesis temperature window is critical to produce small diameter single wall nanotubes and also a narrow set of metallic nanotubes.

Half-Centimeter-Tall Single-Walled Carbon Nanotubes Grown at Low Temperature Regime of the Growth Window

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Rapid, millimeter-tall growth of single-walled carbon nanotubes (SWCNT) in 10 min was realized by adding a small amount of water to C_2H_4/H_2/He during chemical vapor deposition (CVD) [1]. By using our real-time monitoring [2] coupled by combinatorial method for catalysts [3], we found a window for millimeter-tall SWCNTs growing in several minutes using only C_2H_2/Ar without water addition [4]. This time, we systematically studied the effects of catalyst and CVD conditions on growth and termination of SWCNTs and discussed what is necessary for the millimeter-scale SWCNT growth. A gradient thickness profile of Fe was prepared on Al-Si-O layer on a substrate and CVD was carried out on it. The sample was set in a tubular CVD reactor, heated to and kept for 5 min at 700-850 °C in 5 vol% H_2/ 50 ppmv H_2O/ Ar, and then CVD was carried out by switching the gas to 0.05-0.60 vol% C_2H_2/ 50 ppmv H_2O/ Ar under ambient pressure. Samples were monitored in real-time by a digital camera and CVD was continued until growth stopped. SWCNTs grew to 1.4 mm rapidly with a high C_2H_2 concentration at high temperature (18 min, 800 °C, 0.30 vol% C_2H_2) and grew taller to 4.0 mm more slowly with a high C_2H_2 concentration at low temperature (4.5 h, 700 ºC, 0.05 vol% C_2H_2). The effect of temperature and C_2H_2 pressure on growth rate and growth lifetime was investigated. Initial growth rates increased almost linearly with C_2H_2 partial pressure. Growth lifetime decreased with temperature at low C_2H_2 pressures, and it initially increased and then decreased with temperature at high C_2H_2 pressure. Catalyst particles changed their size by Ostwald ripening, evidenced by the increasing sizes of both small and large catalyst particles in conjunction with decreasing size for medium-sized particles in atomic force microscopy (AFM) observations. This coarsening behavior of catalyst particles should largely affect the growth lifetime.

These results show the importance of two mechanisms for the growth termination: carbon by-product formation under excess C_2H_2 supply, and catalyst structural changes at high temperatures. Keeping the C_2H_2 partial pressure not to exceed its upper limit, which increased with increasing temperature, was the key to achieve millimeter-scale SWCNTs. However, Ostwald ripening was enhanced at high temperature. Therefore, there were two options for millimeter-scale growth: slow growth over a long period at low temperature with low C_2H_2 pressure and fast growth over a short period at high temperature with high C_2H_2 pressure. The former option yielded taller SWCNTs and half-centimeter-tall SWCNTs were grown.

[1] K. Hata, et al., *Science* **306**, 1362, (2004).
[2] K. Hasegawa and S. Noda, *Jpn. J. Appl. Phys.* **49**, 085104, (2010).
[3] S. Noda, et al., *Appl. Phys. Lett.* **86**, 173106, (2005).
[4] K. Hasegawa and S. Noda, *ACS Nano* **5**, 975, (2011)

Small-Diameter and Highly Crystalline Double- and Triple-Walled Carbon Nanotubes

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Double walled carbon nanotubes (DWNTs) are considered as an ideal model for studying the interactions and coupling behaviours between different concentric shells in multi-walled carbon nanotubes (MWNTs). The synthesis of high purity and highly crystalline DWNTs allowed us to study novel physics in DWNTs [1]. Specifically, their intrinsic coaxial structures make them mechanically, thermally and structurally more stable than single walled carbon nanotubes (SWNTs). Geometrically, the buffer-like function of the outer tubes in DWNTs allow inner tubes to exhibit exciting transport and optical properties that make them promising in the fabrication of field-effect transistors, stable field emitters and lithium ion batteries. In addition, the utilization of outer tube chemistry makes DWCNTs useful for anchoring semiconducting quantum dots as well as for effective multifunctional fillers in producing tough, conductive transparent polymer films, while the inner tubes with diameter below 0.9 nm preserve their excitonic transitions. More recently, the formation of triple-walled carbon nanotubes (TWNTs) has been the hottest topic in nanotube science and technology, because TWNTs are considered to be the ultimate MWNTs and they are expected to show unique physical and chemical properties. However, the controlled production of uniform, optically active TWNTs has not been reported hitherto. Here, we have demonstrated the ability of synthesizing TWNTs by thermally treating peapods at temperatures of 1500-2400 °C in argon [2]. We have confirmed that the innermost tubes in TWNTs are small in diameter (0.4-1.0 nm), and that they show strong and novel optical signals (e.g., Raman and fluorescent signals). In order to prepare a uniform TWNT sample, we have enlarged the diameters of DWNTs by thermally treating catalytically grown high purity DWNTs at 2400 °C in argon, and such a diameter-enlarged DWNT sample exhibited the optimal diameter distribution for encapsulating fullerenes. We have confirmed that our synthesized TWNTs are uniform and highly crystalline, and also exhibit newly appearing Raman and luminescent signals coming from the innermost tubes that result from the coalescence of fullerenes contained inside the hollow core of DWNTs.

Up to now, the physics of DWNTs and TWNTs have been less explored in nanotube science. Because of their intrinsic complex geometries, DWNTs are able to have the four electronic configurations and TWNTs have the possibility of having the nine electronic configurations. In this talk, the synthesis of high purity and crystalline DWNTs and TWNTs is described and their structural characterizations including optical features are discussed in detail as compared with those of SWNTs.

[1] M. Endo, H. Muramatsu, T. Hayashi, Y. A. Kim, M. Terrones, M. S. Dresselhaus, *Nature* **433**, 476 (2005).

[2] H. Muramatsu, D. Shimamoto, T. Hayashi, Y. A. Kim, M. Endo, M. Terrones, M. S. Dresselhaus, *Adv. Mater.* **23**, 1761–1764 (2011).

Synthesis of Ultra-High-Density Single-Walled Carbon Nanotube Forests

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Single-walled carbon nanotubes (SWNTs) have numerous potential applications. Some applications such as interconnects or thermal interface material require highly dense, vertically aligned nanotube forests. Various groups can grow such forests, [1-3] in which the vertical alignment arises from crowding. However on closer inspection, the forests are only 3-5% space filling and well below the theoretical limiting density. Maximizing the density to 10^{13} cm^{-2} is particularly important for applications such as nanotube interconnects, in order that the nanotube interconnect resistance is as low as that of the copper equivalent. However, the highest density of SWNT forests achieved so far is ~10^{12} cm^{-2} [4,5]. This paper presents a simple method of catalyst design and cold-wall chemical vapour deposition (CVD) that greatly increases the nanotube density.

We have used a modified nanolaminate catalyst design and a cold-wall CVD system to grow the densest SWNT forests. The catalyst consists of three layers of 0.5 nm Al (top), 0.3-0.4nm Fe and 5 nm Al sputtering-coated on Si substrates. Before coating the Fe catalyst, the 5 nm Al layer was pretreated by O_2 plasma to obtain an enhanced diffusion barrier layer of Al_2O_3. This enables the use of a thinner Fe catalyst, which is of great importance for forming ultra dense and fine catalyst nanoparticles during the substrate preheating for as short as a few minutes. Ultra-high-dense SWNT forests were then prepared on these substrates by increasing the C_2H_2 partial pressure to as high as 8%. The SWNT filling fraction reaches 71.7% after capillarity-driven densification. The measured density is over 1×10^{13} cm^{-2}, the highest presently reached.

[1] Y. Murakami, et al., *Chem. Phys. Lett.* **385**, 298 (2004).
[2] K. Hata, et al., *Science* **306**, 1362 (2004).
[3] G. Zhong, et al., *J. Phys. Chem. B* **111**, 1907 (2007).
[4] G. F. Zhong, et al., *Carbon* **44**, 2009 (2006).
[5] D. N. Futaba, et al., *Nature Materials* **5**, 987 (2006).

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Separation Force Spectroscopy of Brush-like Carbon Nanotubes

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Complex morphology and interaction of carbon nanotubes (CNTs) within a brush (vertically aligned CNTs) have always been matters causing confusion among scientists. Wavy structure of CNTs in the brush and difficulties in manipulating them are still big barriers to perform tribological studies on as-grown CNTs. These difficulties resulted in lack of information about interaction force between CNTs in a brush. In this work, we adopted an in situ drawing method for measuring the amount of the force required for separating of CNTs from the as- grown CNT brush. In this method, measurements are performed on pristine brushes without altering the morphological and intrinsic properties of CNTs inside of the brush. A dedicated nano-manipulator inside of the scanning electron microscope (SEM) was used to attach/detach an atomic force microscope to the sidewall of the CNT brush. We could separate as few as 20 CNTs from different location of the brush. Cantilever's deflection was recorded to extract separation force. Morphological changes at the drawing site were captured and then examined precisely to determine the number of CNTs that were being drawn and to correlate force variations to the morphological changes happening at the site. Concurrent availability of separation force and morphological changes made it possible to have a better understanding of the nature of CNTs interaction inside of a brush. We measured separation force on different samples with different levels of spinnability. Measurements revealed that the separation force in spinnable samples, 40 µm far from the top of the sample, can be as low as 3 nN per CNT. When we move to the top, separation force gradually increases. The highest force measured in our samples was 15 nN per CNT at the top of spinnable samples. In contrast to spinnable samples, the amount of separation force in un-spinnable samples is not a variable of separation site distance from the top of the sample. In these samples, separation force is constant and between 9-11 nN per CNT. Comparison of the force between spinnable and un-spinnable samples revealed that the spinnable one benefits from the high separation force at the top of the brush and the low separation force in the middle.

High separation force at the top of spinnable samples comes from high entanglement and waviness at the top. By migrating from the top, alignment of the CNTs increases and separation force decreases as well. In un-spinnable samples, degree of the CNTs' alignment does not show any respectful change all over the sample and that is why separation force is nearly constant and location independent. Based on our observation, formation of permanent inter-bundle links happens everywhere in spinnable samples and not only at the top. In contrast to previous reports, these links also form in un-spinnable samples, but because of wavy nature of these samples, these links cannot withstand high separation forces and disrupt shortly after formation.

Fascination for Nanotubes

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Since the discovery of fullerenes in 1985, much has been done on carbon nanostructures and also those involving other inorganic layered materials. We shall briefly examine some aspects of nanotubes with emphasis on the electronic properties and on selective synthesis of nanotubes with specific properties. In this context, Y-junction nanotubes are of significance. We shall highlight some of the properties of carbon nanotubes, specially the sensitivity of electronic structure to molecular charge transfer and to interaction with metal nano particles. Separation of metallic and semiconductor nanotubes by two new procedures will be discussed. Novel mechanical properties of composites of nanotubes in the presence of other nanocarbons will be indicated. We briefly examine analogues of nanotubes made of a few layered inorganic materials.

Carbon nanotube and graphene contact structure analysis by using cross sectional TEM-EELS

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In our research, we tried to use carbon nanotube (CNT) bundles and multilayer graphene as low-resistivity interconnects for high-performance LSIs. In this study, we grew vertically aligned CNTs on multilayer graphene for 3D interconnects, and analyzed the contact structure between CNTs and multilayer graphene by taking cross-sectional TEM-EELS measurements.
The multilayer graphene was synthesized by thermal chemical vapor deposition (CVD) at 600 °C on Co catalyst metal. After that, CNTs were synthesized on the multilayer graphene by thermal CVD method at 450 °C using Co and Ti catalyst metals [1]. From the cross-sectional TEM-EELS measurements, we clearly observed the catalyst metal particle at the CNT/multilayer graphene interface. We especially found that the Co and Ti migrated into graphene few layers. This result suggests that CNTs were electrically contacted to the multilayer graphene with the metal particle at the interface.

[1] A. Kawabataet al., NT10.

Magnetic Resonance Nanoactuation of As Grown Arrays of Carbon Nanotubes Loaded with Ni Particles

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Suspended carbon nanotubes (CNTs)provide unique capabilities as high frequency mechanical resonators for a number of applications. Although substantial progress has been made in using high frequency CNT resonators, mechanical vibrations of CNT resonators remain very difficult to excite and to detect. The problem of excitation becomes much more complicated for as grown arrays of suspended CNT resonators, which appear to be very attractive because of their potential for ultra-sensitive mass detection. We propose to use ferromagnetic resonance (FMR) actuation of the arrays of CNTs loaded with Ni particles (Ni-CNTs). This contactless actuation method is closely related to the magnetic resonance force microscopy technique [1]and does not require any additional nearby microfabricated electrodes or coils.
The Ni-CNT arrays are grown by chemical vapor deposition from Ni catalyst particles that are attached by electrochemical deposition on the sidewalls of TiN electrodes [2]. The multiwalled CNTs grow underneath the catalyst particles and remain horizontally freestanding and loaded with Ni particles at their tips. The grown Ni-CNTs arrays are composed of highly homogeneous CNTs with uniform lengths (around 600 nm) and almost equal diameters (around 20 nm).The vibrations of Ni-CNTs are actuated by relying on the driving force which appears due to FMR excited at about 2GHz in the Ni particles (diameter around 100 nm).The Ni-CNTs oscillations in the frequency range of 30 to 60 MHz are detected mechanically by atomic force microscopy (AFM) in dynamic mode [3]. The frequency of the magnetic field modulation fixes the driving frequency for the Ni-CNTs, while the microwave power modulation is used for the AFM detection of the Ni-CNTs oscillations and imaging of the envelopes of the Ni-CNTs vibrations. Our new CNT excitation method based on magnetic resonance is advantageous in cases where the traditional electrical actuation methods are not effective or cannot be implemented.

[1] J.A. Sidles, J.L. Garbini, K.J. Bruland, D. Rugar, O. Zuger, S. Hoen, and C.S.Yannoni, *Reviews of Modern Physics*, **67**, 249-265 (1995).
[2] C.A.Santini, D.J.Cott, A.Romo-Negreira, B.D.Capraro,S.R. Sanseverino, S.De Gendt, G.Groeseneken, P.M.Vereecken, *Nanotechnology,* **21**, 245604/1-9 (2010).
[3] A. Volodin, C. Van Haesendonck, R. Tarkiainen, M. Ahlskog, A. Fonseca, and J.B. Nagy, *Applied Physics A*, **72**, S75-S78, 2001; D. Garcia-Sanchez, A.S. Paulo, M.J. Esplandiu, F. Perez-Murano, L. Forro, A. Aguasca, and A. Bachtold, *Phys. Rev. Lett.* **99**, 085501/1-4, 2007.

Carbon Nanotube Based NEMS as Magnetic Force Detector

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Nanoelectromechanical Systems (NEMS) based on carbon nanotubes (CNT) are suitable for many applications, for instance high sensitivity mass detection [1] (~1 zg) or force detection [2] ($<10^{-15}$ N).

Here we studied high quality NEMS based on CVD grown, suspended carbon nanotubes. Actuated by a radio frequency signal from a nearby antenna, our devices achieve quality factors of $Q = 10^5$ at low temperature which is among the highest reported Q factors for CNT based NEMS [3]. We also found evidence for a strong coupling between longitudinal stretching mode phonons and conduction electrons in a suspended double wall CNT quantum dot in a few electron regime. Such high-Q carbon nanotube NEMS could be of great importance when investigating the properties of single molecule magnets [4] (SMM). Induced by the reversal in magnetic fields of such a SMM, grafted to the CNT's sidewall by functional groups, a torque/force will act on the CNT and cause a shift of its resonance frequency. By this technique, one could ultimately determine the hysteresis cycle of a single molecule magnet with a sensitivity approaching 1 μB.

[1] B. Lassagne, D. Garcia-Sanchez, A. Aguasca, and A. Bachtold, *Nano Letters*, **8**, 3735-3738, (2008).
[2] H. Chiu, P. Hung, H. W. Ch. Postma, and M. Bockrath, *Nano Letters*, **8**, 4342-4346, (2008).
[3] G. Steele, A.K. Hüttel, B. Witkamp, M. Poot, H.B. Meerwaldt, L.P Kouwenhoven, H.S.J van der Zant, *Science*, **325**, 1103-1107, (2009).
[4] L. Bogani and W. Wernsdorfer, *Nature Materials*, **7**,179-186, (2008).

Tuning the Band Structure and Optical Properties of Graphene

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The distinctive band structure of graphene, with its massless Dirac fermions, has yielded a wealth of new science and important application directions. While this band structure is optimally suited for some purposes, the ability to modify it in controlled ways and to create a band gap is of obvious interest. In this paper, we show through optical spectroscopy measurements how interlayer interactions significantly change the low-energy band structure in few-layer graphene. In addition to layer thickness, the crystallographic stacking order strongly influences the band structure, as does the application of electrical fields and doping. In particular, the development of a tunable band gap in bilayer graphene and rhombohedrally stacked trilayer graphene will be described.

Photoluminescence due to Exciton Recombination in Metallic Single-Walled Carbon Nanotubes

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In one-dimensional (1D) metallic systems, screening of the Coulomb interaction between an electron and a hole by free electrons is significantly reduced. Recent theoretical [1] and experimental [2, 3] studies suggest that a stable electron-hole bound state, the exciton state, can be realized in metallic single-walled carbon nanotubes (M-SWNTs). Nevertheless, an alternative explanation remains; the resonance behavior observed in the optical spectra is also attributable to van Hove singularities in the 1D density of states. Photoluminescence spectroscopy, which is widely used to reveal the nature of excitons in semiconducting materials, is a powerful technique to test the exciton picture in 1D metallic systems. In this presentation, we experimentally demonstrate that photoluminescence from M-SWNTs is excitonic in nature, by using femtosecond time-resolved luminescence and absorption spectroscopies.

The SWNTs used in this study were formed by the enhanced direct inject process. They had an average diameter ~1.78 nm with a full width at half-maximum of ~0.59 nm. Separation of M-SWNTs and semiconducting SWNTs from the pristine material was carried out using the density gradient ultracentrifugation procedure. The sorted SWNTs are dispersed in an aqueous surfactant. Photoluminescence and its kinetics were measured using femtosecond time-resolved luminescence spectroscopy based on the frequency up-conversion technique [4]. The light source was a mode-locked Ti:sapphire laser (82 MHz, 80 fs, 800 nm), and the spectral range for luminescence measurements was 0.7—1.4 eV. Transient absorption measurements were done using a regenerative amplifier (1 kHz, 120 fs, 800 nm).

We measured luminescence decay kinetics in the1.0-1.4 eV photon energy range in the M-SWNTs sample. Ultrafast decay of the luminescence signal due to the M11 transition of M-SWNTs is observed above 1.1 eV, while no luminescence signal is detected at 1.0 eV or below. The time constants are 40 ± 10 fs for all the decay curves observed at 1.1-1.4 eV. To test whether the recombination process is due to excitons or unbound e-h pairs, we performed transient absorption(pump-probe) measurements. The decay curves show bleaching of the M11 band absorption at the time origin; the bleaching is recovered with the time constant of ~500 fs. This time constant is in good agreement with the decay time corresponding to hot carrier thermalization within the electron system in M-SWNTs [5]. Since this decay time is one order of magnitude longer than the luminescence decay time, we conclude that the ultrafast decay observed by the luminescence measurements is due to recombination dynamics of exactions in M-SWNTs. This finding indicates that the excitons coexist with metallic electrons in the 1D system and can emit photons within ~40 fs. The present work is the first direct observation of luminescence of exciton recombination in metallic systems.

[1] C. D. Spataru et al., *Phys. Rev. Lett.* **92**, 077402 (2004).
[2]. F. Wang et al., *Phys. Rev. Lett.* **99**, 227401 (2007).
[3] Y. Wu et al., *Phys. Rev. Lett.* **99**, 027402 (2007).
[4] T. Koyama et al., *J. Phys. Chem. Lett.* **2**, 127 (2011).
[5] L. Lüer et al., *Phys. Rev. B* **80**, 205411 (2009).

CT13

All Carbon Nanotube Electrochromic Device: Controllable Visible Color Changes in Metallic Single-Wall Carbon Nanotubes

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Electrochromism is the phenomenon of reversible changes in the optical properties of a material during electrochemical redox processes. Typical electrochromic devices rely on transparent electrodes such as indium tin oxide (ITO) glasses to apply a potential to electrochromic materials. However, it is desirable to develop a system without using ITO due to emerging competing demands on rare metal resources. Here we demonstrate that electrochromic devices can be made using metallic single-wall carbon nanotubes (SWCNTs). The color changes can be produced by colorful metallic SWCNTs without ITO layers. The metallic SWCNTs act as electrochromic components, working, counter, and contact electrodes, indicating a route to all carbon nanotube electrochromic devices. We demonstrate very clear, stable and reversible color changes in metallic SWCNTs with diameters of 0.84, 1.0 and 1.4 nm, exhibiting yellow, magenta, and blue-green colors, respectively. The color changes are reversible and repetitive, and a relatively good coloration efficiency $(1.9 \pm 0.2)\times10^2$ $\mathrm{cm^2\ C^{-1}}$ is achieved.[1]

[1] Yanagi et al, *Adv. Mater.* (accepted in 2011).

Vibrational and Optical Excitations of Nanocarbons under External Perturbation

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The properties of materials can be manipulated by external perturbations such as applied fields, external screening and applied stress. These stimuli help in studying the intrinsic properties of nanomaterials and in further tailoring them to our needs. In my talk I will present two examples of external manipulation. I will discuss Raman scattering in uniaxially strained graphene. The observed splitting of the 2D Raman mode is dominated by changes in the phonon dispersion, whereas changes in the electronic band structure play only a minor role contrary to previous suggestions. In the second example I will present the optical and vibrational properties of carbon nanotubes functionalized with nonionic amphiphiles. Adding components to the molecules that switch their conformation allows to tune the optical properties of the functionalized tubes. We also observe a charge transfer between the tubes and the molecules as we prove by luminescence and Raman scattering.

Origin of Strain-Dependent Splitting of the Double-Resonance Raman Scattering Band in Graphene

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The effects of external mechanical perturbations on physical properties of graphene are attracting much attention because of the possible realization of synthetic electromagnetic fields and determinations of its fundamental material parameters. Since electronic structures and phonon dispersion are modified under applied strains, the Raman spectrum—an important diagnostic tool for graphitic systems—will show significant variations. Recent experiments demonstrate that the Raman G band red shifts and splits into two peaks under strain because of symmetry breaking of the doubly degenerate E_{2g} phonons. Furthermore, one can determine the Gruneisen parameter of graphene and identify its crystallographic orientation. Unlike the Raman G band, the scattering process of the Raman 2D band involves electronic states and TO phonons near the K and K' points of the Brillouin zone so that the strain-induced anisotropy of the electronic band structure and the phonon dispersion must manifest themselves in the Raman spectra of strained graphene. Although there have been experimental analyses assuming isotropic TO phonon softening and independent theoretical studies regarding the 2D band of strained graphene, a comprehensive and systematic study considering changes in both electronic and phonon structures is still lacking. Moreover, because several resonant scattering processes contribute to the 2D band, a fundamental question concerning the dominant double-resonance process remains to be resolved.

We present a comprehensive analysis of the changes in electronic energy bands and phonon dispersion of a single-layer graphene under homogeneous uniaxial strains by combining polarized Raman measurements with an analysis based on first-principles calculations and determine the dominant scattering path of the double-resonance Raman scattering process [1]. As the magnitude of the strain increases, the Raman 2D band is split into two peaks, both of which redshift. Moreover, two distinct strains applied along armchair and zigzag crystallographic directions are identified and the frequency shift rate for each split Raman 2D peak is strongly dependent on the strain direction. From theoretical analysis, we demonstrate that the anisotropic TO phonon softening together with distortions of Dirac cones is a dominant factor responsible for the observed effects. Furthermore, the polarization dependence of the relative intensities of the split 2Dband components reveals contributions of different resonant scattering paths, thereby establishing a fundamental understanding of the double-resonance Raman scattering process in graphene.

[1] D. Yoon, Y.-W. Son, H. Cheong, *Physical Review Letters*, **106**, 155502 (2011).

Probing charge transfer between shells of double-walled carbon nanotubes sorted by outer-wall electronic type

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Double-walled carbon nanotubes (DWCNTs) are prime candidates for many applications since they are expected to have improved performance compared to SWCNTs. However, these applications require an understanding of the fundamental properties of DWCNTs. In particular, knowledge of the charge distribution between inner and outer tubes in doped DWCNTs is crucial to future electronic and sensing applications of these materials. Until now the detailed studies of the DWCNTs have been complicated by presence of different electronic types of inner and outer tubes mixed in the samples. Recent advances in density gradient ultracentrifugation, however, have resulted in the isolation of pure DWCNTs having and even more recently to isolation of DWCNT having either metallic or semiconducting outer walls. Such samples are ideal systems for studies into the effect of charge on the inner and outer tubes of DWCNTs.

Here, we present Raman and in situ Raman spectroelectrochemical characterization of sorted chemical vapor deposition grown DWCNTs having either M-outer tube or S-outer tube. The narrow distribution of outer and inner diameters of the sorted DWCNTs allowed straightforward identification and study of semiconducting and metallic tubes for both inner and outer tubes by Raman spectra. Consequently, we were able to follow separately the effects of charge on all four inner/outer tube electronic type combinations.

We show that the electronic type of both inner and outer tubes plays an important role in the doping behavior of DWCNTs. We demonstrated that DWCNT with different combinations of electronic type of inner and outer tubes must be considered as distinct nanostructures with specific properties. Our work also shows that different combinations of inner and outer tubes in a polydisperse mixture of DWCNTs may result in complicated ensemble behavior, which is consequently difficult to analyze. This phenomenon points to the importance of using separated DWCNTs in studies of their properties and encourage the development of techniques to produce DWCNTs enriched according to the four distinct permutations of inner and outer wall electronic type.

Coherent phonon spectroscopy of single wall carbon nanotubes

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Femto second measurement of radial breathing modes (RBM) of single wall carbon nanotubes (SWNTs) by coherent phonon (CP) spectroscopy has revealed an interesting phenomenon that the diameter of a SWNT initially either increases or decreases in the RBM vibration depending on the type, the chirality, and the transition energies of the SWNT [1]. The time-dependent motion of atoms is relevant to electron-phonon (or exciton-phonon) interaction for photo-excited carriers, which is important to understand the fundamental nature of electron-phonon interaction for the excited states of SWNTs and other nano-carbon materials. In this paper, we have calculated CP amplitude of RBM phonon modes for 20 SWNTs whose diameter is between 0.7nm – 1nm in which we reproduced that CP vibration starts either increases or decreases depending on the transition energies and the chirality. Especially, the electron-phonon interaction for hole gives a main contribution for determining the CP amplitude and phases [2]. Comparing with the electronic wave function of the excited states, we have made a map of the CP amplitude as a function of (n,m) and transition energies from which we explain the origin of the initial force. We also discuss on what is a key factor for determining the phase of CP vibration. Further we present the CP spectra of optical phonons (G-band) of graphene and SWNTs and compared with resonance Raman spectra.

[1] G. D. Sanders, C. J. Stanton, J.-H. Kim, K.-J. Yee, Y.-S. Lim, E. H. H´aroz, L. G. Booshehri, J. Kono, and R. Saito, *Phys. Rev. B* **79**, 205434 (2009) and related papers therein.
[2] A. R. T. Nugraha et al, in preparation.

Nanotubes Spin As They Grow During Field Emission

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The key issue for realizing the potential of carbon nanotubes has always been, and still remains, a better control of their growth, especially the selective control of their chirality which is related to their electronic properties.

The growths of individual carbon nanotubes (CNTs) on metallic tips can be observed directly from the nucleation stage till the end of the growth by field emission microscopy (FEM). The most notable fact is that the CNTs often rotate axially during their growth, thus showing a full compatibility with a proposed model of 'screw-dislocation-like' (SDL) mechanism [1]. Detailed analysis shows that we directly observe the insertion of carbon dimers at the CNT base [2] thus causing a rotation of the corresponding field emission pattern.

Once the growth is finished, we characterize our sample with in-situ mechanical studies. The mechanical resonances of these singly clamped nanotubes give us access to the vibration frequency and an estimated Q factor up to 25800 [3]. By plotting the vibration frequency versus the applied voltage, we find that we can tune the mechanical resonances by electric field pulling as already demonstrated for carbon nanotubes [4]. We obtain a very fine aspect ratio with the slope of the first order curve, and estimate the nanotube’s length at 400 nm, in concordance with the growth speed of 0.06 nm/s and the growth duration [2].

[1] Ding F., Harutyunyan A.R., and Yakobson B.I., *Proceedings of the National Academy of Sciences*, **106** 2506–2509 (2009).
[2] Marchand M., Journet C., Guillot D., Benoit J.M., Yakobson B.I., and Purcell S.T., *Nano Letters*, **9** 2961-2966 (2009).
[3] Perisanu S., Vincent P., Ayari A., Choueib M., Purcell S.T., Bechelany M., and Cornu D., *Applied Physics Letters*, **90** 043113 (2007).
[4] Purcell, S.T., Vincent, P., Journet, C., Binh, V.T., *Physical Review Letters*, **89** 276103 (2002).

Gate-Dependent Spin-Orbit Coupling In Multi-Electron Carbon Nanotubes

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Carbon nanotubes are attractive systems for studying quantum effects at low temperature due to their unique electronic properties. The coupling between the orbital motion and the spin of the electron was only recently (experimentally) discovered in a few-carrier quantum dot [1]. The near absence of disorder in the device and the measurements focusing on the few-electron regime led to the question whether coupling between motion and spin can be observed in a many-electron disordered quantum dot.
We present electron transport measurements of a carbon nanotube quantum dot showing that spin-orbit coupling is present in the multi-electron regime, and that the spin-orbit coupling can be deduced even in presence of strong disorder. The gate (electron filling) dependence of the spin-orbit coupling is furthermore compared to predictions based on the Dirac band structure [2].

[1] F. Kuemmeth et al., *Nature* **452**, 448 (2008); *Mat Today* **13**, 18 (2010)
[2] T. Sand Jespersen, K. Grove-Rasmussen et al., *Nat. Phys.* **7**, 348 (2011)

Electrical Transport Properties of Double-wall Carbon Nanotube

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Electronic transport properties of carbon nanotube (CNT) quantum dot (Qds) is strongly dominated by the single electron charging and energy level quantization. Electronic spectroscopy at low temperature provide detailed information on their quantum level structures. Single-wall carbon nanotubes (SWCNTs), which can be viewed as a graphene sheet wrapped into a cylinder, are convenient systems to study these features due to their simple geometries with less spatial imperfection and weak spin-orbit coupling compared to other QD systems. In the Coulomb blockade regime, devices based on SWCNT QDs connected to metallic leads show regular Coulomb blockade patterns, which originate from their electronic structures. Because of the spin degeneracy of two bands near the Fermi points, the stability diagrams of SWCNT QDs exhibit four-electron periodicity of the Coulomb diamond patterns.

Besides SWCNTs, multi-wall carbon nanotubes (MWCNTs) consist of two or more concentric walls. Although transport properties of SWCNT QDs in the Coulomb blockade regime have been well understood, the energy spectra of MWCNT QDs still lack of full understanding. Double wall carbon nanotubes (DWCNTs) with two concentric walls are the simplest MWCNTs and therefore the best candidates to study the electrical transport properties. Depending on the ratio between the unit cell lengths of the two shells, a DWCNT may be either commensurate (c-DWCNT) or incommensurate (i- DWCNT). At low energy, nonzero intershell coupling occur in c-DWCNTs while intershell coupling vanishes in i-DWCNTs.

In this work, we have carried out a systematic electronic transport study of DWCNT QDs at low temperature. Our stability diagrams show only eight-electron periodicity, which means nonzero intershell coupling in our DWCNT QDs. By using Bosonization method [1], we determine the possible schemes for single electron tunneling processes. Furthermore, we extract all the important parameters of DWCNT QDs, namely, electron addition energy (E_{add}), energy level spacing (ε_0), and the intershell coupling strengths. To our knowledge, it is the first time that the intershell coupling strengths are extracted from electron transport spectroscopy measurements. By using the excitation lines, we also determine the full energy shell and half filled QD states.

[1] S. Wang and M. Grifoni, *Phys. Rev. B* **77**, 085431 (2008).

Spin-Transport In Carbon Nanotube Quantum Dots

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Magnetoresistance in carbon nanotube quantum dots contacted to magnetic Permalloy electrodes is observed when the D.C. source-drain bias (VSD) is far greater than the charging energy of the dot (EC) with the ratio of conductance ΔG/GPara≈5%. As VSD is reduced into the coulomb blockade regime an increase in ΔG/GPara is seen in the MR hysteresis loops, as well as a transition into a sweep with more structure in its switching, possibly due to the multi- domain state of the pads being seen at lower VSD. The highest conductance ratio observed was ~70% at a 2mVSD bias. This conductance ratio equates to a spin polarisation of nearly 75% from Julliere's model [1], which suggests the quantum dot is enhancing the magnitude of the magnetoresistance.

[1] M. Julliere, *Physics Letters A*, **54**., 225-226, (1975).

Effects of Chirality and Impurities on the Performance of Carbon Nanotube-Based Piezoresistive Sensors

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Carbon nanotubes (CNTs) offer the potential to overcome many of the limitations of nanoscale mechanical sensing due to their high strain sensitivity and small size. However, the relationship between the structure of a CNT and its strain sensitivity is not well understood making it impossible to take advantage of this potential. In this paper, we will present a quantum mechanics-based model that can be used to predict the strain sensitivity of a carbon nanotube based on it chiral indices (*n*,*m*). Using this model it is possible to identify the types of CNTs that will have the highest strain sensitivities for use in nanomechanical sensor systems.

This framework is extended to capture the behavior of sensors composed of multiple CNTs in a parallel resistor network. Parallel resistor networks of CNTs are often used to reduce the noise in CNT-based sensor systems. This is because increasing the number of CNTs in the sensor increases the number of charge carriers which reduces the flicker noise. The extended theoretical framework is used to predict that a parallel resistor network of 100 randomly selected CNTs will have a gauge factor of 78.5 ± 0.4 which is within the experimental error of the measured gauge factor of 75 ± 5 for such sensors.

In order to maximize the sensitivity of these sensors it is necessary to produce single chirality CNT-based sensors which eliminate the CNTs with low and negative gauge factors from the sensor. In order to do this, ultracentrifugation was used to separate out CNTs from a bulk solution into a solution of 85% pure (6,5) CNTs. Based on the theoretical model presented in this paper, the (6,5) CNTs should have a gauge factor of 57. However, due to the impurities in the sample, the 85% pure (6,5) solution is predicted to have a gauge factor of only -22.3 which within experimental error of the measured gauge factor of -22.7 ± 0.5 for the 85% pure (6,5) CNT sample. This result indicates that impurities can have a large effect on both the sign and the magnitude of the strain sensitivity of the sensor.

Many of these impurities can be removed using the electrical breakdown technique. In this technique, a high voltage is applied across the resistor network which produces a large current in the low resistance CNTs causing them to heat up and burn out. At low strains, this method is used to remove the low resistance impurities in the sensor. At high strains, this method is used to remove the negative gauge factor CNTs from the sensor. Using this technique it is possible to increase the measured gauge factor of the (6,5) CNT sensor from -22.7 ± 0.5 to 34 ± 1. However, this measured gauge factor is still significantly below the predicted gauge factor of 57 for a (6,5) CNT sensor indicating that not all of the impurities have been removed. This result shows that even a small number of impurities in the CNT- based sensor can significantly degrade the sensor’s performance.

Thermoelectric Properties and Environmental Effects in Carbon Nanotube Devices

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Charge transfer doping by atmospheric gas is ubiquitous in carbon nanotube field-effect transistors (FETs) but this important phenomenon is yet poorly understood. This talk will mainly discuss our recent work on the origin and signatures of air-doping in the electrical and thermoelectric properties of nanotube devices.

By using both carbon nanotube and graphene layers as testbeds, we first measured the influence of the chemical nature of the substrate and the impact of different gas exposure on the switching behaviour of both nanoscale and thin-film FETs. Our study reveals that electrochemical charge transfer doping by the water/oxygen redox couple is the underlying mechanism behind most environmental effects in nanodevices. The kinetics of the charge transfer process was monitored using graphene FETs and the results are quantitatively described using the Marcus-Gerischer theory. [1] Here we will present the results and provide solutions to control air-doping in nanotube and graphene devices.

In a second study, N-doping by local potassium (K) deposition was used to prepare a suspended carbon nanotube film having a PN doping profile between two metal contacts. The electrical response of this PN device was studied using laser excitation and temperature gradients. Unexpectedly, the dependence of the photoresponse with the laser position measured before and after doping and for different device geometries indicates that the device response is best described in terms of a thermal mechanism that is independent of the nanotube-metal barrier. Moreover, we show using estimates of the local Seebeck coefficients that a PN junction in a suspended nanotube film behaves as a thermopile. The performances of the novel nanotube thermopile will be presented and compared to state-of-the-art SWNT bolometers. [2]

[1] *Nano Letters*, **11**, 132-135 (2011); this work done in collaboration with P. Lévesque, C. Aguirre, (UdeM) S. S. Shabri, J. Guillemette, T. Szkopek (McGill U.)
[2] *Nano Letters*, **11**, 609-613 (2011) this work was done in collaboration with B. C. St-Antoine and D. Ménard (École Polytechnique).

Trapping Heat in a Conductor: Unusual Light-Induced-Heat Localization in Carbon Nanotube Forests

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Although a material can be thermally conducting and electrically insulating, the reverse is not common: Good conductors of electricity are typically also good conductors of heat. Yet, it is very desirable for some applications, such as thermoelectric devices, to have a situation where electricity is conducted and heat is not. We show that arrays of aligned carbon nanotubes (carbon nanotube forests) provide a possible candidate at high temperatures.

One way to heat a small spot on the surface of a substance is through illuminating it with a collimated beam of light. Although this can be achieved easily for a spot on the surface of an insulating material, it requires significantly higher optical power for a similar spot on a metallic surface, due to efficient dissipation of heat to the surroundings. We found that the situation is drastically different in carbon nanotube forests, although they are known to be good thermal conductors to the point of being investigated for heat sink applications. We observed that a spot on the surface of a millimeter-long nanotube forest can effectively become thermally isolated from the surroundings and heated to temperatures in excess of 2,000 K using a low-power beam of light, while retaining good electrical conductivity. The hot spot exhibits an incandescent glow with a spectrum closely matching that of black-body radiation, while the surrounding areas on the surface of the nanotube forest stay at low temperature and appear dark, making the effect visually extraordinary. We explain this phenomenon based on a very rapid drop in the thermal conductivity of the nanotube forest with an increase in temperature, leading to a positive feedback cycle that thermally isolates an island on the forest surface. As an example application, we performed light-induced thermionic electron emission experiments where a continuous-wave visible laser beam with a diameter in the range of 50-100 µm resulted in a heated spot with the same size on the nanotube forest. We observed an emission current of 100 nA for an optical power as low as 4 mW from a small handheld laser. This is remarkable as conventional light-induced thermionic emitters typically require sophisticated high-power pulsed lasers to be heated to the required temperatures for electron emission. The emission current from our device showed a strong nonlinear increase with laser power and reached 25 µA at 350 mW. This finding has important implications for a wide range of other devices such as solar cells, optical switches, pyroelectric detectors and energy harvesters, thermoelectrics, miniaturized susceptors, and potentially even solar displays.

Designing the interaction between organic chromophores and carbon nanotubes

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Nanostructured allotropic forms of carbon (e.g., nanotubes, graphene, nanoscrolls, nanoonions) are promising active components of light-weight, flexible and resistant functional materials in such application as photoelectrochemical cells, electrochemical sensors, photodetectors and organic light-emitting diodes. Despite their high electrical and thermal conductivity, the lack of solubility and strong absorption in the visible region (350-800 nm) of carbon nanotubes prevents them to be effectively and extensively employed in commercial devices.

In this work, we will present three different strategies to design the interaction between photoactive chromophores and carbon nanotubes, as following. The exohedral covalent approach: we exploited both the carboxylic approach [1,2] the readily accessible 1,3-dipolar cycloaddition of azomethine ylides to introduce functional groups in sp^2-bonded carbon surfaces and to convey additional chemical and physical properties to the starting material. We implemented the use of a controllable, high throughput, environmentally friendly technology to obtain functionalized carbon nanostructures with a considerable improvement in productivity compared to traditional reactors.

The exohedral non-covalent approach: we exploited the interaction between a trisulphonated porphyrin-cyclodextrin conjugated (TPPS3CD) and HiPCO single-walled carbon nanotubes to obtain stable water dispersions and we repeatedly observed the formation of complexes with a fixed stoichiometry suggesting that a selective recognition occurs between TPPS3CD and HiPCO. The endohedral approach: we encapsulated heteroaromatic dyes (i.e., quarter-, quinque-, and sexithiophene) in single-walled carbon nanotubes by vapor-phase technique. We studied the novel peapods by means of steady-state and time-resolved UV-vis spectroscopy, Raman spectroscopy, and HRTEM. All the results point out that we did succeed in the encapsulation processes.

In conclusion, we were able to design three approaches to the synthesis of novel carbon nanostructure-chromophore adducts to be incorporated in functional materials exhibiting improved electro-optical response over the visible spectrum. [3, 4]

[1] M. D'Este, M. De Nardi and E. Menna, *Eur. J. Org. Chem.*, 2517-2522, (2006).

[2] F. Cordella, M. De Nardi, E. Menna, C. Hébert and M. A. Loi, *Carbon*, **47**, 1264-1269, (2009).

[3] M. A. Loi, J. Gao, F. Cordella, P. Blondeau, E. Menna, B. Bartova, C. Hebert, S. Lazar, G. A. Botton, M. Milko and C. Ambrosch-Draxl, *Adv. Mater.*, **22**, 1635-1639, (2010).

[4] J. Gao, P. Blondeau, P. Salice, E. Menna, B. Bártová, C. Hébert, J. Leschner, U. Kaiser, M. Milko, C. Ambrosch-Draxl, M. A. Loi, *Small*, accepted, (2011)

Synthesis and Characterisation of Photoactive Systems Combining Carbon Nanotubes

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Single-Walled Carbon Nanotubes (SWNTs) constitute a relatively new class of material exhibiting exceptional mechanical and electronic properties; they are promising candidates for the realization of composites, electronic devices and sensors, for energy conversion and biomedical applications. Combining carbon nanotubes with photoactive molecules leads to a new generation of donor-acceptor nanohybrids which can be used for the development of photo-switchable devices, memories or carbon-based photovoltaics. However, upon illumination, charge transfer between the nanotube and the grafted dye is not the only possible de-excitation pathway. A second process of major importance is energy transfer (ET) where both an electron and a hole are simultaneously transferred, which is usually a competing effect against charge transfer. For example, the nanotubes/porphyrins-based assemblies are one of the most studied systems,[1] and in these systems, the relaxation mechanism of photo-excited porphyrin is still under discussion in the literature.[2] Upon excitation of the porphyrin, the relaxation can occur following two mechanisms: electron or energy transfers to the nanotube. Their occurrences could both be related to the relative position of the energy levels of the donor and acceptor in their ground and photo-excited states and/or to the chemical nature of the chromophore/nanotube conjugation.

Recently, we reported several examples of SWNTs functionalised with phthalocyanines and/or porphyrins via "click chemistry".[3] The nanotube conjugates were studied for their energy conversion properties: upon illumination these systems give rise to fast charge separations. These results are very promising and further research in this field to obtain practical conversion of light energy into electricity is not only justified but also desirable. Here, we describe the last works performed in our group on photoactive systems combining carbon nanotubes. In particular, we present two original methods to synthesize photoactive polymers on the nanotube sidewalls either by covalent or non-covalent means. The objective of this study is the realisation of nanohybrids possessing new features while retaining the intrinsic properties of the nanotubes.

[1] a) T. Umeyama and H. Imahori, Energy Environ.Sci., **1**, 120-133 (2008); b) V. Sgobba and D. M. Guldi, *Chem.Soc.Rev.*, **38**, 165-184 (2009).

[2] a) S. Campidelli, et al., *J.Am.Chem.Soc.*, **128**, 12544-12552 (2006); b) T. Umeyama, et al., *J.Phys.Chem.C*, **111**, 11484-11493 **(**2007); c) C. Roquelet, et al., *ChemPhysChem*, **11**, 1667-1672 (2010).

[3] a) S. Campidelli, et al. *J.Am.Chem.Soc.*, **130**, 11503-11509 (2008); b) T. Palacin et al, *J.Am.Chem.Soc.*, **131**, 15394-15402 (2009); c) K. H. Le Ho, L. Rivier, B. Jousselme, P. Jégou, A. Filoramo and S. Campidelli, *Chem.Commun.*, **46**, 8731-8733 (2010).

Carbon Nanotubes directly grown on Sharp Neural Microelectrodes Enable Superior Electrochemical and Electrophysiological Performance

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The design of intracortical electrodes has to fulfill many conflicting requirements, and there is ample room for improvement, especially on the materials side. An ideal recording electrode should be as small as possible to reduce perturbation of the local electric field and minimize tissue damage during insertion but, at the same time, should have low impedance to enhance signal quality during recordings. Moreover, for neural stimulation, electrodes should be capable of injecting relatively large currents while minimizing electrode degradation due to Faradaic effects, requirements generally satisfied by increasing the electrode size. Finally, in order to allow long-term operation, the surface of the microelectrodes should be able to facilitate charge transport and minimize tissue reaction. The vast majority of electrodes rely on metals as interface material for recording and stimulation and fall short in satisfying such conflicting requirements. In the past few years, research has been directed to introduce new electrode materials such as iridium oxide [1,2], conductive polymers [3-5], and carbon nanotubes (CNTs) [6-9] and develop methods for creating a new generation of implantable devices which can help overcoming aforementioned problems. A variety of coatings based on carbon nanotube composites have been proposed, but even if CNTs are always present in composition of the electrode material, care must be taken in correlating results as the final properties of the devices strongly depend on the treatments that CNTs have undergone, that is, their chemical functionalization, their interaction with other chemical compounds used, and the electrode coating process. In this paper we compare the electrochemical and electrophysiological performance of coatings made of pure CNTs directly synthetized by chemical vapour deposition on the tip of quartz glass insulated platinum/tungsten microelectrodes for neural recording, with others made of polypyrrole CNT (PPy-CNT) and gold CNT (Au-CNT) composites prepared by electrochemical co-deposition methods on identical devices [10].

The electrochemical characterization clearly demonstrates that pure carbon-coated microelectrodes outperform the other CNT coatings, especially from the point of view of stability and reliability in time. CVD-CNT-coated microelectrodes retain unaltered the same impedance values after 1 year storage or after being used to deliver one million current pulses at their charge injection limit. We report the effect of such high surface area coatings on electrophysiological recordings, with special attention to signal to noise ratio, number of single and multiunit neurons recorded and power spectral density. Latest results on long-term tissue effects in neuro-implants for the different coatings will be discussed.

[1] S.F. Cogan et al. *J. Neurosci. Methods* **137**, 141 (2004).
[2] S. Gawad, *Front. Neuroeng.* **2**, 1 (2010).
[3] X, Cui et al. *J. Biomed. Mater. Res.* **56**, 261 (2001).

[4] X. Cui et al. *Sens. Actuators B* **89**, 92 (2003).
[5] J. Yang et al. *J. Mater. Res.* **21**, 1124 (2006).
[6] K. Wang et al. **6**, 2043 (2006).
[7] E.W. Keefer et al. *Nat. Nanotechnol.* **3**, 434 (2008).
[8] T. Kmecko et al. *Mater. Res. Soc. Symp. Proc.*, **926** (2006).
[9] T. Gabay et. al. *Nanotechnology*, **18**, 035201 (2007).
[10] A. Ansaldo et al. *ACS Nano* **5**, 2206 (2011).

Liquid Phase Exfoliation of Low Dimensional Nanostructures: From Nanotubes and Graphene to Bismuth Telluride

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Many of the nanomaterials that have generated so much interest in recent years are not found as individual nanostructures but as van der Waals bonded aggregates or crystals. For example nanotubes generally exist in cylindrical aggregates known as bundles while graphene sheets are almost always confined to graphitic crystals. While individual nanotubes and graphene sheets have unprecedented mechanical, electrical and thermal properties, the aggregated forms are almost always less interesting. Thus, exfoliation of nanotubes has been well studied for the last decade while exfoliation of graphene has been gaining momentum in the last two years. In this talk I will describe the exfoliation of both nanotubes and graphene using both special solvents and surfactants. Solvent choice for both nanotubes and graphene can be described using standard solubility parameters while DLVO theory can be used to aid the understanding of surfactant exfoliation. Once nanotubes and graphene have been exfoliated they can be processed into functional forms such as fibres, films or composites. For example, we have prepared polymer-nanotube composite fibres with strength ~5 GPa, thin nanotube films with transparency of 75% coupled with sheet resistance of 40 Ohm/sq and graphene- polymer composites which display a doubling in strength and modulus for <1wt% added graphene. We have used the techniques developed in this work to explore the exfoliation of other van der Waals bonded materials. This has lead to the liquid phase exfoliation of layered compounds including MoS_2, WS_2, $MoSe_2$, $MoTe_2$, $TaSe_2$, $NbSe_2$, $NiTe_2$, BN, MnO_2 and Bi_2Te_3. This can be achieved either in solvents or in water using certain surfactants. In all cases, few layer flakes are obtained. Once exfoliated, these materials can be deposited as individual flakes or formed into films or composites. By blending with other dispersed nanomaterials we can form hybrids. For example, MoS_2/nanotube hybrids have electronic conductivity 10 orders of magnitude higher than MoS_2. However, many of the attributes of the MoS_2 remain intact. For example the hybrid retains the high Seebeck coefficient associated with MoS_2. This means that such exfoliation is potentially useful for thermoelectric materials. In addition, these hybrids are also of interest as electrodes in supercapacitors and Li ion batteries. We envisage the combination of high conductivity of the nanotube network and the intrinsic properties of the layered material will be of interest for a wide range of applications.

High-Performance Medium-Scale Integrated Circuits Using Carbon Nanotube Thin-Film Transistors

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Carbon nanotube (CNT) thin-film transistors (TFTs) have attracted growing interest because of their potential for use in the fabrication of high-performance electronic components on flexible and transparent substrates. However, high-speed potential has not been demonstrated in realistic integrated circuits so far because of the difficulty encountered in integrating many high-performance CNT-TFTs with high uniformity; this difficulty is associated with metallic CNT incorporation which compels researchers to use devices with small CNT density and large channel length. In this presentation, we report on the successful implementation of high-speed medium-scale integrated circuits with 108 CNT-TFTs [1] based on CNT growth using a plasma-enhanced chemical vapor deposition (PECVD) technique; this technique allows the preferential growth of CNTs that exhibit semiconducting behavior in the FET current-voltage characteristics.[2]

Owing to the advantage of preferential growth, a normally-off operation with good pinch-off characteristics with an on/off current ratio of 4.2×10^5 was confirmed even for the device with a channel length of 10 μm. A normally-off operation is indispensable for all driver TFTs in the circuits to realize error-free logic operations. The drain on current was as high as 800 μA/mm owing to the high-density CNTs, which is expected to lead to high-speed operations. High uniformity was confirmed in the electrical properties of the devices with small fluctuations of 12% for the drain current and 0.5 V for the threshold voltage, leading to the successful implementation of medium-scale integrated circuits.

A 53-stage ring oscillator consisting of 108 CNT-TFTs demonstrated a switching speed of 0.51 μs/gate. This speed is approximately two orders of magnitude higher than that demonstrated by previous TFT integrated circuits [3], and the integration level is the highest among all the nanocarbon-based devices. The switching speed increased with an increase in the drain current and a decrease in the channel length, indicating the importance of using short-channel devices with high-density CNTs; which has become possible by taking advantage of the preferential growth. The successful demonstration of the operation of a ring oscillator with more than 100 transistors confirms the suitability of the present TFT technology for implementing CNT-TFT integrated circuits with various functions.

[1] T. Mizutani, Y. Okigawa, Y. Ono, S. Kishimoto, and Y. Ohno: *Appl. Phys. Express*, **3**, 115101 (2010).
[2] H. Ohnaka, Y. Kojima, S. Kishimoto, Y. Ohno, and T. Mizutani: *Jpn. J. Appl. Phys.*,**45**, 5485 (2006).
[3] M. Ha, Y. Xia, A. A. Green, W. Zhang, M. J. Renn, C. H. Kim, M. C. Hersam, and C. D. Frisbie: *ACS Nano*, **4**, 4388 (2010).

Label-free Electrical Detection of Few Copies of DNA Based on Electrochemically Functionalized Single Wall Carbon Nanotubes

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The detection of specific nucleic acids is highly important for the diagnostics of infectious and genetic diseases, food control and forensics. Commonly used techniques (quantitative polymerase chain reaction (qPCR) and microarray) have a number of disadvantages such as long duration of tests due to multiple DNA amplification steps, bulky optical reading instrumentation, necessity of labelling etc. These aspects make it difficult to implement existing techniques in so called lab-on-a-chip systems, which can be used for point-of-care diagnostics. Due to their high surface-to-volume ratio single wall carbon nanotubes (CNTs) are considered as promising materials for their role as transducers in electrical biosensors. The electronic properties of CNTs are very sensitive to their environment. Even very small amounts of analyte molecules in the vicinity of nanotubes can be efficiently detected. Utilizing this high sensitivity, we present here a CNT-based label-free on-chip DNA detection strategy that does not require PCR.

Our nanobiosensor comprises of CNTs that are trapped dielectrophoretically between platinum electrodes pre-fabricated on a Si/SiO2 substrate. The electrodes were passivated in order to avoid background current caused by electrolytes in the analyte solution. Subsequently, using a two-step procedure, the CNT surface is modified with probe oligonucleotides that are complementary to the target sequence. For the detection of the changes in the electrical signal upon DNA hybridization on the CNT surface, we measured the nanotube impedance at different gate voltages (-0.4 to 0.2V). The analyte solution is poured into a microwell cut in PDMS placed on the device substrate. An Ag/AgCl reference electrode was used to apply the gate voltage. The measurements were taken in 10mM phosphate buffer (pH 7) containing 100 mM NaCl. The melting of the double stranded DNA and the sensor recovery were performed by washing the well with a hot (80 °C) water.

A strong threshold voltage shift (around 120 mV) at certain frequencies was observed after introducing 100 fM of complementary DNA solution. This effect is reversible, highly specific and concentration-dependent, with detection limit of 100 aM. The sensing of specific DNA with our devices is also possible in a heterogeneous environment. 200 aM of complementary DNA comprising just 2% of the total DNA concentration in a solution of 3 different oligonucleotide sequences (9fM in total) caused a significant threshold shift (65 mV) compared to the same DNA mixture without the target sequence (12mV).

In conclusion, we have demonstrated the direct electrical detection of few thousand copies of target oligonucleotide sequences from a small sample droplet (30 µL) with the help of a compact and a durable CNT-based biosensor. The fabrication protocol was developed in a way that most of the steps can be automated and up-scaled, showing promise for future diagnostic applications.

Development of Carbon Nanocapsules for Therapy and Ultrasensitive Imaging

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The use of carbon nanotubes in the biomedical field is receiving an increased attention. One added advantage of using CNTs is that their inner cavity can be loaded with a given payload of medical interest for in vivo imaging or therapy, and additionally, their sidewalls can be functionalised and chemically derivatised to make them dispersible, biocompatible and even for targeting purposes.

A key step towards the characterisation and application of filled CNTs is the complete removal of the large amount of unwanted external material present after the filling step, whilst preserving the encapsulated payload. An absence of species outside the CNTs will reduce the side effects during targeting. We have developed two complementary methodologies for the containment of materials inside single-walled carbon nanotubes (SWCNTs), namely by closing their ends by thermal annealing [1] and by using fullerenes as corks [2]. These nanocapsules (filled and sealed SWCNTs) can then be readily purified by stirring the sample in a suitable solvent.

In the context of drug delivery systems we have investigated methods that, for instance, allow a controlled discharge of the encapsulated payload by lowering the pH of the media. Here, we demonstrate the use of acid-sensitive functionalized fullerenes as removable ‘‘corks’’ for the containment and controlled release of the cargo contained within SWCNTs by lowering of the pH in aqueous media [3]. It is well known that the pH of primary tumours and regions of inflammation and infection is lower than physiological.

We will also present recent results on the development of“hot” filled SWCNTs for in vivo radioemitter localization and imaging [4]. The nanocapsules were prepared by first filling the SWCNTs with Na125I, followed by their sidewall functionalisation with carbohydrates. Short SWCNTs were employed in this study to further improve the biocompatibility of the materials. Effectively, the nanocapsules guaranteed essentially zero leakage of the radionuclide and remained stable in vivo for extended periods. The sealing of iodide within single-walled carbon nanotubes enabled its biodistribution to be completely redirected from tissue with innate affinity (thyroid) to lung. Surface functionalization of these nanocapsules offers versatility towards modulation of biodistribution of the radioemitting crystals in a manner determined by the capsule that delivers them.

[1] L. Shao, G. Tobias, Y. Huh, M. L. H. Green. *Carbon*, **44**, 2855-2858, (2006).

[2] L. Shao, T.-W. Lin, G. Tobias, M. L. H. Green. *Chem. Comm.*, 2164-2166, (2008).
[3] P. Luksirikul, B. Ballesteros, G. Tobias, M.G. Moloney, M.L.H. Green, *Carbon*,**48**, 1912-1917, (2010).
[4] S.Y. Hong, G. Tobias, K. T. Al-Jamal, B. Ballesteros, H. Ali-Boucetta, S. Lozano-Perez, P.D. Nellist, R.B. Sim, C. Finucane, S.J. Mather, M.L.H. Green, K. Kostarelos, B.G. Davis. *Nature Materials*, **9**, 485-490, (2010). (Highlighted in: “News and Views” *Nature Materials*, **9**, 467-468, (2010); *Nature Chemistry*, **2**, 604, (2010)).

Separation of Single-Wall Carbon Nanotubes using Gel Chromatography

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Production of mixed structured single-wall carbon nanotubes (SWCNTs) is one of the most serious problems towards their electronic device applications. Density gradient ultracentrifugation (DGU) first realized large scale metal/semiconductor (M/S) separation [1]. After that, stimulated by the success of the DGU, M/S separation using agarose gel was developed as a lower cost method [2-4]. Interestingly, it was shown that Sephacryl gel can also be used for M/S separation medium as well as agarose [5]. After the intensive research on the separation using Sephacryl gel, single-chirality separation of SWCNTs was realized [6]. We overlook the separation methods developed to date, where we can find some similarities and differences between them. We think the large scale single-chirality separation is a tentative goal of separation method. However, now we need supporting technologies such as high efficiency dispersion method without inducing defects and perfect removal of surfactant molecules after the separation. In this presentation, we would like to summarize previous separation methods including ours and try to show perspectives.

[1] M.S. Arnold et al, *Nat. Nanotechnol.* **1**, 60 (2006).
[2] T. Tanaka et al., *Appl. Phys. Express* **1**, 114001 (2008).
[3] T. Tanaka et al., *Nano Lett.* **9**, 1497 (2009).
[4] T. Tanaka et al., *Appl. Phys. Express*, **2**, 125002 (2009).
[5] K. Moshammer et al., *Nano Res.* **2**, 599 (2009).
[6] H. Liu et al. *Nat. Commun.*, accepted

Assembly, Characterization and Applications of Chirality-Sorted Carbon Nanotube Device Arrays

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In order to fully realize the potential of single-walled carbon nanotubes (SWCNT) for electronics-based applications, it is essential to overcome the polydispersity problem. Integrated circuits or sensor/resonator arrays should ideally consist of SWCNTs of the same chirality or electronic type. Such selective integration should also be scalable to large integration densities.[1] Here, we demonstrate how this can be achieved by a combination of solution-phase sorting and directed assembly by Dielectrophoresis (DEP). SWCNTs are sorted into metallic and semiconducting species with 99% purity, using density-gradient ultracentrifugation, [2] and to individual chirality using targeted polymer wrapping with purity up to 80%, [3] resulting in solutions of SWCNTs in water and toluene respectively. DEP is used to deposit device arrays out of these sorted solutions, and characterized by Raman and PLE spectroscopy, electronic-transport and voltage-contrast SEM to confirm the chirality-sorted arrays.[4, 5] DEP is scalable to ultra-large-scale integration densities. Devices can be assembled at any arbitrary location or orientations simultaneously.[6]

In order to establish the importance of sorted SWCNTs in applications, we also demonstrate that hydrogen sensing with SWCNT devices is strongly dependent on nanotube chirality, with an optimum band-gap of 1 eV for highest sensitivity and fastest response. [7]

[1] McEuen P L *Physics World* **13** 31-6 (2000).
[2] Arnold M S, Green A A, Hulvat J F, Stupp S I and Hersam M C *Nat. Nanotechnol.* **1** 60-5 (2006).
[3] Hennrich F, Lebedkin S and Kappes M M *Physica Status Solidi (B)* **245** 1951-3 (2008).
[4] Vijayaraghavan A, Hennrich F, Stürzl N, Engel M, Ganzhorn M, Oron-Carl M, Marquardt C W, Dehm S, Lebedkin S, Kappes M M and Krupke R *ACS Nano* **4** 2748-54 (2010).
[5] Ganzhorn M, Vijayaraghavan A, Green A A, Dehm S, Voigt A, Rapp M, Hersam M C and Krupke R *Adv. Mater.* Early View (2011).
[6] Vijayaraghavan A, Blatt S, Weissenberger D, Oron-Carl M, Hennrich F, Gerthsen D, Hahn H and Krupke R *Nano Lett.* **7** 1556-60 (2007).
[7] Ganzhorn M, Vijayaraghavan A, Dehm S, Hennrich F, Green A A, Fichtner M, Voigt A, Rapp M, Lohneysen H v, Hersam M C, Kappes M M and Krupke R *ACS Nano* Articles ASAP (2011).

A Rational Concept to Recognize Single-Walled Carbon Nanotubes with a Specific Chirality

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A family of single-walled carbon nanotubes (SWNTs), though existing as a mixture of different chiralities, has unique electronic, photophysical, mechanical and thermal properties. Because these properties markedly depend on its own chirality, facile preparation of highly pure SWNT with single chirality becomes one of the most important issues in the current carbon nanotube science and technology. However, any rational materials design enabling to efficiently extract/solubilise pure SWNT with a desired chirality has yet not been demonstrated.
In this paper, we demonstrate, fort the first time, a method for the selective chiral recognition and solubilization of selected (*n*,*m*) SWNTs [1]. The approach is to use new p-conjugated copolymers which have the selective recognition and solubilization abilities of (*n*,*m*) SWNTs with a few specific chirality. The p-conjugated copolymers are polyfluorene-based copolymers carrying achiral and bulky chiral side chains. We have discovered a regulated SWNT chirality recognition/dissolution by changing the copolymer composition ratios due to the SWNT chiral angle recognition by the copolymers. A molecular mechanics simulation partially explained this behavior based on binding energies and close packing.

[1] H. Ozawa, T. Fujigaya, Y. Niidome, N. Hotta,M. Fujiki, N. Nakashima, *J. Am. Chem. Soc.*, **133**, 2651–2657 (2011).

The Toxicology Of Fibre-like Nanomaterials

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Carbon nanotubes are one example of fibre-like or high aspect ratio nanomaterials (HARN).The toxicology of nanotubes and other HARN has received much attention for two reasons. Firstly, industry and governments are keen to understand the risks associated with the use of nanomaterials in order to develop nanotechnology in a safe and sustainable manner, allowing the technology to reach its full potential. Secondly, nanotubes and HARN exhibit characteristics that are similar to pathogenic fibres such as asbestos. These characteristics include the ability to generate a respirable aerosol, a high aspect ratio (length: width >3:1), the potential to be relatively long (greater than 10um) and to be relatively durable and therefore biopersistant. Asbestos exposure is associated with fibrosis (scar tissue formation) and cancer, particularly mesothelioma. Mesothelioma is a tumour that surrounds the lung and is derived from the mesothelial cells that line body cavities. This tumour kills thousands of people per year in the UK alone. In addition, nanotubes are often contaminated with catalyst metals which are also bioreactive due to their ability to partake in redox cycling Fenton chemistry. This presentation will demonstrate how manipulation of the morphology, length and composition influences the biological activity of HARN.

Cell based (in vitro) studies have focused on macrophages (immune cells) due to their role in the clearance of fibres and particles from the respiratory system, as well as their role in driving inflammation and disease. Long straight multiwalled carbon nanotubes (MWCNT) resulted in incomplete uptake by the macrophages (frustrated phagocytosis) associated with the production of damaging reactive oxygen species (superoxide anions) and pro-inflammatory cytokine proteins (tumour necrosis factor alpha). Treatment of the cells with entangled or shorter nanotubes resulted in no significant impact on the macrophages and the particles were readily ingested. Subsequent studies in mice have demonstrated the ability of long straight nanotubes to induce inflammation as well as changes in the number of the cells associated with influx of inflammatory cells and fibrosis. This response was comparable to a pathogenic form of asbestos but was not observed with entangled nanotubes.

This data therefore shows that long straight fibre-like HARN are more pathogenic than shorter or entangled samples, when tested in cellular and animal models, therefore indicating that the characteristics of HARN are important in determining their toxicity.

Graphene-based Materials: lessons at the interface

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Graphene-based materials are promising due to their electronic and thermal transport, mechanical properties, high specific surface area, that they can act as an atom thick layer, barrier, or membrane, and for other reasons. Our micromechanical exfoliation approaches [1,2] conceived of in 1998 yielded multilayer graphene and one paper described in detail how monolayer graphene could be obtained [1]. Two main research areas of our group are: (i) Growth of large area graphene on metal substrates, characterization and physical properties, and studies of devices having graphene as a central component; and (ii) the generation, study, and use of graphene-based platelets (typically derived from graphite oxide) including as dispersed in liquids, and powders derived from such colloids or generated by microwave or thermal treatment of graphite oxide. I will briefly present each pioneering study (composites, thin films, transparent conductive films, electrical energy storage, large area monolayer CVD growth on copper, graphene as a protective coating, others) as well as discuss our on-going research in these areas.

[1] Lu XK, Yu MF, Huang H, and Ruoff RS, *Nanotechnology*, **10**, 269-272 (1999).

[2] Lu XK, Huang H, Nemchuk N, and Ruoff RS, *Applied Physics Letters*, **75**, 193-195 (1999).

Graphene and Carbon Nanotube Hybrid Papers for Electrodes in Li Ion Batteries and Supercapacitors

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Graphene and carbon nanotubes (CNTs) possess exceptional properties, including excellent electronic and thermal conductivities, high specific surface area and large aspect ratio and excellent mechanical properties. These properties make them ideal building block for various nanostructured active materials for energy storage devices, such as Li ion batteries and supercapacitors [1]. A particularly attractive option is to design and develop highly flexible electrodes consisting of both or either of graphene and CNTs as vital components of high performance energy storage systems [2-4]. This work reports the synthesis of highly flexible graphene/CNT hybrid sandwich papers prepared via vacuum filtration of aqueous dispersions containing these carbon nanofillers, and the measurement of their electrochemical properties. It is found that the supercapacitors made from the hybrid papers exhibit much improved performance in terms of specific capacitance and rate capability, compared with the neat graphene paper or CNT bucky paper alone. The hybrid paper with a layered structure presents several important synergies that are responsible for the improvement, including improved electronic conductivity especially through the paper thickness direction by the formation of extensive 3D networks, and enhanced surface area necessary for electrochemical reaction by creating sufficient gaps between the graphene layers. The improvements are highly dependent on the surface chemistry, degree of reduction and the relative compositions of graphene and CNTs.

When metal oxide nanoparticles with a high specific capacity, such as SnO_2, are incorporated into the graphene/CNT hybrid building block, the anode cells for Li ion batteries made from the SnO_2/graphene/CNT hybrid composites showed a remarkable capacity of 635 mAh g^{-1} after 80 charge/discharge cycles at 0.25 A g^{-1}. Combining SnO_2 nanoparticles into the graphene/CNT paper illustrates a synergy of improving both the capacity and cycleability by taking advantage of the extremely high specific capacity of SnO2 nanoparticles (with poor cyclic performance) and the excellent cyclic performance of graphene/CNT paper (with relatively low capacity) [5].

[1] Zhang LL, Zhou R, Zhao XS. *Journal of Materials Chemistry*, **20**, 5983-5992 (2010).
[2] Byon HR, Lee SW, Chen S, Hammond PT, Shao-Horn Y. *Carbon*, **49**, 457-467 (2011).
[3] Yu DS, Dai LM. *Journal of Physical Chemistry Letters*, **1**, 467-470 (2010).
[4] AbouimraneA, ComptonOC, AmineK, NguyenST. *Journal of Physical Chemistry C*, **114**, 12800-12804 (2010).
[5] Zhang B, Huang ZD, Zheng QB, Yousefi N and Kim JK, *Carbon*, in press.

Noncovalent Functionalization of Carbon Nanostructures: A DFT Investigation of Charge Transfer with Electron Donor-Acceptor Molecules and Protonation by Superacid

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Noncovalent doping of carbon nanostructures by charge transfer from/to donor/acceptor molecules (EDA) or protonation by H_2SO_4, be it with holes or electrons, is usually thought as potentially interesting for many applications of carbon based nano-devices. However, from a theoretical point of view, little is known about such “charge transfer” processes. Employing first-principles method based on Density Functional Theory (DFT), we have studied in details the interaction between a prototypical donor molecule the tetrathiafulvalene (TTF), a standard acceptor organic molecule, tetracyanoethylene (TCNE) and carbon nanostructures: grapheme layer and SWNTs with various chiral indices. Additionally, we have studied the adsorption properties of sulfuric acid molecules. Main results concern structural and thermodynamic aspects including dispersion forces effects, and evidently electronic structure modifications of the nanostructures. At very low coverage values, we have estimated a charge transfer of 0.45e from the graphene to TCNE, a value of 0.12e from TTF to graphene and more interestingly no charge transfer is observed in the H_2SO_4@graphene case. We have found a charge transfer decreasing while the curvature of nanotubes is increasing, and a strong influence of the metallic/semi-conductor character of the SWNTs is obtained. The results of this work could help to understand the charge transfer of carbon nanostructures by means of noncovalent functionalization, which is a promising method for their future applications.

Carbon Nanotube-Incorporated Conductive Composites: Epoxy Matrix Pastes, Stretchable Conductive Films, and Further Applications

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Carbon nanotube-incorporated conductive composites have been of interest for decades due to the excellent mechanical/electrical properties and high aspect ratio of nanotubes. However, poor contact interface hindered a dramatic increase in electrical conductivity for polymer matrix composites. Here we present highly conductive silver/epoxy pastes [1] and stretchable conductive films [2] by using micron-sized silver (Ag) flakes and a small amount of nanotubes functionalized with Ag nanoparticles. The one-dimensional, flexible and conductive nanotubes constructed effective electrical networks among the micron-sized Ag flakes, and the contact interface was improved by the Ag nanoparticles self-assembled on the sidewall of nanotubes. The achieved conductivity of silver/epoxy pastes (2.5×10^5 S/cm) was even higher than those of bulk tungsten, lead and platinum which are commercially used electrical interconnect materials [1]. For the stretchable conductive films, the maximum conductivities were 5710 S/cm at 0 % strain and 20 S/cm at 140 % strain where the film was ruptured [2]. The strategy of hybrid structures could be expanded to synthesize thermoelectric materials for energy conversion, including the thermoelectric power wave concept [3], as well as metallic inks [4] and thermally anisotropic substrates for thermal quenching control [5].

[1] Y. Oh et al, *J. Mater. Chem.*, **20**, 3579 (2010)
[2] K. Chun et al, *Nature Nanotechnology*, **5**, 853 (2010).
[3] W. Choi et al, *Nature Materials*, **9**, 423 (2010).
[4] R. Ma et al, *J. Mater. Chem.*, DOI:10.1039/C1JM10850F
[5] S. Hong et al., *Energy Environ. Sci.*, DOI: 10.1039/C0EE00781A

Boosting Bucky Gel Actuators: Cross-Linked CNTs and Linear Motion

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Bucky gel is a physical gel that is obtained by grounding single-walled carbon nanotubes (SWCNTs) with imidazolium based ionic liquids (ILs) [1]; the gelification is possibly due to a specific interaction between the imidazolium ion component and the π–electronic nanotube surface.

This composite material was used to make bimorph electrochemical actuators where a polymer-supported internal IL electrolyte layer is sandwiched between two bucky gel layers [2]. These actuators were promising because could operate in air (without any liquid electrolyte) showing a good frequency response and high strain, but, due to their electrode configuration could generate only bending motion and were thus strongly limited for applications as artificial muscles. We have introduced a novel actuator capable of both linear and bending motion by designing a three electrode device in which we have added to the two usual active electrodes a metal spring embedded in the solid electrolyte that is used as a passive counter plate.

Moreover, we have successfully cross-linked Super-Growth single walled carbon nanotubes (SGCNTs) and used the resulting material in our actuators [3]. The cross-linking, devised to prevent sliding between tubes, results also in an increase of the specific capacitance of the composite material that dramatically improves the performance of bucky gel actuators in terms of strain and efficiency. The same chemical treatment applied on commercially available SWCNTs, has similar positive effects in improving performance of actuators. Chemical, morphologic and mechanical characterizations of CNTs and composite materials will be reported. Electrochemical characterizations of the composite materials and on actuators devices will be shown. Actuation tests performed applying a square wave of 4 Volt peak-to-peak at frequencies between 0.1 Hz and 100 Hz and blocking force measurements show that cross-linked SGCNTs based actuator has superior response than actuator based on pristine SGCNTs. Finally, we propose a way to model actuation performance in terms of purely material-dependent parameters instead of geometry-dependent ones [4]. Applying the promoted approach, we demonstrate how proper cross-linking treatments on carbon nanotubes endow bucky gel actuators with superior performance. The latest research results on bimorph and linear bucky gel actuators composed of chemically modified CNTs will be given and discussed.

[1] T. Fukushima et al. *Science*, **300**, 2072 (2003).
[2] T. Fukushima et al, *Angew. Chem.* **117**, 2410 (2005).
[3] M. Biso et al., *Carbon*, **49**, 2253 (2011).
[4] L. Ceseraccu et al., *Sensors and Actuators B*, in press doi: 10.1016/j.snb.2011.03.012 (2011).

A Novel 'Seamless Integration' Technology Platform For Dielectric Elastomer Actuators

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Dielectric Elastomer Actuators (DEA) are large strain solid-state actuating systems with unprecedented strains of 100% (and more [1]) while being cost-efficient because of the use of polymer technologies. Due to their simple multi-layered structure, the polymers are potentially easily adaptable to many geometric configurations like micro-valves, artificial muscles (e.g. prosthetics) and active noise / vibration damping [2]. Beyond the use for actuators, the same platform can also be used for polymer sensors, polymer capacitors, printed polymer circuitry and elastomer power generators. However, despite these advantages, multi-layered systems for DEA haven't found wide- spread use in technology up to now. This is mainly due to (i) a very low relative permittivity ε_r of the elastomer dielectrics thus requiring high voltages, and (ii) the lack of a compatible electrode material. Currently, thin metal layers or graphite suspensions are typically used as electrodes, resulting in limited reliability, robustness and lifetime of actuating dielectrics – electrodes stacks. The idea is to replace current electrode materials with a flexible nano-network.

In our experiments, purified Single-Walled Carbon Nanotubes (SWCNTs) have been dispersed in both the silicone-based dielectrics (low SWCNT content) and in the silicone-based electrode layers (high SWCNT content). Ceramic high ε_r materials have also been added to the silicone dielectrics instead of SWCNTs. The specific technological advantage here is the use of one basic material (silicone) for both the dielectrics and the electrodes. The flexible, conductive SWCNT network does the electrical job while allowing the basic material (silicone) to infiltrate all layers. This allows a seamless integration of all layers containing different fillers in one single bulk silicone body. Given the developed technology, no delamination and electrical degradation occurred for SWCNT-filled bodies irrespective applied strains and shear forces. This solution is easily adaptable to large-area roll-to-roll technologies. For DEA structures, both a much-improved relative permittivity of the dielectrics (orders of magnitude with fillers) and good conductivities of the < 2µm thick electrode layers were obtained. The threshold for dielectric breakdown of 50x30 mm^2, 100 µm thick dielectric layers was adjusted to 150 kV/mm (1 minute). For systems with a Young's modulus of 2 MPa and no applied pre-strain, a thickness contraction of 34% was observed, which is excellent for DEA with no applied pre-strain.

[1] R. Pelrine, R. Kornbluh, Q. Pei and J. Joseph, *Science* **287**, 836-839 (2000)/
[2] P. Carpi, D. de Rossi, R. Kornbluh, R. Pelrine, P. Sommer-Larsen, "Dielectric Elastomers as Electromechanical Transducers: Fundamentals, Materials, Devices, Models and Applications of an Emerging Electroactive Polymer Technology," Elsevier, Amsterdam, 2008.

Inkjet-printed Single Walled Carbon Nanotube Electrode of Supercapacitors for Flexible Application

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Recently, next-generation high power energy devices such as lithium-ion batteries and supercapacitors are widely studied. While the lithium-ion batteries are used for hybrid electric vehicles (HEVs) due to the high energy density, the supercapacitors are suited for the power sources of electronic devices such as flexible display and sensors due to the high power densities and cycling ability. Supercapacitors can be divided into electric double-layer capacitors (EDLCs) and pseudocapacitors by their charge storage mechanism. For EDLCs, various carbonaceous materials such as carbon fibers, activated carbon, and carbon nanotubes can be used for the electrode materials. Among the carbonaceous material, the single walled carbon nanotubes (SWCNTs) have unique merits in the high surface area, high conductivity, and availability in solution-based process (such as printing or spray method) for the electrode preparation.

The printed electronics are widely used in the various applications such as displays, sensors and flexible devices because of low process cost, large scale-ability, and high processing speed. However, compared to the other solution-based processes such as spray method and meyer rod coating, the inkjet printing process are less reported for the application in the supercapacitors.

In this study, we fabricated inkjet-printed single-walled carbon nanotubes (SWCNTs) thin film electrodes on various substrates and operated in various organic electrolytes. First, we synthesized water-base SWCNTs solution by using tip sonication with aqueous surfactant for sidewall functionalization, which showed dispersion stability of ~6 months. For fabricating SWCNTs films, the SWCNTs solution was printed on the substrates (Al foil or paper). The shape of the electrode was controlled to be a square form by continuous printing through several nozzles. For obtaining suitable electrochemical and conductivity properties, ink-jet printing was reiterated. The thickness of 20-layered thin films was ~1 μm. We fabricated EDLC cells consisting of two symmetric ink-jet printed SWCNTs films on metal or paper substrates, which were enclosed with various organic electrolytes. For evaluating the electrochemical properties of inkjet printed supercapacitors, the specific capacitance was obtained by galvanostatic charge/discharge measurements and the cycling stability was confirmed by cyclic voltammetry. The characteristic frequency using an impedance measurement showed faster charge/discharge characteristics. The characteristic frequency (f_p) of the cell was 13 Hz, which was far larger than that of conventional EDLC electrodes (0.1–0.01 Hz). And the specific capacitance of supercapacitors on the Al foil showed 2.7 mF cm^{-2} with 100-layered film in 1 M $LiPF_6$ in EC:DEC (1:1 in volumetric ratio) organic electrolyte. The specific capacitance can be increased by optimizing process and effective elimination of surfactant included in the SWCNTs solution (Weight ratio of SWCNT and surfactant was 1:10). The detailed results on the properties of inkjet printed SWCNTs supercapacitors will be discussed in the paper.

Nucleation Growth of SWNTs with Controlled Structure: From Metal Catalysts to Carbon Nanomaterials Seeds

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How to grow single-walled carbon nanotubes (SWNTs) with controlled diameter, chirality, and metallic/ semiconducting property, is still in its infancy. Also, there is a huge gulf between production and applications. To meet the needs for applications, SWNTs' diameter, chirality, and metallic/semiconducting property should be controlled in the growth process. We present herein a brief review on the controlled growth and fabrication of SWNTs array on surface in our group, including 1) Temperature mediated chemical vapor deposition (CVD) growth of SWNTs with controlled diameter; 2) Cap engineering for SWNTs growth with controlled chirality; 3) Direct growth of semiconducting single-walled carbon nanotube array; and 4) Separation of semiconducting and metallic SWNTs by assistance of "scotch tape".

[1] J Zhang et. al, Temperature-mediated growth of single-walled carbon-nanotube intramolecular junctions, *Nature Materials* **6**(4), 283-286, (2007).
[2] J Zhang et. al, Direct Growth of Semiconducting Single-Walled Carbon Nanotube Array, *J. Am. Chem. Soc.* **131**, 14642-14643 (2009).
[3] J Zhang et. al, Cap Formation Engineering: From Opened C60 to Single-Walled Carbon Nanotubes, *Nano Lett.*, **10**, 3343-3349 (2010).
[4] J Zhang et. al, 'Cloning' of single-walled carbon nanotubes via open-end growth mechanism, *Nano Lett.* **9**(4), 1673-1677 (2009).

Grafting Carbon Nanotubes On Carbon Fibers: Influence Of The Growth Parameters On The Mechanical Properties

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Because of their unique mechanical properties, high aspect ratio and low density, carbon nanotubes (CNTs) are of particular interest as additional nano-reinforcements in fiber-reinforced polymer composites. Most potential of CNTs is seen in improving the toughness/damage resistance of these materials. It is already been demonstrated that a small amount of CNT dispersed in the matrix can hinder the formation of transverse cracks and hence improve the damage resistance of fiber-reinforced composites [1]. CNTs can be integrated into these materials in a variety of ways, e.g. dispersed in the matrix, CNTs dispersed in the fiber sizing, CNTs as a special ply etc. [2,3]. One of the most challenging ways is growing CNTs directly on the surface of carbon fibers, to obtain so-called CNT- grafted carbon fibers. The CNTs could help to hinder fiber/matrix debonding in the early stages of damage development, leading to an improved damage resistance of the fiber- reinforced material. The main drawback of growing CNTs directly onto carbon fibers is the decrease in mechanical properties of the carbon fibers. At typical growth temperatures of CNTs in the catalytic Chemical Vapor Deposition (CVD) process, i.e. 700-900 °C, the catalyst particles can interact with the carbon fibers, causing damage to the fiber surface resulting in a degradation of tensile strength. At the same time, carbon originating from the fibers can poison the catalyst particles, preventing the CNT growth [4-7].
In the present work, we studied systematically the growth of CNTs on PAN-based carbon fibers by means of catalytic CVD technique. By varying the growth conditions, the effect of various parameters has been investigated, e.g. catalyst composition, catalyst deposition technique, reaction gases, growth temperature etc. Special attention is paid to the equimolar C_2H_2-CO_2 reaction, which allows us growing CNTs at much lower temperatures [8]. CNTs and their distribution are characterized using SEM and TEM. The effect of the grafting process on the mechanical properties of the carbon fibers is investigated by single-fiber tests before and after catalyst deposition, and after CNT growth. In order to exploit the full potential of the CNTs in the polymer composite, a sufficiently high bonding strength to the carbon fiber is required. We explore various bonding strength measurements, e.g. nanoscratch test, fiber pull-out test as well as individual CNT pull-out test using a nano-manipulator. Our results indicate that the grafting of CNTs onto carbon fibers is possible without affecting the carbon fiber mechanical strength.

[1] N. De Greef, L. Gorbatikh, A. Godara, L. Mezzo, S.V. Lomovand I. Verpoest, (to be

submitted to Carbon).
[2] T.-W. Chou, L. Gao, E.T. Thostenson,Z. Zhang and J.-H. Byun,*Composite Science and Technology*, **70**, 1-19, (2010).
[3] H. Qian, E.S. Greenhalgh, M.S.P. Schaffer and A. Bismarck A, *Journal of Materials Chemistry*, **20**, 4751–4762, (2010).
[4] H. Qian, A. Bismarck, E.S. Greenhalgh, G. Kalinka and M.S.P Shaffer, *Chemistry of Materials*, **20**, 1862–1869, (2008).
[5] H. Qian, A. Bismarck, E.S. Greenhalgh and M.S.P. Shaffer, *Composites: Part A,* **41**, 1107-1114, (2010).
[6] Q.H. Zhang, J.W. Liu, R.J. Sager, L.M. Dai and J.W. Baur, *Composite Science and Technology*, **69**,594–601, (2009).
[7] R.J. Sager, P.J Klein, D.C. Lagoudas, Q.H. Zhang, J.W. Liu, L.M. Dai and J.W. Baur, *Composite Science and Technology*, **69**, 898–904, (2009).
[8] A. Magrez, J.W. Seo, V.L. Kuznetsov and L. Forro, *Angewandte Chemie Int. Ed.*, **46**, 441-444, (2007).

Balloon Launched on Multiwall Carbon Nanotube Tether in Antarctica

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Drs Okada and Inoue have invented a one-step chemical vapor deposition growth of Multiwall Carbon Nanotubes (MWCNTs) to produce vertically aligned multi-walled carbon nanotube arrays on quartz substrates. The height of the carbon nanotube array exceeds 1 mm in less than 20 min. The fabricated MWCNT array can be easily drawn into a large scale MWCNT web. During drawing, nanotubes pull each other with the aid of van der Waals and magnetic forces (single domain magnetite crystals). The endless drawn web has been fabricated into the nanotube tethers. The achieved tether strength reaches 475 MPa. We have spun a tether designed to be strong enough for tethering a simple balloon launched in Antarctica conditions. Each nanotube was about 40 nm in diameter and 1-2 mm long. These MWCNTs structures allowed drawing them into a single two-dimensional sheet and spinning I tto produce several metre long tethers with circular cross sections. Resulting tethers were about 20-30 micrometers in diameter. Four tethers were spun together, producing one, about 40 m long tether that was 50 micrometers in diameter. This tether was cut into 4 segments and these segments were spun together producing a final 10 m long tether, about 0.1 mm in diameter. The SEM images and the images of balloon pulling with the MWCNT tether indicate that the resulting tether was almost strong enough to be used for launching of simple balloons and small payload. Such activity was performed while monitoring the resistance of the tether. Increasing of the pulling force due to sheer force of the wind acting on balloon and its tether resulted in decreasing of the tether's electrical resistance. The decrease of the tether's electrical resistance was also observed when the MWCNT tether was exposed to several days of Antarctica weather.

Monodisperse SWNT: Applications and Device Performance

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Broad availability of pure, monodisperse carbon nanotubes offers the possibility of improving device performance, enabling new CNT applications, and opening new avenues of scientific research [1]. In 2007, NanoIntegris was founded to commercialize a scalable and flexible technique for sorting SWNTs by their physical and electronic structure developed in the Hersam Research Group [2]. During the past 4 years, NanoIntegris has dramatically scaled up production capacity and lowered costs meet the growing global demand for refined CNTs. Today, NanoIntegris supplies materials to over 400 organizations from university research groups to Fortune 500 companies. The availability of these materials has enabled new research directions, resulting in over 30 publications to date.

Semiconducting-enriched SWNTs (s-SWNTs) have been demonstrated in thin film transistor (TFT) devices showing high mobility [3], high on/off ratios [4,5], printability [5], and high-frequency performance [6]. These devices have been utilized for applications ranging from OLED backplanes [7], CMOS logic circuits [8], and analog RF electronics [9]. Additionally, opto-electronic devices have also been demonstrated that exhibit electrically tunable infrared (IR) transmittance [10], and polarized IR emission from a CNT LED [11].

Highlights of recent academic research using electronically-enriched CNTs will be discussed, along with recent progress in scale-up and commercialization of new CNT materials at NanoIntegris [12].

[1] M. C. Hersam, *Nature Nanotechnology*, **3**, 387 (2008)
[2] M.S. Arnold, et al., *Nature Nanotechnology*, **1**, 60 (2006)
[3] C. Wang et al., *ACS Nano*, **4**, 7123 (2008)
[4] C. Wang et al., *Nano Letters* **9**, 4285 (2009)
[5] M. Ha et al., *ACS Nano*, **4**, 4388 (2010)
[6] L. Nougaret et al., *Applied Physics Letters*, **94**, 243505 (2009)
[7] C. Wang et al., *Nano Letters* **9**, 4285 (2009)
[8] S. Lee et al., *ACS Nano*, **5**, 2369 (2011)
[9] P. Burke et al, *Nature Nanotechnology*, **4**, 811 (2009)
[10] F. Wang et al., *Nano Letters*, **10**, 937 (2010)
[11] M. Kinoshita et. al., *Opt. Express*, **16**, 25738 (2010)
[12] www.nanointegris.com

Hetero-junctions of Carbon Nanotubes and Boron Nitride Nanotubes

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Heterojunctions of boron nitride nanotubes (BNNTs) and carbon nanotubes (CNTs) are predicted to have appealing properties that are not available from pure BNNTs and CNTs. These BNNT/CNT junctions are expected to have tuneable electronic, photonic, magnetic, and spintronic properties. Here we report on the first success of growing two types of BNNT/CNT junctions and their properties.

Theory predicts that BNNT/CNT junctions [1, 2] and BN sheet/graphenejunctions [3, 4] are energetically stable. Various configurations of such BNNT/CNT nanotubular junctions have been evaluated and concluded as follows:1) BNNT/CNT junctions are energetically stable either in the armchair or the zigzag configurations. 2) Zigzag BNNT/CNT junctions posses flat band structures with tuneable direct band gaps (~0.5 to 2.0 eV). Thus these BNNT/CNT junctions arepromising ferromagnetic, spintronic, electronic, and photonicmaterials. 3) Armchair BNNT/CNT junctions will have direct band gap and can form Schottky barrier devices, diodes, and quantum dots etc.

Experimentally, the growth of BNNT/CNT junctions was hindered by the absent of a common growth techniques for both BNNTs and CNTs. Based on our recent capabilities in growing CNTs [5-7] and BNNTs [8-11], we have succeeded in producing BNNT/CNT junctions using a series of common catalysts. Results indicated that two types of new nanotubular structures were realized 1) branching, and 2) co-axial BNNT/CNT junctions. The details of the synthesis methodology, the growth model, and properties of these junctions as realized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), Raman spectroscopy, Fourier-transformed IR (FTIR), and scanning probe microscopy (SPM) will be discussed in the conference

[1]. X. Blase, J.-C. Charlier, A. De Vita, R. Car, *Appl. Phys. Lett.***70**, 197 (1997).
[2]. J. Choi, Y-H Kim, K. J. Chang, D. Tománek, *Phys. Rev. B* **67**, 125421 (2003).
[3]. S. Okada, M. Igami, K. Nakada, A. Oshiyama, *Phy. Rev. B* **62**, 9896 (2000).
[4]. S. Okada, A. Oshiyama, *Phy. Rev. Lett.* **87**, 146803 (2001).
[5]. V. Kayastha, Y. K.Yap, S. Dimovski, and Y. Gogotsi, *Appl. Phys. Lett.* **85**, 3265 (2004).
[6]. V. K. Kayastha, et al, *Appl. Phys. Lett.* **86**, 253105 (2005).
[7]. V. K. Kayastha, S. Wu, J. Moscatello, Y. K. Yap, *J. Phys. Chem. C* **111**, 10158 (2007).
[8]. J. Wang, et al, *Nano Letters.* **5**, 2528 (2005).
[9]. C. H. Lee, et al, *Nanotechnology* **19**, 455605 (2008).
[10]. C. H. Lee, M. Xie, V. K. Kayastha, J. Wang, Y. K. Yap, *Chem. Mater.* **22**, 1782 (2010).
[11]. J. Wang, C. H. Lee and Yoke Khin Yap, *Nanoscale* **2**, 2028 (2010).

Materials in the Flatland

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Graphene is a novel material with a number of unique properties. However, the most important one is that it has opened a floodgate for other two-dimensional (2D) crystals to be obtained. The current progress in 2D crystal isolation and growth can lead to a new paradigm of "complex materials on demand" by combining such 2D crystals into 3-dimensional layered structure. The number of different structures that one can obtain based on these strategies is practically unlimited and their physical properties are hard to predict a priori. Nevertheless, by understanding the properties of the 2D components, one should be able to create materials that have interesting structural, electronic, optical, mechanical and other properties.

Auger-Induced Carrier Multiplication in Graphene

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Graphene as a zero-bandgap semiconductor with a linear energy dispersion is an ideal model structure to study the carrier relaxation channels, which are suppressed in conventional semiconductors due to restrictions imposed by energy and momentum conservation. In particular, it is of fundamental interest to address the question whether Auger-type processes significantly influence the carrier dynamics in graphene. These scattering channels bridge the valence and conduction band allowing carrier multiplication - a process that generates multiple charge carriers from the absorption of a single photon. This process has been intensively discussed in literature for improving the efficiency of solar energy conversion in quantum dots and carbon nanotubes.

Here, we present microscopic calculations of the coupled population and coherence dynamics describing the time-, momentum-, and angle-resolved relaxation of photo-excited carriers toward equilibrium [1,2]. Our approach, based on the density matrix formalism, microscopically includes both carrier-carrier as well as carrier-phonon relaxation channels. We observe a redistribution of optically excited carriers to energetically lower states resulting in a hot Fermi distribution within the first hundred femtoseconds followed by a slower phonon-induced energy dissipation. We observe that the initial fast thermalization is governed by Coulomb-induced carrier-carrier scattering. However, our calculations reveal that the carrier-phonon relaxation also has a considerable contribution resulting in a rapid loss of the excess energy right after the excitation pulse. The results are in good agreement with recent high-resolution (< 10 fs) pump-probe experiments [3].

Our investigations show, in particular, that the Auger-type processes have a considerable influence on the relaxation dynamics in graphene. While the Auger recombination annihilates an electron and a hole, the impact excitation creates charge carriers. We find a strong asymmetry between these two processes resulting in a much higher probability for the impact excitation. This can be traced back to the Pauli blocking, which suppresses the Auger recombination, since its final states in the valence band are occupied at the beginning of the relaxation dynamics. As a result, a significant multiplication of charge carriers is obtained. This non-equilibrium effect depends on the excitation strength and is found to be stronger for weaker excitations. Including the carrier-phonon scattering leads to a decay of the carrier density on a picosecond timescale, i.e. the carrier multiplication remains efficient up to a few picoseconds

Our microscopic calculations give new insights into the ultrafast relaxation dynamics of optically excited carrier in graphene, which can be helpful for designing and engineering novel graphene-based optoelectronic devices. In particular, we show that despite the competing phonon-induced processes the impact excitation is very efficient. It gives rise to a significant carrier multiplication confirming the potential of graphene as a new material for photodevices, such as high-efficiency solar cells and high-sensitivity photodetectors.

[1] T. Winzer, A. Knorr, and E. Malic, *Nano Lett.* **10,** 4839 (2010).
[2] S. Butscher, F. Milde, M. Hirtschulz, E. Malic et al., *App. Phys. Lett.* **91**, 203103 (2007)
[3] M. Breusing, S. Kuehn, T. Winzer, E. Malic, et al., *Phys. Rev. B*, in print (2011)

Ink-Jet Printed Graphene Electronics

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Ink-jet printing is one of the most promising techniques for inexpensive large area fabrication of flexible plastic electronics [1], due to its versatility, the limited number of process steps [2,3], the ease of mass fabrication [2,3]. Despite much progress, ink-jet printed organic Thin Film Transistor (TFT) still show poor air stability, limited lifetime, mobility.

Here we fabricate graphene-based ink-jet printed transparent and conductive electrodes and TFTs. The grapheme ink is produced by Liquid phase exfoliation (LPE). High quality graphite flakes are dispersed in organic solvents by ultrasonication followed by ultracentrifugation to remove large graphite fragments that are likely to clog the nozzle of the ink-jet printer. We investigate N,N-dimethylacetamide, Ethyl Acetate, 1-Methyl-2-pyrrolidone (NMP), Dimethylformamide as organic solvents. By Optical Absorption Spectroscopy (OAS), Transmission electron microscopy (TEM) and Raman spectroscopy we find that NMP gives the highest yield of monolayer graphene [4]. Graphene-ink stripes are then ink-jet printed on Si/SiO_2 modified by Self-Assembled Monolayers (SAM), which reduce the wettability of the substrate and allow uniform printing of graphene electrodes. The ink-jet printed graphene-ink stripes are then utilized to fabricate graphene-based TFTs achieving mobility up to 95 $cm^2 V^{-1} s^{-1}$ [5]. The electrical and optical performances observed in our devices, demonstrate the viability of graphene-ink to fabricate electronic devices, paving the way to graphene ink-jet printed electronics.

[1] H. Sirringhaus et al. *Science*, **290** (2000) 2123.
[2] B. J. DeGans et al. *Adv. Mater.* **16** (2004) 203.
[3] M. Singh et al. *Adv. Mater.* **22** (2010) 673.
[4] Y. Hernandez et al. *Nat. Nanotechnol.* **3** (2008) 563
[5] F. Torrisi et al., submitted, (2011).

Ab Initio Quantum Transport in Defective and Chemically-modified Graphene

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In the present work, quantum transport properties of disordered graphene with structural defects (Stone-Wales and divacancies) are investigated using a realistic π-π^* tight-binding model elaborated from accurate ab initio calculations [1]. Mean free paths and semiclassical conductivities are computed as a function of the nature and density of defects (using an order- N real-space Kubo-Greenwood method). By increasing the defect density, the decay of the semiclassical conductivities is predicted to saturate to a minimum value over a large plateau of carrier density ($> 0.5 \times 10^{14}$ cm^{-2}). Additionally, strong contributions of quantum interferences suggest that the Anderson localization regime could be experimentally measurable for a defect density as low as 1%. The effects of extended line of defects on the electronic properties of graphene are also briefly described [2].

The electronic and transport properties of graphene after epoxide functionalization via ozone treatment is also studied using the same numerical method [3]. The orbital rehybridization induced by the epoxide groups triggers a strong intervalley scattering and changes dramatically the conduction properties of graphene. By varying the coverage density of epoxide defects from 0.1 to 4%, charge conduction can be tuned from a diffusive to a strongly localized regime, with localization lengths down to a few nanometers long. Our theoretical predictions provide a physical interpretation to the metal-insulator transition observed experimentally.

[1] A. Lherbier, S.M.-M. Dubois, X. Declerck, S. Roche, Y.M. Niquet, and J.-C. Charlier *Phys. Rev. Lett.* **106**, 046803 (2011).
[2] A. Botello-Mendez, X. Declerck, M. Terrones, H. Terrones, and J.-C. Charlier *Nanoscale*, in press (2011).
[3] N. Leconte, J. Moser, P. Ordejon, H. Tao, A. Lherbier, A. Bachtold, F. Alsina, C.M. Sotomayor Torres, J.-C. Charlier, and S. Roche, *ACS Nano* **4**, 4033-4038 (2010).

Controlling The Function Of Carbon Nanotube Devices With Lithographically Defined Charge Patterns

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We use AFM lithography to write charge patterns in close proximity to carbon nanotube field effect transistor devices. The silicon dioxide substrate retains the charge for days, allowing various charge configurations to be tested. We show that the written charge can move the Fermi level in the nanotube by hundreds of meV and we use this charge lithography to reconfigure a field effect transistor into a p-n junction. The substrate charge can be erased and rewritten, offering a new tool for prototyping nanodevices and optimizing electrostatic doping profiles.

Dissipation And Breakdown In Carbon Nanotube Network Transistors

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Single-wall carbon nanotube networks (CNNs) are of interest for integrated circuits [1] and displays [2] on transparent or flexible substrates, particularly where they could exceed the performance of organic or amorphous thin-film transistors (TFTs). A key parameter for such devices is the ON/OFF current ratio, which can be enhanced by geometric striping or Joule breakdown to reduce metallic pathways in the film.[1,3,4] During Joule breakdown, high electric fields and temperature gradients raise fundamental questions about the behaviour of CNNs under such stress. Moreover, substrates with low thermal conductivities, e.g. glass or plastic, are known to result in self-heating effects [5] and reduced reliability,[6] topics not yet explored in CNN TFTs. In this study, we explore several aspects of CNN TFT performance and reliability. We demonstrate a pulsed electrical breakdown method for enhancing the ON/OFF current ratio in CNN de- vices to levels comparable with geometrically striped CNNs (from 10x to 1000x). Additionally, we use infrared (IR) thermal imaging [7] to investigate Joule breakdown and power dissipation in such devices. Our findings reveal the formation of distinct hot spots in the device channel during operation. However, the average CNN temperature at breakdown is much lower than expected from the breakdown of individual nanotubes, suggesting extremely high regions of power dissipation at the nanotube junctions. Statistical analysis and comparison with a thermal model allow the extraction of the average tube-tube junction thermal resistance, $\sim 4.4\times 10^{11}$ K/W (thermal conductance ~2.27 pW/K). Our findings suggest that transport, dissipation, and reliability of CNN devices are limited by the CNT junctions rather than extrinsic factors such as low substrate thermal conductivity. These results offer a path towards understanding dissipation and optimizing performance of CNN TFTs.

[1] Q. Cao, et al., *Nature*, **454**, 495 (2008),
[2] S. Kim, et al., *ACS Nano*, **4**, 2994 (2010).
[3] G. H. Buh, et al., *IEEE TNano.*, **7**, 624 (2008).
[4] P. G. Collins, et al., *Science*, **292**, 706 (2001).
[5]A. Valletta, et al., *APL*, **89**, 093509 (2006).
[6] K. Takechi, et al., *IEEE TED*, **53**, 251 (2006).
[7] D. Estrada and E. Pop, *APL*, **98**, 073102 (2011).

Carbon Nanotube Based Device For The Highly Responsive And Selective Detection Of Terahertz Radiation

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Recently, much attention has been paid to microsized and nanosized devices that could operate with terahertz radiation. A number of tiny detectors [1-3] of electromagnetic radiation in THz range were proposed. Among terahertz detectors it is worth noting such class of devices as resonant detectors. Their work based on the effect of bounded mechanical and electrical oscillators. For the first time this idea was proposed by Nathanson [4] in his model of resonant transistor. Previously proposed resonant detectors utilize plasma waves in detectors channel and mechanical oscillations of floating cantilever that also serve as a gate for waves in channel. This influence of a gate on waves in channel make a possibility for detection of electromagnetic radiation. We propose a novel scheme of resonant terahertz detector based on metallic carbon nanotubes suspended over insulator or well conducting plane. In this case both plasma and mechanical resonances are realized by carbon nanotubes. According to the theory of the Tomonanga-Luttinger liquid that explains successfully electron behavior in CNT [5], the plasmons can be generated in carbon nanotubes (CNT). This leads to the coupled plasma and mechanical resonances. Besides possibility to generate plasmons CNTs possesses unique mechanical properties. Sufficiently high Young's modulus of nanotubes allows the mechanical resonances of CNT in the gigahertz frequency range. Also we propose the scheme of powering the detector that is based on the transmission line (TL) model used for the plasmon description in nanotubes [6]. According to this model we choose the length of TL to be equal to a quarter wavelength of plasmon in nanotube. In this case we consider an open-circuited TL. The major characteristic quantity for such detector is a responsivity that is defined as the ratio of signal current amplitude in external circuit to the THz power incoming to the detector antenna. So for the typical sizes of our system (nanotube length equals 0.5 um, its diameter equals 3 nm, distance between nanotubes or between nanotube and underlying plane approximately equals 10 nm) we obtain the responsivity 0.3 [A/W] $R\approx$ that considerably exceeds those for previously proposed detectors [2-3].

[1] Ryzhii V. et al., *Appl. Phys. Lett.* **90**, 203503, (2007).
[2] Hu Y.et al., *Phys. Status Solidi C* 5, **277**, (2008).
[3] Leiman V.G. et al., *J. Appl. Phys.* **104**, 024514, (2008).
[4] Nathanson H.C. et al., *IEEE. Trans. Electron Devices* ED-14, **117**, (1967).
[5] Bockrath M.W. Carbon nanotubes: electrons in one dimension. Berkeley, Ph.D. Dissertation, 1990.
[6] Burke P.J. *IEEE Trans. on Nanotech* 1, 129, (2002).

Polyaniline-Nanotube Single Molecular Field Effect Transistor

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At the present time intensive research of charge transport mechanism in single molecules that demonstrate semiconducting properties are carried out. The actual problem is still in contact organization to single molecule for measurements. One of variants for interface organization between molecule and electrodes made by traditional lithography methods is usage of carbon nanotubes (CNT) with well-known electro-physical properties [1]. We investigate the polyaniline molecules (PANI) as the molecular channel for formation one- dimensional transistor. Emeraldine formed polyaniline (PANI EB) with length of chain near 10000 (given by T. Berezina, University of Parma, Italy) was dissolved in 1-methyl-2- pyrrolidone (NMP) with mass concentration PANI in solution 10-3 %.CNT with mass ~ 1 µg in 2 ml PANI solution in NMP is exposed by ultrasonication several hours at frequency 35kHz and power 75 W. The given solution was stable within a week without leading to formation of conglomerates. Deposition was carried out on chip 1,5*1,5 mm size by dielectrophoresis between gold electrodes, made by group lithography methods of microelectronics with distance between electrodes ~ 2 µm. Parameters of dielectrophoresis: voltage amplitude 6 V, frequency 100 kHz, duration 3 minutes. The molecular dipole energy in experimental field of $1,7*10^8$V/m are 7 meV. Thus there is a probability of molecular structuring in line along with CNT electrode deposited in the gap between the gold electrodes. The energy difference between HOMO and LUMO levels in PANI EB are no more than 3,6eV [2]. In the contact area of CNT and PANI when the-10 V gate potential is applied the charge transport through HOMO occurs because of jumping to LUMO levels at CNT contact region. Moreover the energy levels simulation demonstrate that CNT presence increase the molecular orbital delocalization and decrease the effective energy gap in comparison with pure PANI molecule. Thus we demonstrate electric field induced one-dimensional semiconducting molecular channel assembling. This molecular channel demonstrate strong dependence on external (gate) electric field. The change of conductivity is no less than four orders of magnitude when gate potential changes on 5 Volts. The measured conductivity at zero gate potential was obtained 3,2 $(\text{Ohm}\cdot\text{см})^{-1}$ and is less than doped PANI. But if note the contribution in resistance of CNT-gold electrode contact is about 1 MOhm we can conclude that intrinsic conductivity of molecular channel between CNT can be an order higher.

[1] I.I. Bobrinetskii, V.K. Nevolin, S.V.Khartov, Yu.A. Chaplygin. Field-modulated conductivity in quasi-one-dimensional molecular conductors, *Technical Physics Letters*, **31**(10), 885-887, (2005).
[2] Y.Cao, P. Smith, A.J. Heeger,*Synth. Met.* **32**,263 (1989).

High-Performance SWCNT Thin Film Transistors: Correlation between Alignment and Transport Characteristics

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For the sustainable society, printing electronics is one of the most important issues to be realized to save energy and resources. Semiconductor enriched single-wall carbon nanotubes (s-SWCNTs) can be used as resources for the printing electronics because of their high performance in electronic transport properties. Most of previous works used two dimensional random networks of s-SWCNTs for fabrication of thin-film transistors (TFTs). In the recent our work, however, TFT using a slightly aligned s-SWCNT thin film showed drastically improved transfer characteristics [1]. The on-off current ratio and the mobility were higher than 10^5 and 10 cm^2/V, respectively, although the purity of semiconductor was lower than 90 %.This indicates that the network topology is very important as well as the concentration of semiconductor to fabricate high-performance printing SWCNT devices. In this study, we present a detailed analysis of aligned s-SWCNT films to see the topological effect on SWCNT-TFTs.

In this work, the s-SWCNT solution was prepared by the gel chromatography methods [2] and was dropped onto a SiO_2/Si substrate covered with self-assembled monolayer of 3-aminopropyltriethoxysilane. Because the alignment process of SWCNT should be simple and easy towards the industrial applications, in this work, the aligned thin film was prepared by N_2 blow in the drying process. The alignment of s-SWCNTs was numerically analyzed from AFM image using Scanning Probe Image Processor (SPIP) software. The Fourier transformed image clearly indicated alignment of s-SWCNTs. The network topology was further analyzed using autocorrelation function. We will discuss the correlation between alignment and device characteristics of s-SWCNT TFTs.

[1] S. Fujii et al.,in preparation
[2] T. Tanaka et al., *Appl. Phys. Express*, **2**, 125002, (2009)

Light Emission From Carbon Nanotubes in Silicon

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Modern single wall carbon nanotube became an exciting material for optic and photonic applications due to significant advances in nanotubes sorting and thin-films preparation. Recently, it has been shown that semiconducting nanotubes (s-SWNT) could be used as strong light emitters in the near-IR, thanks to their efficient excitonic recombination across a direct band gap.
In particular, strong photoluminescence has been demonstrated in polyfluorene embedded s-SWNT extracted using an ultracentrifugation process. This extraction technique leads to almost metallic-free nanotubes, as confirmed by photoluminescence, absorption and Raman spectroscopies [1,2]. Thanks to this improvement, an experimental demonstration of optical gain as high as 160 cm^{-1} in (8,7) s-SWNT at a wavelength of 1300 nm has been achieved. Evidences were gathered using several methods on a thin film doped with pure s-SWNT[3]. The emergence of “Carbon Nanotube Photonics” for broad application domains (e.g. optical interconnects, telecommunications and biophotonics) will have to go by the integration of carbon nanotubes with existing photonics technology. The emerging and more and more considered photonic material is the silicon. It is obvious that the development “Carbon Nanotube Photonics” has to be done within the framework of silicon platform, with optoelectronic devices based on carbon nanotubes (light source, modulation and detection) while the integrated light guiding structures will be performed by silicon waveguides. In order to achieve this mutation of silicon photonics towards carbon, we will present the first integration of s-SWNT in silicon photonics structures. We will emphasize how to achieve an efficient coupling between carbon nanotubes and silicon waveguide and we will demonstrate the light generation in silicon from carbon nanotubes with a temperature-independent emission up to 100 °C at a wavelength of 1.3 µm [4]. This is another important milestone towards emergence of a new age of “Carbon Nanotube Photonics”

[1] N. Izard, S. Kazaoui, K. Hata, T. Okazaki, T. Saito, S. Iijima, N. Minami, *Appl. Phys. Lett.*, **92**, 243112, (2008).
[2] E. Gaufrès, N. Izard, L. Vivien, S. Kazaoui, D. Marris-Morini, E. Cassan, L. Vivien, *Opt. Lett.*, **34**, 3845, (2009)
[3] E. Gaufrès, N. Izard, X. Le Roux, D. Marris-Morini, S. Kazaoui, E. Cassan, L. Vivien, *Appl. Phys. Lett.*, **96**, 231105, (2010)
[4] E. Gaufrès et al. *Submitted*

High-performance, Functional Carbon Nanotube Integrated Circuits On Plastic

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Carbon nanotube thin-film transistors (TFTs) are expected to enable the fabrication of high-performance, flexible, and transparent devices for future plastic electronics with relatively simple and low-cost techniques. However, the conventional solution-based fabrication processes lead to contamination and destruction of the nanotubes, thus reducing TFT performance. Here we present a new method for producing high-performance carbon nanotube TFTs and integrated circuits.[1]

The fabrication technique we developed is based on a gas-phase filtration and transfer process.[1] The single-walled carbon nanotubes were continuously grown in an atmospheric pressure floating-catalyst chemical-vapor deposition process.[2] The nanotubes were then collected on a membrane filter for a few seconds, and subsequently transferred onto any kind of substrates. The fabricated carbon nanotube TFTs show the uniform and excellent performance, with an on/off ratio of $\sim 10^7$ and mobility of 35 cm^2/Vs evaluated by a parallel plate model (634 cm^2/Vs by a rigorous model[1,3]), better performance than previous nanotube-based TFTs, and comparable to low-temperature poly-Si and zinc oxide TFTs. The high on/off ratio is realized even using the as-grown nanotubes (~30% metallic nanotubes), because the nanotube density can be precisely controlled by adjusting the collection time to make the metallic nanotube density lower than the percolation threshold. The high mobility is attributed to the clean nanotubes and unique morphology of the nanotube networks consisting of individual, long nanotubes interconnected by ‘Y’-shaped junctions.

We also fabricated flexible and transparent integrated circuits, including inverters, ring oscillators, NAND gates, NOR gates, reset-set flip-flops, and master-slave delay flip-flops. For 21-stage ring oscillator in which 44 TFTs were integrated, the high-speed operation was achieved with a delay time of 12 μs per logic gate. Finally, the master-slave delay flip-flops, triggered on the rising edge of the clock signal, was demonstrated to show the first sequential logic integrated circuits based on carbon nanotubes to date, which has storage or memory functions in contrast to the combinational logic.

This simple and fast technique to fabricate circuits is easily scaled up and adaptable to high-speed roll-to-roll manufacturing systems, which could lead to the development of large-scale, inexpensive, and flexible electronics, bringing plastic electronics a step closer to reality.

[1] D.M. Sun, M.Y. Timmermans, Y. Tian, A.G. Nasibulin, E.I. Kauppinen, S. Kishimoto, T. Mizutani, Y. Ohno, *Nature Nanotech.*, **6**, 156-161, (2011).
[2] A. Moisala, A.G. Nasibulin, D.P. Brown, H. Jiang, L. Khriachtechev, E.I. Kauppinen, *Chem. Eng. Sci.*, **61**, 4393-4402, (2006).
[3] Q. Cao, M. Xia, C. Kocabas, M. Shim, J.A. Rogers, *Appl. Phys. Lett.*, **90**, 023516, (2007).

Electrical Properties Of Vertically Aligned Carbon Nanotubes For Strain Measurements

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A strain gauge is one of the most powerful sensors for experimental mechanical analysis, e.g. pressure, force or acceleration. Versatile applications in sectors like medical technology or weighing technology make further developments of strain gauges interesting. Conventional strain gauges are limited because of the low strain sensitivity (gauge factor) or high temperature dependence of resistance (TCR) of the used material.

In the last years the interest of CNTs based sensors increased, because of their remarkable properties. CNTs exhibit, besides high temperature and chemical stability, also high flexibility and conductivity. A flexible gauge sensor based on a single carbon nanotube has been demonstrated having a high piezoresistive gauge factor of about 269 [1]. Aligned unstructured polymer-CNT-composites [2] and non embedded CNTs [3] show also high gauge factors, but strong temperature dependence.

In this work, we present structured and vertically aligned carbon nanotubes (CNT) as a highly strain-sensitive material for strain gauge application. The charge transport occurs orthogonal to the CNTs. Arrays of aligned CNTs offer structural advantages due to the possibility of using only standard microsystems technology and hence the integration in to MEMS devices. The main challenge of such a strain gauge is the high CNT process temperature at 725 °C. This makes a direct deposition of the CNTs on a flexible polymer impossible. Hence the CNTs are grown on an oxidized Si wafer, contacted by a thin film Pt resistor, passivated by a plasma polymer and then transferred on a flexible film. In [4] we demonstrated that the negative TCR of the CNTscan be compensated with thin film Pt resistors, which are added in series on either side of the CNT carpet. Due to the positive temperature coefficient of Pt the total TCR can be tuned nearly to zero by an appropriate layout of the Pt resistors.

In this work, we investigate the influence of the CNT quality on their charge transport, sensitivity of strain, and temperature dependence. For this, we verify the carrier properties, the dimensions of the catalyst and the CNT growth parameters themselves. We show the significance of a roughened carrier surface for better clustering conditions of thin sputtered catalyst layers in order to obtain a good CNT growth. Ashort sputter time of the catalyst leads to an increase in length and a more regular growth of the CNTs. Additionally, with increasing length of the CNTs the gauge factor increases and the temperature dependence decreases linearly. In the temperature range of 20 °C-100 °C the resistance is linear and free of hysteresis. For characterization, we used SEM and AFM as well as wire connected electrical measurements.

[1] C. Stampfer, T. Helbling, D. Obergfell, B. Schoberle, M. K. Tripp, A. Jungen, S. Roth, V. M. Bright, and C. Hierold, *Nano Lett*, **6**, 233- 237, 2006.
[2] M. Park, H. Kim and J. P. Youngblood, *Nanotechnology*, **19**, 055705, 2008.
[3] R. J. Grow, Q. Wang, J. Cao, D. Wang, and H. Dai, *Applied Physics Letters*, **86**, 093104, 2005.
[4] S. Riekeberg, J. Büttner, J.Müller, *Sensors IEEE*, 647 – 651, 2010

Flexible, Transparent, and Metal-Free Single-Walled Carbon Nanotube Field-Effect Transistors

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With the recent development of novel electronic devices there is a desire for flexible, transparent, high-performance field-effect transistors (FETs). A single-walled carbon nanotube (SWNT) is a strong candidate for realizing such next-generation devices due to their mechanical robustness and excellent electrical properties.

Based on our unique patterned-growth technique using a self-assembled monolayer (SAM) [1], we have reported that high-performance FETs can be easily fabricated using as-grown SWNTs for the channel as well as both source and drain electrodes [2]. Such "all-SWNT" devices are expected to work on flexible substrates without degradation of electrical properties, and may contribute to realization of sustainable development because of metal- free electronics.

In this study, we fabricated flexible, transparent, and metal-free FETs that utilize SWNTs as both the channel and all three electrodes (drain, source and gate). Poly(vinyl alcohol) (PVA) film was employed as the gate insulator and the substrate. Since the polymer substrate was very thin ($t \sim 10$ μm) compared to other commonly used transparent plastic supports— poly(ethylene terephthalate) (PET) or poly(ethylene naphthalate) (PEN)—the device was highly flexible and was characterized in various shapes (flat, bent, and wrinkled). We found only a small degradation of the electrical properties was observed although the film could be heavily crumpled. An indium tin oxide (ITO) film, which is the conventional transparent conducting materials, does not demonstrate such flexibility [3]. Possibility of the all-SWNT device as novel applications will be discussed.

[1] R. Xiang, T. Wu, E. Einarsson, Y. Suzuki, Y. Murakami, J. Shiomi, and S. Maruyama: *J. Am. Chem. Soc.* **131**, 10344–10345 (2009).
[2] S. Aikawa, R. Xiang, E. Einarsson, S. Chiashi, J. Shiomi, E. Nishikawa, and S. Maruyama: to be published in *Nano Res.* [DOI: 10.1007/s12274-011-0114-0].
[3] N. Saran, K. Parikh, D.-S. Suh, E. Muñoz, H. Kolla, and S. K. Manohar: *J. Am. Chem. Soc.* **126**, 4462–4463 (2004).

Complimentary logic circuits by inkjet print viologen doping on semiconducting carbon nanotubes transistor

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Use of random network carbon nanotube (CNT) transistors and their applications to complementary logic gates have been limited by several factors such as control of CNT density, existence of metallic CNTs producing a poor yield of devices, absence of stable n- dopant and control of precise position of the dopant, and absence of a scalable and cost- effective fabrication process. Here, we report a scalable and cost-effective fabrication of complementary logic gates by precisely positioning an air-stable n-type dopant, viologen, by inkjet printing on a separated semiconducting CNTs network. The obtained CNT transistors showed a high yield of nearly 100% with an on/off ratio of greater than 10^3 in an optimized channel length (<9 μm). The n-doped semiconducting carbon nanotube transistors showed a nearly symmetric behavior in the on/off current and threshold voltage with p-type transistors. CMOS inverter, NAND, and NOR logic gates were integrated on a HfO_2/Si substrate using the n/p transistor arrays. The gain of inverter is high, which is around 45, and NAND and NOR logic gates revealed excellent output on and off voltages. These series of whole processes were conducted under ambient conditions, which can be used for large-area and flexible thin film technology.

Torsional Actuator Based on Transition between Flattened and Tubular States in Carbon Nanotubes

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Carbon nanostructures are of great interest for their potential to design nanosized electromechanical devices because of their unique mechanical and electrical properties. A synthetic rotational motor or linear motor consisting of carbon nanotubes have been reported [1,2]. In this study, we propose a nanosized actuator utilizing the transition between flattened and tubular states in carbon nanotubes (CNTs).

It has been suggested that CNTs are deformed along their axis [3,4], and fully or partially flattened and twisted CNTs were experimentally observed by a transmission electron microscope (TEM)[4]. We have revealed that such flattened and twisted state change to tubular state by applying electric current to CNTs, and this transition is reversible and generates torque. We demonstrated the actuator motion using a nanomanipulator equipped in TEM. At first a fully flattened and twisted CNT with the circumference of 13 nm was bridged between two electrodes. When the current was increased up to 50 mA, a part of the flattened state region changed to tubular state. When the current was decreased to 36 mA, the boundary between the flattened state region and the tubular state region shifted to expand the flattened state region, and upon further decrease of the current to 20 mA, the CNT was returned to the initial flattened state. The fact that applying current causes the transition strongly suggests that its driving force is thermal energy induced by Joule heating. One can expect that the initial twist generates torque when the states change. In this experiment, this torque was balanced with the torsional stress because the both ends of the CNT were fixed.

In addition we have performed a molecular dynamics simulation of transition process between the flattened and tubular states in single walled CNTs. Our simulation shows that the initial twist of flattened CNT is caused by taking specific graphitic stacking orders for the CNT inside. For example a CNT with near armchair chirality prefers the AB stacking. Furthermore it is suggested that the fully flattened CNT changes its state to the tubular state above 2000 K. The results brought us a new concept of torsional actuators that has one end fixed and the other supported by a bearing structure to be free to rotate. Controlling the amount of current applied to the CNT enable us to adjust the rotation angle of the free end.

[1] A. M. Fennimore et al., *Nature* **424**, 408-410, (2003)
[2] H. Somada et al., *Nano Letters* **9**, 62-65, (2009)
[3] G. Gao et al., *Nanotechnology* **9**, 184-191, (1998)
[4] N. G. Chopra et al., *Nature* **377**, 135-138, (1995)

Development of Glucose Sensor Using CNT Compound Materials

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A bio-nanosensor consisting of a silicon-based chip contains a poly[ethylene glycol]- grafted (PEG)-grafted carbon nanotubes (PEG-CNTs) modified with living body materials (ex. enzyme, antibody, and DNA etc.) using plasma ion irradiation (plasma activation) method, developed.[1,2]

We developed a method for measuring changes in the electrical conductivity of a CNT surfacereaction, which is a time-based detection method (impedance type). Specifically, we immobilized the glucose oxidase (GOD) on a sensor chip with a CNT base and we then measured changes in impedance caused by the catalyst reaction at the point where the glucose was dripped onto the chip. After evaluating variouscharacteristics, we used PEG to enhance the dispersion of the multiwalled CNTs (MWCNTs) used when the sensor was fabricated. According to evaluation of the glucose sensor manufactured by using glucose oxidase (GOD), impedance revealed an increase due to a catalyst reaction of PEG-CNTs surface. Furthermore, the impedance change which originated in the blood glucose of small animal (rat) was confirmed. The results suggested that a bio-nanosensor made sure concentration dependency of blood glucose.

[1] T. Hirata, S. Amiya, M. Akiya, O. Takei, T. Sakai, and R. Hatakeyama, *Appl. Phys. Lett.*, **90**, 233106-1-233106-3, (2007).
[2] T. Hirata, S. Amiya, M. Akiya, O. Takei, T. Sakai, T. Nakamura, J. K. Tsuzuku, T. Yamamoto, and R. Hatakeyama, *Jpn J. Appl. Phys.*, **47**, 2067-2071, (2008).

Rims Of Carbon Nanotubes: A Possible Path To Chiral Selective Growth ?

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The chirality of a carbon nanotube determines its electronic and mechanical properties. To control the properties of a carbon nanotube sample it is necessary to control the chiralities within the sample. Chirality control is desired in the growth process, as nanotubes could be directly grown into devices instead of using post processing methods. The growth can be divided into two stages. The nucleation phase and the elongation stage. The nucleation phase is especially important, as the cap nucleated in this phase determines the chirality of the tube.[1] Almost all studies on the nucleation process model the nucleation without taking into account chiral selectivity. Liu et al attempted to describe chiral selectivity in the nucleation phase concentrating on the rim of the nanotubes. [2] The study, however, did not consider pentagons, needed for the inclination of the cap, and neglected the change in the rim structure with every carbon addition.[3,4] To understand the chiral selectivity in the nucleation process we determine the interaction between the cap and the catalytic particle. We calculate the atomic binding energies of the atoms in carbon nanotube caps with various chiralities on metallic clusters using density functional theory. The rim is directly connected to the cluster forming carbon-metal bonds. We find that carbon-metal bonds are the main influencing part for the cap-cluster interaction, as they have the weakest binding energies. The armchair and zigzag parts of the rim have varying bond energies depending on their neighboring atoms. Especially rim atoms in pentagons have lower bond energies. Small changes of the atom positions between rim and catalytic particle can influence the bond energies significantly. We conclude that the chiral selective carbon nanotube nucleation phase cannot be modeled by only considering the rim of a nanotube. It is necessary to consider the rim atoms of the cap structure and the neighboring atoms of the catalytic particle to model the nucleation phase. But this leads to the conclusion that chiral selective growth of a single chirality is not possible, as experimental evidence suggests that catalytic particles have a dynamic structure.[5] Our study will help to improve/rethink the models for chiral selective growth of carbon nanotubes.

[1] Stephanie Reich, Lan Li, and John Robertson, *Chemical Physics Letters* **421**, 469 (2006).
[2] Yuanyue Liu, and Alex Dobrinsky, and Boris I. Yakobson, *Phys. Rev. Lett.* **105**, 235502 (2010).
[3] Heiko Dumlich and Stephanie Reich, *Phys. Rev. B* **82**, 085421 (2010).
[4] Heiko Dumlich and Stephanie Reich, *Phys. Stat. Solidi B* **247**, 2722 (2010).
[5] Stephan Hofmann, Renu Sharma, Caterina Ducati, Gaohui Du, Cecilia Mattevi, Cinzia Cepek, Mirco Cantoro, Simone Pisana, Atlus Parvez, Felipe Cervantes-Sodi, Andrea C. Ferrari, Rafal Dunin-Borkowski, Silvano Lizzit, Luca Petaccia, Andrea Goldoni, and John Robertson, *Nano Lett.* **7**, 602 (2007).

Dynamic And Charge Doping Effects On The Phonon Dispersion Of Graphene And Metallic Carbon Nanotubes: A Theoretical Study

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The dynamic and charge doping effects on the phonon dispersion of graphene and metallic carbon nanotubes were studied within a non-orthogonal tight-binding model. We found that the dynamic corrections are largest for the in-plane optical phonon branches in the vicinity of the Γ point and K point of the Brillouin zone of these systems and that they essentially depend on the doping level. We reproduced previous results of the dynamic and doping effects on the G-modes of graphene and selected metallic carbon nanotubes. In addition, we obtainednew results for these effects for the phonon dispersion of graphene [1] and the G-modes of a large number of metallic nanotubes [2].

[1] V. N. Popov and Ph. Lambin, *Nano Res.* **3**, 822–829(2010).
[2] V. N. Popov and Ph. Lambin, *Phys. Rev. B* **82**, 045406/1-9(2010).

Understanding Carbon Nanotube Chirality through Molecular Dynamic and Kinetic Monte Carlo Simulations

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We are going to present a theoretical study on carbon nanotube growth mechanism through both molecular dynamic (MD) simulation and kinetic Monte Carlo (KMC) simulation. From 2003, we have successfully simulated the nucleation and growth of carbon nanotubes (CNTs) by a MD simulation and have revealed two necessary conditions for catalytic CNT growth: the strong tube edge-catalyst interaction [1] and the weak tube wall- catalyst interaction [2]. While the MD simulated CNTs suffer a drawback of numerous defects and thus we can't use it to explore the origin of CNT chirality, (n,m), and potential means of tube chirality control.
On the other hand, a KMC method has been developed to deal with the coalescence of fullerenes and perfect CNT formation has been seen in a KMC simulation [3]. By combining the MD and KMC, methods together, we are now able to simulate defect free CNTs and thus the origin of tube chirality and means of CNT chirality control by changing the tube-catalyst interaction has been emerged [4].

[1] F. Ding, *et al. Nano. Lett*. **8**, 463-368, (2008)
[2] Ribas MA, *et al, J. Phys. Chem*., **131**, 224501, (2009)
[3] Ding F, *et al. Phys. Rev. B,* **82**, 041403, (2010)
[4] Xu ZW, Ding F, submitted (2011)

Carbon Nanotubes As Substrates For Molecular Switches

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The adsorption of molecules to the surface of carbon nanostructures opens a new field of hybrid systems with distinct and controllable properties. Carbon nanotubes (CNTs) consisting of a single layer of carbon atoms show a high sensitivity to changes in their surrounding medium, which makes them optimal substrates. In particular, the functionalization with photochrome molecules, such as spiropyrans, is promising for engineering switches on the molecular level. First experiments have been realized illustrating how the spiropyran molecules can be used to switch the conductance of carbon nanotube transistors [1]. Here, we present a microscopic study on optical properties of pristine and spiropyran-functionalized carbon nanotubes. Our approach is based on a combination between the density matrix formalism (CNT optics) and quantum-chemical DFT calculations (molecule geometry). Spiropyrans can be reversibly switched between two different conformations: planar merocyanine (MC) and orthogonal spiropyran (SP). The conversion is induced by visible and ultraviolet light, respectively, and is accompanied by a significant change in the molecular dipole moment. As a result, the attached molecule has - depending on its conformation - an unique influence on the carrier mobility and the optical transitions in the substrate CNT. We derive many-particle Bloch equations for hybrid nanostructures including excitonic effects and dipole-induced molecule-substrate coupling. Applied to spiropyran-functionalized nanotubes, we observe considerable red-shifts of transition energies in excitonic absorption spectra of functionalized CNTs. In particular, the MC molecule with its large dipole moment (13.9 Debye) significantly influences the optical properties of the substrate CNT leading to a red-shift of up to 65 meV [2]. In contrast, the SP molecule (6.2 Debye) only slightly changes the absorption spectrum (approx. 5 meV). This clear difference between the spectra of MC- and SP-functionalized CNTs suggests the possibility of an unambiguous optical read-out of spiropyran-based molecular switches. To assure that the observed red-shift of the transition energy is stable and to find optimal functionalization scenarios, we performed calculations for different dipole densities, distributions, and orientations [2]: We observe the largest shift in the case of perpendicularly oriented dipoles with respect to the CNT axis. The distribution of molecules along the CNT surface turns out to have no measurable influence on the peak position. Furthermore, we find a surprising non-linear dependence of the observed red-shift on the dipole density predicting an optimal molecule coverage with respect to the design of spiropyran-based molecular switches. Our microscopic investigations offer new insights, which can guide future optical experiments and help realize efficient nanotube-based molecular switches. The developed many-particle Bloch equations describing the coupling mechanism between excitons in the one-dimensional nanosubstrate and the externally induced molecular dipole field can be applied to other hybrid structures.

[1] X. Guo et al., *J. Am. Chem. Soc.* **127**, 15045 (2005)
[2] E. Malic et al., *Phys. Rev. Lett.* **106**, 097401 (2011)

Plasmon Generation By Optically Excited Excitons In Individual Single Wall Carbon Nanotubes

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Optical properties of semiconducting carbon nanotubes (CNs) originate from excitons and may be tuned by either electrostatic doping [1], or via the quantum confined Stark effect (QCSE) by means of an electrostatic field applied perpendicular to the CN axis [2]. In both cases exciton properties are mediated by surface plasmon excitations [2,3,4]. We have shown recently that the QCSE allows one to control the exciton-interband-plasmon coupling in individual CNs and their optical absorption, accordingly [2]. Here, we extend our studies to demonstrate the possibility of low-energy localized surface plasmon generation by optically excited excitons in small-diameter (~1nm) semiconducting single wall nanotubes. The phenomenon is similar to the known SPACER effect (Surface Plasmon Amplification by Stimulated Emission of Radiation) reported previously for a number of metallic nanosystems [5]. The stimulated character of the exciton-to-plasmon energy transfer causes the buildup of the macroscopic population numbers of coherent localized surface plasmons. As a consequence, high-intensity coherent localized optical-frequency fields are created at nanoscale across the nanotube diameter along the nanotube surface. These strong local fields can be controlled and manipulated by fine tuning the exciton-plasmon coupling by means of the QCSE and by changing the sample temperature. The effect can be used in a variety of new optoelectronic applications of CNs, including exciton photoluminescence control and enhanced electromagnetic absorption, optical switching, near-field nonlinear-optical probing and sensing, materials nanoscale modification.

[1] M.Steiner, M.Freitag, V.Perebeinos, et al., *NanoLetters* **9**, 3477 (2009).
[2] I.V.Bondarev, L.M.Woods, and K.Tatur, *Phys. Rev. B* **80**, 085407 (2009).
[3] C.D.Spataru and F.Leonard, *Phys. Rev. Lett.***104**,177402 (2010).
[4]A.Popescu, L.M.Woods, and I.V.Bondarev, Phys. Rev. B83, 081406(R) (2011).
[5]D.J.Bergman and M.I.Stockman, Phys. Rev. Lett.90, 027402 (2003).

Monte Carlo Simulation of Water Nanosorption in Carbon Nanotubes

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A Grand Canonical Monte Carlo (GCMC) algorithm has been developed for studying the nano-scale sorption of water molecules inside smooth single wall carbon nanotubes (SWCNTs) with different diameters. Armchair (*n*,*n*) SWCNTs with indices n = 6, 8, 10, 12 and 20 (corresponding to tube radii of 4.07, 5.43, 6.79, 8.14 and 13.57 Å, respectively)and length equal to 40 Å were used. Atomistic interactions among water molecules were computed by making use of the accurate three-site SPC/E forcefield [1]; interactions between the oxygen atom of the water and the SWCNT carbon atoms (which were assumed fixed during the simulations) were modelled by a Lennard-Jones 12-6 potential with parameters taken from the work of Liu et al. [2]. All simulations were conducted in the Grand Canonical (μVT) ensemble where the water chemical potential (μ), the temperature (T = 298 K) and the volume (V) of the SWCNT were kept fixed. The water chemical potential was set equal to that of bulk water at the same temperature (T = 298 K) and pressure P = 1 atm; its value was computed via the direct particle deletion method [3]. The initial configuration consisted of an empty SWCNT which was gradually filled up with water molecules in the course of the MC simulation based on appropriate energetic (Metropolis) criteria. Results will be presented for the local density and local packing of the water molecules in the CNT, as a function of the CNT diameter. Our simulations indicate strong ordering of the water molecules which depends on CNT diameter. For example, inside the (6,6) SWCNT we observe the formation of a single water layer, but inside an (8,8) SWCNTone water ring and one water layer are formed.

[1] H.J.C. Berendsen, J.R. Grigera, T.P. Straatsma, *J. Phys. Chem.***91**, 6269-6271 (1987).
[2] Y. Liu, Q. Wang, T. Wu, L. Zhang, *J. Chem. Phys.***123**, 234701 (2005).
[3] M.G. De Angelis, G.C. Boulougouris, D.N. Theodorou, *J. Phys. Chem. B* **114**, 6233–6246 (2010).

Selective-area-grown Graphene Transistor by Thermal Chemical Vapor Deposition Method

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Graphene is a single atomic layer of carbon atoms that form a honeycomb structure, and thus, it is the ultimate thin layer. Thanks to its high carrier mobility, graphene is one of the materials with most promise to open a new era of electrical and optical integrated circuits. A method needs to be developed to grow graphene directly on sub-nm-order flat insulating layers in order to fabricate electrical and optical devices that utilize graphene. In addition, using a Si wafer as a substrate is strongly desirable. The current big Si-electronics industry has accumulated enormous amounts of knowledge and know-how concerning Si. Thus, starting graphene-electronics on a Si substrate seems practical.

We recently reported on a growth method for graphene on a sapphire substrate [1] and on an Al_2O_3 layer sputter-deposited on a SiO_2/Si substrate [2]. This paper presents a new selective-area growth method for graphene on a fine-patterned Al_2O_3 layer fabricated on a SiO_2/Si substrate. We fabricated graphene transistors successfully utilizing this selective-area growth method and obtained their excellent electrical characteristics.

Our fabrication process for graphene transistors is follows: A sputter-deposited Al_2O_3 layer (15 nm thick) on SiO_2 (100 nm thick)/Si substrate is patterned to channel, source, and drain regions. The source and drain regions are connected by the channel region. Graphene layers are grown on the patterned Al_2O_3 regions selectively with no growth on SiO_2 surface by thermal chemical vapor deposition method. The growth temperature is 800 °C and using propylene flows (4 ml/min) as the source gas and argon (400 ml/min) as the carrier gas. The graphene layers have piled structure of small platelets with a domain size of 30 nm. The averaged number of layers is 2.6 for 2-minute growth. The source and drain regions are covered with Au (100 nm thick)/Ti (10 nm thick) electrodes by using electron beam evaporation method and lift-off process.

The fabricated graphene transistors gives electrical conductance of more than 10,000 S/m which corresponds to effective electron mobility of a few tens cm^2/Vs. The drain current is modulated by gate voltage and $(I_{max}-I_{min})/I_{min}$ is more than 70% when the gate voltage changes from -40 V to + 40 V. The drain current is minimum when the gate voltage is around +30 V.

[1] M. Okai, et al., Tenth International Conference on the Science and Application of Nanotubes 2009 (Beijing, China), paper D13, (2009).
[2] M. Okai, et al., *Carbon* (Clemson, USA), paper Th-2A-5, (2010).

Determination of the Quantum Capacitance of Gated Bilayer Graphene Using a Five-Nearest Neighbor Tight-Binding Model

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Graphene-based systems have recently attracted much attention from both the experimental and the theoretical points of view. Bilayer graphene is particularly interesting because it becomes a tunable band-gap semiconductor under the application of an external electric field perpendicular to the system due to a voltage difference (ΔV) between the top and bottom gates of the bilayer device. The system thus forms a capacitor with the usual electrostatic capacitance (*CG*) depending on its geometry. However since it is an atomic layer system, quantum effects come into play giving rise to the so-called quantum capacitance (CQ) which is directly related to the change of the density of states $D(E)$ at the Fermi energy EF. In this work, an analytical expression of CQ for monolayer graphene will first be derived followed by the evaluation of CQ for our bilayer device system allowing us to compare the different responses of mono- and bi- layer graphene subject to ΔV. Our Hamiltonian is of the tight-binding (TB) type with five nearest intra-layer (within the same layer) neighbours and three inter-layer (between the two layers) hopping parameters contrary to what most authors use to evaluate quantum capacitances which is a total of two intra-layer and one interlayer parameters at most. We expect our model to give a rather clearer and more exact form of the dependence of CQ on ΔV, liberate new information about gated bi layer graphene systems and possibly explain some discrepancies- found in the literature- between experimental and theoretical Raman shift curves for some particular values of ΔV.

Electronic Structure of Graphene Adsorbed on (0001) Surfaces of SiO_{2} Substrate

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Following the first isolation of graphene in 2004, graphene has been keeping a premier position not only in the low-dimensional sciences but also in electronic device engineering due to its unique electronic properties. Recent experiments unravelled that the insulating substrates occasionally modulate the electronic properties of graphene, such as band gap opening and decrease of carrier mobility. Although much effort devoted to elucidate the physical properties of graphene adsorbed on SiO_2 surfaces, the fundamental and unified comprehension on this hybrid system is still unclear yet. Here, we investigate energetics and electronic structures of graphene adsorbed on SiO_2 (0001) surfaces using first-principles total-energy calculations [1]. We find that graphene is bound to SiO_2 surfaces via weak interaction. Despite the weak interaction between them, graphene adsorbed SiO_2 (0001) surfaces exhibits the semiconducting electronic properties. The semiconducting property is ascribed to the spatial undulation of onsite energy on C atomic site induced by the substrate atoms.

[1] N.T. Cuong, M. Otani, and S. Okada, *Phys. Rev. Lett.*, **106**, 106801, (2011).

Functionalization of graphene using nitrogen ion

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We introduce nitrogen ion to modify the electronic properties of the graphene. We could clarify the three nitrogen induced species on the few-layer epitaxial graphene(EG) on SiC(0001), such as N_2, the graphite-like nitrogen and pyridine-like nitrogen in our previous paper.[1] In this paper, we prepared the monolayer and the multilayer EG and irradiated the energy of 100 eV nitrogen ion on the EGs. We gradually annealed the sample to the temperature of 1000oC and measured the surface property changes using photoemission spectroscopy (PES), and atomic force microscopy(AFM). After 1000 °C annealing on the multilayer EG, N 1s core level spectra show that the graphite-like nitrogen remains as a major species and the work function change (Df) shows the n-type doping property by decreasing 0.75 eV. The measured shift contains both the band bending at the graphene surface 0.4 eV and an additional contribution from the interface dipole generated by the charge transfer (i.e., 0.35 eV) from nitrogen ion to graphene.

[1] Ki-Jeong Kim, Hangil Lee, Junghun Choi, Hankoo Lee, Min Cherl Jung, H J Shin, T-H Kang, B Kim and Sehun Kim, *J. Phys.: Condens. Matter* **22** 045005 (2010).

Resonant Raman Spectroscopy on ^{13}C Enriched Carbon Nanomaterials

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Isotopically enriched singlewall carbon nanotubes (SWCNTs) and graphene were investigated via Resonance Raman spectroscopy. The effect of the reduced mass variation of the isotope mixture on the phonon frequencies is described through a simple harmonic oscillator approximation. For ^{13}C modified SWCNTs linear reductions of the Raman frequencies with an increase of ^{13}C concentration are observed for the different nanotube Raman modes. In addition to the frequency dependence, the Raman linewidths as a function of the concentration of ^{13}C were also investigated and an expression describing this is presented. We observed a reduction of the G band linewidth, associated with the isotopic mass variation and a decrease of the phonon lifetime, when the isotope mix ratio has increased. Through an analysis of the Raman spectra of the radial breathing modes (RBM) obtained with different excitation energies, and the optical absorption spectra of the isotope samples, a relation between the RBM frequency and the diameter of^{13}C enriched nanotubes was also established. Measurements with different excitation energies were performed and the frequency dispersions of the D and G' bands with laser energy were observed to be the same for ^{12}C and ^{13}C nanotubes, suggesting no changes in the electronic structure after isotope enrichment.

A sample of graphene containing a spatially varying mixture of ^{13}C-graphene vs. normal graphene (having 1.1 at% ^{13}C) grown by chemical vapor deposition of methane on Cu foil was interrogated using different laser energies. A comparison between isotopically labeled SWCNTs and isotopically labeled graphene will be presented.

Element Mapping of Coated Multiwall Carbon Nanotubes

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To facilitate any real application in the nm-range, be that using graphene or carbon nanotubes, it is vital to have means to characterise the element distribution with high spatial resolution. Modern energy-dispersive X-ray spectroscopy (EDS) in electron microscopy is a straightforward method for chemical analysis. Scanning transmission electron microscopy (STEM) using high brightness electron sources and aberration correction in combination with modern spectroscopy techniques such as electron energy loss spectroscopy and liquid nitrogen free silicon drift detectors (SDD) for EDS allows the characterisation on micrometer, nm and even atomic scale [1].

As one example coated multiwall carbon nanotubes, to be used as flexible interconnects [2], were investigated. 2-D element maps of the as grown carbon nanotubes containing Co and Ni catalysts and of CuO-coated tubes will be shown. Aberration corrected STEM and EELS at 80 kV allows to count the number of tube walls and to judge the quality of the coatingfilm produced by atomic layer deposition (ALD) [3]. EDS in SEM and conventional STEM reveals within minutes the whereabouts and type of the catalyst particles and the element distribution in the ALD coating.

A combination of SEM- and TEM-spectroscopy techniques can provide reliable data on the structure and element composition of nanotube arrays in a reasonable amount of time.

[1] M. Falke, *Imaging & Microscopy*, **11**, 35-38, (2009).
[2] S. Hermann, et al.,*Microelectronic Engineering*, **87** (3), 438-442, (2010).
[3] T. Waechtler, et al.,*J. Electrochem. Soc. Vol.* **156** (6), H453-H459, (2009).

Gate-Induced Blueshift and Quenching of Photoluminescence in Suspended Single-Walled Carbon Nanotubes

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Understanding of electric-field effects on optical emission properties in single-walled carbon nanotubes is a key to the development of carbon-based nanoscale optoelectronics. In particular, gate-fields are expected to cause redshifts through screening and Stark effects, allowing for voltage-tuning of emission wavelengths. Here we report on gate-voltage dependence of photoluminescence spectra in individual suspended single-walled carbon nanotubes. As-grown nanotubes within field-effect transistor structures are identified by photoluminescence imaging using a home-built laser scanning confocal microscope. Excitation spectroscopy is used to determine their chirality, and photoluminescence spectra are collected as a function of gate voltage. Surprisingly, we find that the emission blueshifts when the gate voltages are applied. The blueshifts occur in nanotubes with different chiralities and types, suggesting that it is an extrinsic effect. Furthermore, the photoluminescence intensity decreases exponentially with gate voltage, and we find that a model assuming doping-induced exciton relaxation proportional to carrier density cannot account for all of the quenching observed.

Length Analysis of Single-Wall Carbon Nanotubes Cut by Sonication

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Single-wall carbon nanotubes (SWCNTs) were frequently dispersed into suspension by sonication with the help of various dispersing reagents (detergents), not only for fundamental but also for applied research. Although the dispersing process using sonication was thought to cut SWCNTs, to date its detailed effect has not been fully clarified yet. In this work, we have investigated the differences in length distribution of SWCNTs against various detergents and dispersing conditions. In addition, we have fabricated thin film transistor (TFT) devices by using length-determined SWCNTs and investigated the consistency of the device performance because it was suggested that the length of SWCNTs largely affects the reliability on performances of SWCNT-TFTs [1].

Four detergents, sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfate (SDBS), sodium cholate (SC), and ethylene glycol (100) stearyl ether (Brij700) have been intentionally selected to explore the effect of cutting SWCNTs during their dispersing. The length of SWCNTs in each sample, deposited on the aminopropyltriethoxysilane (APTES) functionalized silicon substrate, were statistically characterized by the analysis of topographic images taken by atomic force microscope (AFM). For fabricating TFTs, the extraction of semiconducting SWCNTs was carried out by electric-force-induced layer formation (ELF) method [2]. The average length and percentage of extracted semiconducting SWCNTs were 336 nm and 97 %, respectively, characterized by AFM and Raman. For the shortened semiconducting SWCNTs, the device performances of TFTs fabricated on silicone substrates with SiO2 layer of 100 nm thickness were measured.

As a result of dispersing by bath sonication at 70 W, while the length distributions of SWCNTs, especially in SDS dispersing, highly depended on the dispersing process, dispersing by using SC and Brij700 showed shorter length distributions compared with SDS and SDBS. In particular, the detailed analysis proved the considerable decrease in the longer part of SWCNTs (> 1mm) in the sample dispersed by Brij700. Furthermore, when SWCNTs were dispersed by using Brij700 with the horn-type sonication homogenizer at 300 W for 10 hours, all measured SWCNTs were even shorter and in the range less than 600 nm with the average length of 119 nm. To investigate the dependence on SWCNT diameter, we have analyzed lengths of three different SWCNTs with mean diameters of 1, 1.4, and 2.2 nm dispersed by using SC and Brij700. In SC dispersions, average lengths of SWCNTs with diameters of 1, 1.4, and 2.2 nm were 528, 794, and 905 nm, respectively, and the dependency according to the diameter was observed. On the other hand, SWCNTs of Brij700 dispersions were shortened in the average length of less than 400 nm without showing the diameter dependence. These results suggest that Brij700 possesses the considerably strong ability that effectively cuts SWCNTs in their dispersing process. TFTs of shortened SWCNTs exhibited high performances in mobility and on/off ratio with extreme uniformity. Detailed characteristics of devices will be discussed in the presentation. This work has been supported by NEDO project.

[1] M. Ishida and F. Nihey, *Appl. Phys. Lett.* **92**, 163507 (2008).
[2] K. Ihara, et. al., Abstract NT10, CT-38.

Quantum Conductance in Carbon Nanotube Systems

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Quantum conductance in carbon nanotube systems has been under investigation since the seminal publication by Frank et al announced a micrometre-scale room- temperature phase coherence lengthin multi-wall carbon nanotubes (MWNTs): one thousand times greater than those typically observed in metal nanowires [1]. This observation points to the application of carbon nanotubes as dissipationless interconnect for CMOS micoelectronics as well as single-molecule detection using coupled-wall MWNTs.

Quantum conductance is described by the Landauer formalism and expressed as multiples of the conductance quantum, $G_0=2e^2/h$; theory predicts that a single-wall nanotube (SWNT) will exhibit a conductance of $2G_0$. This work aims to tackle the open questions that followed the Frank et al publication, namely: i) is a direct measurement of the SWNT quantum conductance possible, ii) why do MWNTs exhibit only $1G_0$ of conductance rather than the ideal $2G_0$ per wall, and iii) can the quantum conductance of a sample be characterised byunique numbers of current- carrying 'modes' (m) and the associated transmission coefficients (T)?

Mechanically controllable break-junction (MCBJ) methods were used to probe the quantum conductance of freestanding nanotubes not subject to any chemical modification: SWNTs; the simplest multi-wall system, namely the double-wall carbon nanotube (DWNT); and MWNTs. Ideal (m=2, T=1) behaviour was observed in some SWNT systems but non-ideal m=2, T= 0.88 was also observed, sometimes in mixed ideal/non-ideal samples. In DWNTs produced by the coalescence method, one metallic channel contributes to quantum transport and additional field- and temperature-dependent two-channel contributions were observed. The electronic conductance of chemical vapour deposition grown DWNTs comprising two populations of inner- and outer-wall diameter showed two discrete conductances, $0.24G_0$ and $0.91G_0$ with non-ideal corresponding transmission coefficients of 0.12 and 0.45, respectively, were identified as those of the lowest-energy metallic subbands in outer walls. High-bias injection was dominated by two discrete conductance values for a wide range of excitation energy. Conductance in MWNT systems was found to comprise ballistic ($1G_0$ contribution from the outer-wall) and diffusive contributions.

Covalent functionalisation of the MWNTs was found to increase the diffusive nature of the electron transport whereas p-stacked chemical modification increased the number of scattering centres per nanotube but electron transport remained ballistic. In conclusion, ideal behaviour was observed in some SWNT systems but highly non- ideal behaviour was observed in multi-wall systems. The physical origin of the discrete values of the observed transmission coefficients emerged as question for future work.

[1] S. Frank, P. Poncharal, Z. L. Wang, W.A.de Heer, *Science* **280**, 1744, (1998).
[2] M. Baxendale, M. Melli, Z. Alemipour, I. Pollini, T.J.S. Dennis, *J. Appl. Phys.* **102**, 103721, (2007).
[3] M. Baxendale, P. Battini, I. Pollini, M. Endo, Y.A. Kim, T. Hayashi, H. Muramatsu, *Phys. Rev. B*, **80**, 125411, (2009).

Photocurrent Imaging Of Ultra Clean Suspended Carbon Nanotubes

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Carbon nanotubes have been found to be an excellent system for studies of optoelectronics, due to their high carrier mobility and direct bandgap [1]. Photoluminescence as well as electroluminescence from a single walled semiconducting carbon nanotube have been demonstrated [2,3] and have paved the way for future photonic device realization. Controlled injection of electrons and holes in addition to radiative recombination of the charge carriers is a requirement for electroluminescence and hence for the engineering of a carbon nanotube light emitting diode. A p-n-junction is here created by electrostatically induced n-doped and p-doped segments of the carbon nanotube by means of local gates.
Here we report photocurrent measurements on single semiconducting carbon nanotubes, grown to bridge a few micrometer wide trench in between two metal contacts. The nanotube is grown in the final step of the device fabrication, resulting in no post-growth processing and hence an ultra-clean system with potential to reach the single particle regime [4]. The doping of the system can be controlled by means of gate potential.
Results from photocurrent imaging in combination with IV-measurements of a p-n-junction in a suspended carbon nanotube will be presented. We show how the position of the p-n-junction along the nanotube axis can be tuned as a function of gate potential as well as demonstrating a technique to image the transition from a p-n- to a n-p-configuration of the local band bending in the carbon nanotube.

[1] P. Avouris, *Nature Photonics*, **2**, 341-350, (2008).
[2] J. Lefebvre, *Nano Letters*, **6**, 8, (2006).
[3] T. Mueller, *Nature Nanotechnology*, **5**, 27-31, (2009).
[4] G.A. Steele, *Nature Nanotechnology*, **4**, 363-367, (2009).

STM Images of Carbon-Nanotube Quantum Dots: Seeing a Wigner Molecule of Correlated Electrons

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The paradigm of few-electron complexes in quantum dots (QDs) relies on the idea that the lowest-energy quantized levels are filled according to Pauli's exclusion principle. If Coulomb repulsion is sufficiently strong to overcome the kinetic energy cost of localization, a different scenario is predicted: a “Wigner” molecule (WM) forms, made of electrons frozen in space according to a geometrical pattern. Despite considerable experimental effort, evidence of the WM in semiconductor QDs has been elusive so far. Here we demonstrate theoretically that WMs occur in gate-defined QDs embedded in typical semiconducting carbon nanotubes (CNTs). The unambiguous signatures of the WM state must be searched in the scanning tunneling microscopy (STM) images of the electrons. Through exact diagonalisation (ED) calculations, we unveil the inherent features of the electron molecular states. We show that, like nuclei in a usual molecule, electrons have localized wave functions and hence negligible exchange interactions [1, 2]. ED results for single and double QDs provide a simple interpretation for transport experiments in ultraclean CNTs [3, 4].

[1] A. Secchi and M. Rontani, *Phys. Rev. B* **80**, 041404(R) (2009).
[2] A. Secchi and M. Rontani, *Phys. Rev. B* **82**, 035417 (2010).
[3] V. V. Deshpande and M. Bockrath, *Nature Phys.* **4**, 314 (2008).
[4] F. Kuemmeth et al., *Nature* **452**, 448 (2008).

Two Time Scales Translational Dynamics of a One-Dimensional File of C_{60} Fullerenes Encapsulated Inside Single-Walled Carbon Nanotubes

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In addition to their numerous interesting physical properties, single-walled carbon nanotubes offer an inner cavity available to host molecules, providing scientists with an exceptional model system to study one-dimensional physics. This is particularly true when the inner molecules size is comparable to the tubes' diameters, as is the case with C_{60} fullerenes – such insertion compound being called fullerene ‘peapods’. Whereas the rotational dynamics of the encapsulated fullerenes has already been studied by inelastic neutron scattering (INS) [1] and NMR [2], their translational dynamics had yet never been observed. In this communication, we present very recent INS measurements that highlight the astonishing translational behaviour of encapsulated fullerenes on two different time scales.

The translational dynamics of the inserted C_{60} has been studied thanks to the synthesis of a large amount of peapods under the form of buckypapers – in which the tubes are mainly oriented in the buckypaper's plane. We chose experimental configurations where the scattering vector corresponding to the reciprocal parameter of the 1D chain was either parallel or orthogonal to the paper's plane, i.e. where the translational motion of the confined fullerenes was either magnified or extinguished. Experiments were performed on the time of flight spectrometer IN5 and on the spin-echo spectrometer IN11 at ILL, allowing one to have access to a large range of frequencies or time scales.

Considering an ideal 1D system of infinite length, the translational motion of fullerenes is expected to be purely quasi-elastic, its width depending on the sound velocity and on the temperature [3]. The experimental situation is much more complex as we evidenced three different components in the INS data: an elastic one and two quasi-elastic ones corresponding to very different time-scales, of typically 100 and 10 ps at room temperature. Their temperature evolutions, indicating a low temperature dynamical transition, will be presented. These original results will be discussed on the basis of analytical calculations taking into account effects of the finite size of the fullerene chains, as well as on the basis of Molecular Dynamics calculations. The 1D character of this system gives rise to very unusual behaviors, that may also be related to another intriguing phenomenon inside nanotubes: the extraordinary high transport of water [4].

[1] S. Rols, J. Cambedouzou, M. Chorro, H. Schober, V. Agafonov, P. Launois, V. Davydov, A. Rakhmanina, H. Kataura and J.-L. Sauvajol, *Phys. Rev. Lett.* **101**, 065507 (2008)
[2] K. Matsuda, Y. Maniwa and H. Kataura, *Phys. Rev. B* **77**, 075421 (2008) ; E. Abou-Hamad, Y. Kim, T. Wågberg, D. Boesch, S. Aloni, A. Zettl, A. Rubio, D. E. Luzzi and C. Goze-Bac, *ACS Nano* **3**, 3878 (2009)
[3]V.J. Emery and J.D. Axe, *Phys. Rev. Lett.* **40**, 1507 (1978)
[4] M. Majunder, N. Chopra, R. Andrews and B.J. Hinds, *Nature* **438**, 44 (2005)

Photocatalytic Activity MWCNT/TiO_2 Nanocomposites

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Multi-wall carbon nanotubes (MWCNTs) can be considered excellent supports for materials with photocatalytic properties because they can favor the surface electron transfer, they also exhibit high mechanical strength and chemical stability, and they present mesopores favoring the diffusion of reactive species. The dispersion of TiO_2 on the surface of CNTs can create many active sites for photocatalytic degradation [1]. The photocatalytic activity of TiO_2 powder depends strongly on its microstructure and physical properties [2]. In this context, to obtain a highly active photocatalyst TiO_2, it is essential to develop a thermally stable anatase phase at high temperatures with high specific area. The composite material, CNT/TiO_2, have attracted research attention due the possibility of application in various areas: water splitting for hydrogen generation, degradation of environmental pollutants in aqueous contamination and waste water treatment, carbon dioxide photo-reduction, dye sensitized solar cells, self-cleaning activity and air purification [3]. In this work, MWNTs were coated with sol-gel solutions (SGS). The SGS were prepared using two alkoxides precursors: titanium tetra propoxide $Ti(OPr)_4$ and P25 (TiO_2)-Degussa, and isopropyl alcohol, nitric acid, ammonium hydroxide and deionized water. The solutions were homogenized, filtered, dried and thermally treated at different temperatures (400 °C, 500 °C and 600 °C) for 1h. The composites were characterized structurally to analyze their properties. The photocatalytic activity of the nanocomposites was monitored following the photodegradation of methyl orange in aqueous suspension under UV irradiation. The XRD characterization shows the crystalline structure of the nanocomposites. Transmission electron microscopy (TEM) was employed to analyze the morphology of the NTCs, which indicated that the particles coated the surface of the nanotubes. The comparison of the photocatalytic activity of TiO_2 and CNT/TiO_2 composites indicates that the presence of CNTs can greatly enhance the photocatalytic activity of TiO_2.

[1] A. Jitianu, T. Cacciaguerra, R. Benoit, S. Delpeux, F. Béguin, S. Bonnamy, *Carbon*, **42**, 1147-1151, 2004.
[2] K. Zhang, F.J. Zhang, M.L. Chen, W.C. Oh, *Ultrasonics Sonochemistry*, **18**, 765-772, 2011.
[3] R. Leary, A. Westwood, *Carbon*, **49**, 741-772, 2011.

Phonon-Assisted Electron Emission From Individual Carbon Nanotube Shells

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How electrons can escape from solid surfaces into vacuum is an important problem from both fundamental and technological viewpoints. In physical pictures of traditional thermionic and field electron emission models, only electrons moving toward the emission surface may escape from a solid.[1] However, when the dimension of a solid is decreased to only one atom thick (e.g. shells of carbon nanotubes (CNTs), graphenes), electrons are strictly confined by a one-atom-thick quantum well along thickness direction and can only move in a one-atom-thick surface without velocity component normal to it. So it’s difficult to understand perpendicular electron emission from a one- atom-thick surface based on traditional thermionic and field electron emission models. How electrons can escape perpendicularly from one-atom-thick surfaces is still not well understood. Herein, we present a thorough study on perpendicular electron emission from a one-atom-thick surface. We study electron emission from side surface of individual electrically-biased carbon nanotubes both experimentally and theoretically and discover a new electron emission mechanism named as phonon-assisted electron emission.[2] The experiments are performed in situ inside a scanning electron microscope equipped with three nanoprobes. Two probes are used to apply a bias voltage to an individual suspended CNT, while the third one is used to collect emission current from lateral CNT surface. It’s found that, when the bias voltage is higher than a threshold value, emission current increases exponentially with bias voltage. A kinetic model based on coupled Boltzmann equations of electrons and optical phonons is proposed to describe perpendicular electron emission from one-atom-thick CNT shells, and well describes experimentally-measured emission current. It is shown that, the electrons moving along an electrically-biased CNT can overflow from the one-atom-thick surface due to the absorption of hot forward-scattering optical phonons. The exponential law with work function as in thermionic emission model is retained in our new model. Emission density is predicted to increase along tube axis in the direction of electric force according to phonon-assisted electron emission, which is a property peculiar to the new mechanism. A low working voltage, high emission density and side emission character make phonon- assisted electron emission primarily promising in electron source applications.

[1] W. W. Dolan, W. P. Dyke, *Phys. Rev.*, **95**, 327-332, (1954).
[2] X. L. Wei, D. Golberg, Q. Chen, Y. Bando, L. M. Peng, *Nano Lett.*,**11**, 734-739, (2011).

Real Time Manipulation and Characterization of Individual Boron Nitride Nanotubes by SPM-TEM

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Individual boron nitride nanotubes (BNNTs) are characterized by scanning probe microscopy under real-time transmission electron microscopy (SPM-TEM system). The mechanical properties of BNNTs were investigated in the atomic force microscopy (AFM) mode, while their electronic characters were studied using the conducting AFM mode. The dynamic of mechanical deformation, deformation induced current flows, and decomposition initiated by prolongs Joule heating are video captured under TEM to reveal the underlying mechanism. High-quality BNNTs were synthesized by catalytic chemical vapour deposition [1-3]. Then, mechanical test was conducted by cyclic bending using the SPM-TEM system at 1) small bending angle ~65°and 2) large bending angle ~120° [4]. We found that BNNTs survived from the small-angle test and their modulus was determined as ~0.5 TPa. However, a unique fracture failure of individual BNNTs was discovered after the large-angle cyclic bending. TEM analysis indicates that the brittle failure mechanism was initiated from the outermost walls and propagated toward the tubular axis with discrete drops of applied forces. The transport properties of these BNNTs were also investigated by conducting AFM under various bending angles [5]. We found that our BNNTs are insulating even when they are bended up to ~65o, consistent with the 6eV band gap[2]. This is in contrast to a reported data where moderate currents were flown at small bending angles [6]. When our BNNTs are severely bended, we detected up to 15nA of current flow. Under these severe mechanical deformations, we found a series of “V” shape rippling upon buckling on BNNTs [7]. Furthermore, the deformed BNNTs are recoverable upon stress release, indicting the extraordinary elasticity of these BNNTs. The critical strain to form the first ripple was measured as 4.1% and the buckling process was reversible up to 26% strain. Finally, we have investigated on the working limit of BNNTs under excessive joule heating. Results indicate that BNNTs will start to decompose at ~1000 oC, with the formation of boron nanoparicles [8]. Detail TEM analysis suggested that this decomposition are initiated from site wall defects, and progress with time. The real-time dynamics of all these observation are video captured under TEM and will be discussed in the meeting.

[1]. C. H. Lee, et al, *Nanotechnology* **19**, 455605 (2008).
[2]. C. H. Lee, et al, *Chem. Mater.* **22**,1782 (2010).
[3]. J. Wang, et al, *Nanoscale* **2**, 2028 (2010).
[4]. H. M. Ghassemi, et al, *J. Appl. Phys.* **108**, 024314 (2010).
[5]. H. Ghassemi, et al, Nanotubes and Related Nanostructures — 2009, edited by Y. K. Yap (Mater. Res. Soc. Symp. Proc. Volume 1204, Warrendale, PA, 2010), 239-242.
[6]. X. D. Bai, et al, *Nano Lett.* **7**, 2146 (2007).
[7]. H. M. Ghassemi, et al, *Nanotechnology* **22** 145602 (2011).
[8]. H. M. Ghassemi, et al, *JOM* **62**, 69 (2010).

Physicochemical Properties of Aluminum Oxide Substrates Probed with AFM, XPS, and Contact Angle Goniometry

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Water-assisted catalytic CVD using a thin Fe catalyst film supported on an aluminum oxide (AO) layer is one of the preferred methods for producing single-walled carbon nanotube (SWNT) carpets due to the high activity and lifetime of the catalyst. The AO films used as catalyst support are usually deposited using any of the physical or chemical vapor deposition techniques such as electron beam (e-beam), atomic layer deposition (ALD), and magnetron sputtering. The substrate surface during magnetron sputtering is constantly under powerful electron bombardment and the sputtered particles are known to have high kinetic energy. Particles deposited on the substrate by e-beam are generally characterized by limited mobility because of their lower kinetic energy. On the other hand, ALD is a slow, well controlled chemical deposition process whereby atomic layers are deposited one layer at a time and the films are highly uniform in thickness and relatively free of pinholes. These deposition processes are clearly different and the resulting films should have different properties. Our recent work confirmed that Fe catalyst supported on sapphire, and amorphous AO films deposited by ALD, sputtering, and e-beam have catalyst activity and life time that are remarkably different.[1] The rational design of immortal catalysts for improved and controlled growth of SWNT carpets will require a good understanding of the properties of the different AO substrates. Using scanning probe microscopy, spectroscopy, and contact angle goniometry, we have successfully elucidated the surface topography, surface energy, stoichiometry, and surface hydroxyl fraction of c-cut sapphire and amorphous AO films deposited using standard chamber conditions.

[1] Amama, P. B.; Pint, C. L.; Kim, S. M.; McJilton, L.; Eyink, K. G.; Stach, E. A.; Hauge, R. H.; Maruyama, B. *ACS Nano* **4**, 895-904 (2010).

Strength of Nanotubes, Filaments, and Nanowires From Sonication-Induced Scission

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Measurements of the mechanical properties of nanostructures, and of their strength in particular, are an essential requirement for fundamental understanding of the possibilities and performance limits of materials based on such structures. Typically, elastic-modulus and strength measurements are performed through mechanical manipulation of individual nanostructures, for example, using scanning probe techniques. However, because of the challenges intrinsically associated with nanoscale mechanics, such measurements remain technically involved and very time consuming.

In this paper, we examine the fragmentation of filamentous structures under sonication. Sonication is widely implemented in the dispersion of nano and mesoscale particles and filaments. The principal origin of the enhanced dispersion is the ultrahigh shear rate attained during cavitation events. Based on a coarse-grained model of this process, we discuss an alternative approach to probe the strength of elongated nanostructures, such as carbon nanotubes, silver nanowires and protein fibrils; and show that the limiting length that such structures reach after prolonged sonication reports accurately on their effective tensile strength. Our results furthermore shed light on the effect of commonly used sonication treatments on nanostructured materials.

Y.Y. Huang, T.P.J. Knowles and E.M. Terentjev, *Adv. Mater.* **21**, 3945 (2009).
Nature Nanotechnology Research Highlights: doi:10.1038/nnano.2009.300

Transparent Electrode with a Nanostructured Coating

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Recent development in nanostructured materials, such as carbon nanotube, graphene and metallic nanowires, has offered new ways for the realization of flexible transparent electrodes, at the same time opening possibilities of low temperature processing of optoelectronic devices. Although tremendous efforts have been made to improve the performance of these coatings (mainly centered on sheet resistance vs. transparency) through material selection and tuning the fabrication conditions, there is so far no successful technique – and equally no viable theoretical model which can accurately correlate the sheet resistance-transmission behavior to the coating microstructure. The second big question is related to the electromechanical response of the coating, a performance indicator critical to a flexible electrode. Although many papers have suggested such coatings to be more bend-resilient than the traditional oxide thin film coatings, the testing methods through which the results were obtained lack reliability and cannot be cross-compared. We address the above two questions in the present work. Using single-walled nanotubes as an example, we fabricated transparent conductive coatings and demonstrated a new technique of centrifuge coating as a potential low-waste, solution-based batch process for the fabrication of nanostructured coatings. A theoretical model is developed to account for the sheet resistance exhibited by layered random-network coatings such as nano-filaments and graphene. The model equation is analytical and compact, and allows the correlation of very different scaling regimes reported in the literature to the underlying coating microstructure. Finally, we also show a refined experimental setup to systematically measure the curvature-dependent sheet resistance.

Y. Y. Huang and E. M. Terentjev *ACS Nano*, **5**, 2082 (2011).

Auger Electron Emission From Carbon Nanotubes: An Atomistic Approach

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Auger processes are of crucial importance in understanding the electronic properties of both solid state and biological samples. In materials with a band structure, the creation of a core-hole leads to core-valence-valence(CVV) Auger electron emission, wherethe initially empty core level causes a decay that involves two valence electrons: one neutralizing the core-hole and the other being ejected. A fundamental role is played by the broadening of the Auger peak that contains information on a variety of static and dynamic screening effects. In this paper, we use ab initio atomistic methods to calculate the CVV spectra from cylindrical Carbon NanoTubes (CNTs). Specifically, we consider a cluster of Carbon atoms described by a double-zeta basis set, that are allowed to occupy the equilibrium positions of short-length (3,3), (6,6) and (10,10)-tubes. Restricted Hartree-Fock algorithms lead to a super-molecular system, whose spectrum of eigenvalues is compared with tight-binding periodic calculations on infinite nanotubes of the same chiralities. Then, we apply the Fermi's golden rule to determine the so called 'one-electron spectrum' of emitted electrons from the cluster, in which either the neutralizing or the ejected electrons lie on the same atomic-site of the core-hole. Lifetime effects in the initial and final states, as well as the electron-phonon interaction, are effectively included in a Gauss-Lorentz distribution. Particular attention is paid to the final state effect of the valence hole-hole coupling[1]. A quantitative estimation of shake-up processes at the Fermi level is proposed by extending the calculated spectra to match the valence energy range of large-size/infinite nanotubes[2]. The theoretical results show a good agreement with measurements of Auger electrons ejected from bundles of single wall Carbon nanotubes.

[1] E. Perfetto et al., *Phys Rev B* **76**, 233408 (2007).
[2] A. Sindonaet al, *Phys. Rev. A* **71**, 052903 (2005); A. Sindona et al,*Surf. Sci.*, **601**, 2805 (2007); A. Sindona et al, to appear in *JNN* (2011).

Direct Growth Of Vertically Aligned Carbon Nanotubes On Aluminium Foils Over Large Areas

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Synthesis of vertically aligned carbon nanotubes (VACNTs) has been a key subject of interest in the recent years, owing to their several applications as electron field emitters, supercapacitor electrodes, gas sensors, interconnects, atomic force microscope probes and more [1,2,3]. Majority of these applications demands a direct growth of VACNTs on metallic substrates. Synthesis of VACNTs on easily available, conducting substrates has been under investigation in the recent years. Aluminium seems to be the best cost-effective metal for the preparation of such light-weight hybrid materials. However, the reaction temperature employed for thermal catalytic chemical vapour deposition (CCVD) of aligned carbon nanotubes is usually in a range higher than 700 °C, thus precluding the use of aluminium due to its low melting point (660 °C). Moreover, various key parameters such as the composition of the catalyst, the hydrocarbon source, as well as the surface properties of the aluminium substrate used in the deposition process, greatly influence the surface density, distribution, length and diameters of the synthesized nanotubes.

We have discovered a novel catalyst combination, derived from the salts of cobalt and manganese, which resulted in a direct one-step synthesis of VACNTs that are well aligned and uniformly distributed over a large area of aluminium foils. The catalyst is loaded by a simple drop-coating procedure, unlike the usual sophisticated sputtering techniques. The reaction temperature employed for CCVD is as low as 645 °C. The average length of the synthesized nanotube arrays is 30 µm and the average diameter of the individual nanotubes is less than 20 nm. This simple method of drop-coating and depositing uniformly distributed VACNTs over large areas has a potential to be further scaled up to yield bulk amounts of well aligned carbon nanotube arrays on Al foil. A comparative study of the effect of various other supported catalysts on the characteristics of resulting nanotube forests is presented, along with an explanation of the plausible mechanism of alignment, justified by thermodynamic calculations. We also discuss about the key parameters that influence the properties of the resulting VACNT arrays. The so produced hybrid materials could find a good deal of applications in field emission devices or components of supercapacitors.

[1] J. Robertson, *Materials Today,* **7** (10), 46-52, (2004).
[2] R. H. Baughman, et al., *Science* (2), **297**, , 787-792 (2002).
[3] V. O. Khavrus, et al., *Physica E* (2011), DOI:10.1016/j.physe.2011.01.028.

Growth of Carbon Nanotube Inside Diamond

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Carbon nanotube coating is widely used in many fields from tribology to biology and represents a significant part of the already commercialized applications of the carbon nanotube. The hard conditions such as friction, high temperatures, that the coating undergoes can lead to a loss of carbon nanotube and reduce the efficiency of the device. Moreover as carbon nanotube is becoming one of the major coatings for biological sensing especially neural growth and stimulation, a toxicity issue is also raised when devices aim to be implanted into the body. Therefore solutions to strongly bind carbon nanotube to their substrate have to be found to enhance the reliability of CNT coated devices. Depending on the application, the substrate to coat has to be insulating or conductive and have chemical and tribological properties as good as the ones of carbon nanotubes. All those features can be reached with a single material: diamond. Actually diamond can be either insulating or conductive when doped with boron and the carbon chemistry is easily applied on it. In this study a new way to combine carbon nanotube to diamond in a composite material is presented. Carbon nanotube were grown inside pores made in diamond. Those pores are created by metallic etching with nickel or palladium nanoparticles that remain at the bottom of the hole after the etching. The particles are used as catalyst for the growth of multi-walled carbon nanotubes afterwards. In this process, all carbon nanotube follow a base growth mechanism. Their density and diameter depend on the density and diameter of the pores. Raman spectroscopy shows no modifications of the quality of the nanotube compare to tube grown directly on diamond. The improvement of the mechanical binding properties was successfully tested in sonic bath where most of the carbon nanotubes remained on the substrate. This method is forecasted to prevent catalyst diffusion during growth allowing a precise patterning of single carbon nanotube. This new material was also used as electrode for electrochemistry and biosensing.

In situ Evidence for Chirality-Dependent Growth Rates of Individual Carbon Nanotubes

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Chiral-selective growth of single-walled carbon nanotubes (SWNTs) remains a great challenge that hinders their use in applications such as electronics and medicine. Recent experimental [1, 2] and theoretical3, 4 reports begin to address this by suggesting that selectivity may be achieved during nucleation by changing the catalyst composition or structure. Nevertheless, in order to establish a rational basis for chiral-selective synthesis, the underlying mechanisms governing nucleation, growth, and termination of SWNTs must be better understood. To this end, we report the first measurements of growth rates of individual SWNTs through in situ Raman spectroscopy and correlate them with their chiral angles. Our results reveal that the growth rates are directly proportional to the chiral angles, in agreement with recent theoretical predictions.[5, 6] Importantly, the evidence singles out the growth stage as responsible for the chiral distribution—distinct from nucleation and termination which might additionally affect the final product distribution. Our results suggest a route to chiral-selective synthesis of SWNTs through rational synthetic design strategies based on kinetic control.

[1] Chiang, W.-H. & Sankaran, R.M. *Nat. Mater.* **8**, 1-5 (2009).
[2] Harutyunyan, A.R. et al. *Science* **326**, 116-120 (2009).
[3] Reich, S., Li, L. & Robertson, J. *Chem. Phys. Lett.* **421**, 469-472 (2006).
[4] Koziol, K.K.K., Ducati, C. & Windle, A.H. *Chem. Mater.* **22**, 4904-4911 (2010).
[5] Ding, F., Harutyunyan, A. & Yakobson, B. *Proc. Nat. Acad. Sci.***106**, 2506 (2009).
[6] Dumlich, H. & Reich, S. *Phys. Rev. B* **82**, 085421 (2010).

Characterization of Forest-like Carbon Nanotubes Synthesis Using Hexane

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In this workwe have investigated the influence of synthesis parameters in forest-like carbon nanotubes (CNTs) produced with hexane as carbon source by chemical vapor deposition (CVD). The effects of temperature, film catalyst thickness (iron) and the amount of hexane were analyzed by Raman Spectroscopy, Scanning and Transmission Electron Microscopy. The increase on the temperature has showed a clear increase in the CNTs quality, but also has increased the size of iron particles formed from the thin film as well as the amount of hexane converted into carbon, until the formation of amorphous carbon, due to the non-catalytic conversion. For thethin film thickness, inside the investigated range (1.7, 2.3 and 3.7 nm), an improvement in dispersion and a reduction of the iron particles size has occurred as the thickness raised, contrary to ours expectations. Another interesting finding was the importance of the amount of hexane used; it only influences the amount of carbon necessary for the "forest" grows. The excess of hexane results in a greater amount of amorphous carbon, although a low amount of hexane results in a smaller "forest" than would be expected.

Synthesis of nitrogen-doped carbon nanotubes by CVD correlating Raman spectroscopy and XPS

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High purity aligned multi-walled nitrogen doped carbon nanotubes were synthesized by catalytic chemical vapour deposition method (CCVD) using pyridine and Fe/Co (2:1 volume ratio) as the single C/N precursor and catalyst material. The average diameter of the synthesized tubes range between 29 nm and 57 nm while the nitrogen content of the tubes reach a maximum of 9.2 % of (atomic) nitrogen. The effects of growth time and temperature on the structure and diameter of the tubes were studied using transmission electron microscopy (TEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). TEM data reveal a sudden increase in the outer diameter/wall thickness of the tubes at a certain growth time. In addition, effect of nitrogen doping on the Raman response of doped tubes and its correlation with X-ray Photoelectron spectra was investigated. Clear trends for the I_D/I_G and I'_G/I_G (integrated area ratio) could be observed in the Raman spectra at the initial increase in nitrogen content of the samples. However at higher nitrogen contents (> 5 %) these trends were suddenly changed. XPS spectra show similar changes when analyzing the nitrogen bonding type at the same doping content. The correlation between the Raman and the XPS data suggest that at higher nitrogen doping, another nitrogen incorporation mechanism is taking place. Various methods of purification were employed in order to remove the amorphous carbon and catalyst particles. These results reveal that heat treatment in air is able to remove the amorphous carbon from the outer layer of tubes and that acid treatment could partially remove the catalyst particles. The nitrogen level however decrease significantly by acid treatment suggesting that nitrogen doped tubes are much more sensitive for these type of treatments due to their lower stability and higher reactivity.

Controllable Growth of Vertically Aligned Few-Walled Carbon Nanotubes from FePt Catalyst: A Comparative Study with Fe Catalyst

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By comparing the Ostwald ripening behavior of 1, 2 nm Fe and FePt catalyst film on Al_2O_3 support, we find FePt catalyst film has stronger interaction with Al_2O_3 support than Fe catalyst film. Strong catalyst-support interaction guarantees the deposited FePt catalyst film agglomerated into high-density, ultrafine FePt nanoparticles (NPs). While Fe NPs derived from Fe catalyst film of the same thickness are low-density, large-sized and nonuniform. When the FePt and Fe catalysts are employed to grow vertically aligned carbon nanotubes (VA-CNTs), VA-CNTs grown from FePt catalyst are of perfect alignment, high quality, high CNT wall number selectivity and narrow diameter distribution. While VA-CNTs grown from Fe catalyst are curved, poor-quality, wide wall number and diameter distribution.

Separate Control of Catalyst Particle Formation and Single-Walled Carbon Nanotube Growth in Floating Catalyst Synthesis

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Chemical vapor deposition (CVD) method is now widely used in producing single-walled carbon nanotubes (SWCNTs). SWCNTs can be synthesized either on substrates by supported catalysts or in the gas-phase by floating catalysts. The latter method is advantageous in continuous operation, which can be easily realized by feeding both sources for SWCNTs and catalysts simultaneously [1,2]. However, this simultaneous feeding causes inherent contamination of catalysts in SWCNTs, and therefore it is important to enhance the catalytic performance and reduce the amount of the floating catalyst particles based on their better understanding.

In this study, floating catalyst Fe particles were formed by thermal decomposition of ferrocene ($FeC_{10}H_{10}$) vapor and SWCNTs were grown from 0.27 vol% C_2H_2/ Ar balance at ambient pressure. Temperature was set to 1273 K at the center of the 34-cm-long furnace and gas velocity was set to 0.88 cm/s in standard condition. Two types of experiments, i.e. simultaneous feeding and sequential feeding of $FeC_{10}H_{10}$ and C_2H_2, were performed. In the former experiments, $FeC_{10}H_{10}$ and C_2H_2 were fed simultaneously from the inlet of the reactor just like ordinary gas-phase synthesis of SWCNTs. In the latter experiments, on the other hand, only $FeC_{10}H_{10}$ was fed from the inlet and C_2H_2 was fed at 0, 5, 7, 9, 11, 13 cm from the inlet of the furnace using a narrow inner tube. The aim of sequential feeding is to clearly separate the formation of catalyst particles and nucleation and growth of SWCNTs. The product was captured on a membrane filter at the outlet of the reactor and analyzed mainly by scanning and transmitting electron microscopes (SEM and TEM) and Raman spectroscopy.

The sequential feeding at 7, 9, and 11 cm yielded SWCNTs with catalysts of smaller content than the simultaneous feeding experiments, showing that the sequential feeding improved the activity ratio of catalyst particles. Also, the sequential feeding of C_2H_2 at a larger distance increased the diameter of SWCNTs, showing that catalyst particles grew larger at a larger distance from the inlet of the furnace. We also carried out the fluid dynamics simulation for the temperature profile and the gas-phase decomposition of ferrocene and found that addition of C_2H_2 just after the decomposition of $FeC_{10}H_{10}$ is the key to enhance the catalyst activity of Fe particles and reduce the catalyst contamination in SWCNTs.

[1] A. Moisala, et al., *Carbon,* **43**, 2066 (2005).
[2] P. Nikolaev, et al., *Chem. Phys. Lett.,***313**, 91 (1999).

Boron Nitride Nanotube Films Grown From Ink painting

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The growth of BNNT films on different substrates is important for realizing their special properties and applications. However, there are only a few methods that can produce high purity and density of BNNT films. Therefore, we develop an innovative boron (B) ink method that enables high-density BNNT films with any desired pattern to be grown on different surfaces [1]. The B ink is a mixture of ball milled B particles and metal nitrate ethanol solution. In the process, the B ink is first painted, sprayed or ink-jet printed on substrate with the desired pattern and then the substrate with the ink pattern is heated in nitrogen or ammonia gas for BNNT growth. It should be noted that this is the first method that is capable of growing BNNTs on non-flat, irregular shaped surfaces, such as, a fine mesh with 60µm openings, a screw with diameter of 500µm and inside and outside of a syringe needle. New properties are explored from these BNNT coatings. Strong deep ultraviolet (close to 200nm) light emission is discovered from a film of BNNTs with diameter smaller than 10nm [2]. Both superhydrophobicity and superoleophilicity are found in the BNNT film, which enables the BNNT coated mesh to separate water and oil on a microlitre scale. This versatile method is easily scalable and greatly broadens the application of BNNTs.

[1] LH. Li, Y. Chen and A. M. Glushenkov, *Journal of Materials Chemistry*, **20**, 9679–9683, (2010).
[2] LH. Li, Y. Chen, M.-Y. Lin,A. M. Glushenkov, B.-M. Chengand J. Yu, *Applied Physics Letters*, **97**, 141104, (2010).

Electronic and Mechanical Modification of Single-Walled Carbon Nanotubes by Binding to Porphyrin Oligomers

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We report on the non-covalent binding of conjugated porphyrin oligomers to small diameter single-walled carbon nanotubes (SWNTs) and highlight two remarkable observations. First, the binding of the oligomers to SWNTs is so strong that it induces mechanical strain on the nanotubes in solution and, second, a type-II heterojunction is established between long chain oligomers and small-diameter nanotubes [1].

SWNTs are promising candidates for electron acceptors in organic photovoltaics (OPVs) due to their high mobilities and large aspect ratios. Porphyrins are the primary chromophores in photosynthesis and have been proposed as light harvesting components in OPVs, such as by forming non-covalent complexes with SWNTs [2].

In this work, we have used absorption and photoluminescence measurements to carefully monitor the spectroscopic changes in SWNTs and porphyrin oligomers following complex formation. We observe a significant red-shift of the porphyrin Q-band upon binding to SWNTs, attributed to increased conjugation along the length of the oligomer owing to planarization of the porphyrin chains on the tubes [3]. In addition, we find that the porphyrin red-shift causes a significant red-shift in the SWNT transition energies. These nanotube shifts can be split into two components – a component whose sign depends on nanotube family ($q = \pm 1$) and an electronic component.

The former phenomenon follows established strain theory [4], indicating that the binding by oligomers is so strong that it mechanically strains the nanotubes. Comparable strains have not been previously observed in solution nor in any other SWNT–supramolecular complexes. The latter electronic red-shift component is dependent on nanotube diameter and oligomer length and is most pronounced for the smallest diameter SWNTs dispersed with the longest oligomers. This observation can be explained by considering the energy levels calculated from theory and experiment, where a type-II staggered heterojunction exists for this combination of tubes and oligomers only. This result provides a promising avenue for incorporating porphyrin–SWNT composites in efficient OPVs, utilising the high mobilities of both materials and the broad absorption bands of the porphyrin oligomers to capture a wide range of the solar spectrum.

[1] S. D. Stranks, J. K. Sprafke, H. L. Anderson, R. J. Nicholas, *ACS Nano*, **5**, 2307-2315, (2011).
[2] J. K. Sprafke, S. D. Stranks, R. J. Nicholas, H. L. Anderson, *Angew. Chem. Int. Ed.*,**50**, 2313-2316, (2011).
[3] F. Y. Cheng, A. Adronov, *Chem.-Eur. J.*, **12**, 5053, (2006).
[4] L. Yang, J. Han, *Phys. Rev. Lett.*, **85**, 154, (2000).

Novel Single-Walled Carbon Nanotube – Dual Polymer Nanostructures

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We report on the dispersion of single-walled carbon nanotubes (SWNTs) using two semi-conducting polymers sequentially, namely poly(3-hexylthiophene) (P3HT) and poly(9,9'-dioctylfluorene-co-benzothiadiazole) (F8BT) to create a new form of nanostructure. We have used spectroscopic techniques to show that one polymer directly coats the tube and new nanostructures of desired composition can be constructed by surrounding this with a second polymer. These nanostructures show particular promise for organic photovoltaics (OPVs). It has been recently shown that long-lived charge separation can be achieved in a SWNT- P3HT blend provided small diameter SWNT-P3HT nanohybrids are embedded in an excess matrix of P3HT [1]. However, the close alignment of the P3HT and SWNT energy levels means there is only a small barrier for charge recombination across the interface. In addition, only a small proportion of SWNTs can be incorporated into the blend because a large excess of polymer is required for adequate charge separation. In this work, we propose a nanostructure consisting of a SWNT coated in a monolayer of F8BT and embedded in an excess matrix of P3HT, such that the F8BT layer acts as a blocking layer for holes to improve charge separation.
The immediate environment of the SWNTs directly influences the nanotube transitions. In particular, small diameter SWNTs coated in P3HT exhibit a much larger red-shift in their E11 and E22 transitions than those coated in F8BT [2] and we can use this phenomenon as a probe to determine which polymer is directly attached to the SWNTs. By adding asufficient excess of P3HT, we have monitored the absorption and emission spectra of the blends in solution to find that the P3HT polymer slowly substitutes the F8BT polymer on the SWNT. However, we have shown that the desired non-substituted structure can be obtained in the solid-state provided the F8BT-SWNT proportion in the P3HT matrixis not reduced to below 10%. Finally, we have monitored the quenching of emission from the polymers using ultrafast photoluminescence measurements. We have also used transient absorption spectroscopy to show that long-lived charge transfer is observed. By using both techniques, we can fully describe the time-scales of the processes occurring in the nanostructures and provide further evidence that the desired structures have been constructed. Our results show that we can selectively manipulate the SWNT environment to create novel nanostructures which show great promise for OPVs.

[1] S. D. Stranks, C. Weisspfennig, P. Parkinson, M. B. Johnston, L. M. Herz, R. J. Nicholas, *Nano Lett.,***11**, 66, (2011)
[2] T. Schuettfort, A. Nish, R. J. Nicholas, *Nano Lett.*, **9**, 3871, (2009)

Semiconducting Polymer/Carbon Nanotube Blends for Ambipolar Light-Emitting Field-Effect Transistors

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Blends of single-walled carbon nanotubes (SWNT) and semiconducting polymers are interesting hybrid systems for organic electronic devices such as solar cells and field-effect transistors (FETs). We demonstrate that nanotubes at concentration levels well below the percolation limit have a significant impact on charge injection and transport in semiconducting polymers. We studied the effect of selectively dispersed SWNT in semiconducting polyfluorenes on the transport and emission properties of ambipolar light-emitting polymer FETs. Even at very low nanotube concentrations the charge injection of holes and electrons into poly(9,9- dioctylfluorene-co-benzothiadiazole) (F8BT) and poly(9,9-dioctylfluorene) (PFO) was significantly enhanced leading to reduced threshold voltages and lower contact resistances than in FETs with pristine polymer films. At the same time the charge carrier mobility decreased slightly. Nevertheless, the achievable ambipolar currents and thus light emission intensities are considerably higher. This overall beneficial effect is investigated in terms of the energy levels of the nanotubes and their spatial distribution within the active polymer layer. Semiconducting nanotubes selectively dispersed in a polyfluorene matrix are very well de-bundled and show unusually high photoluminescence efficiencies in the near infrared. They form type I heterojunctions with most polyfluorenes, which makes them ideal near-IR emissive dopants in polymer light-emitting devices. The improved charge transport properties of ambipolar polymer FETs with dispersed carbon nanotubes allow us to study charge and excitation transfer from the polymer matrix to the nanotubes as well as the influence of charge carrier density and electric field on their radiative properties. Combining good charge transport within the polymer matrix and efficient near-infrared emission from SWNTs could lead to novel optoelectronic devices operating efficiently in the near-infrared telecommunication wavelength window.

Measurement of the Defect-induced Barrier Height in Metallic CNTs

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We have demonstrated that the carbon nanotubes (CNTs) with semiconducting behavior in the field-effect transistor current – voltage (I-V) characteristics are preferentially grown by grid-inserted plasma-enhanced chemical vapor deposition (PECVD) [1]. It has been pointed out that the defects in the metallic CNTs (m-CNTs) could form the barrier which would be modulated by the gate bias [2], resulting in drain current (ID) modulation. In this study, we have evaluated the barrier height by measuring the temperature dependence of the FET I-V characteristics. The device showed ambipolar conduction with good off characteristics (ON/OFF current ratio: ~105 at 300 K). In the channel of this device, the barrier due to the defects in the m-CNT were detected by scanning gate microscopy (SGM), in which ID modulation by the scanning gate was not observed at the contact edges but in the CNT channel. The barrier height (Φ_B) was obtained from Arrhenius plot of the drain current. Φ_B increased at first with increase in VGS, showed a peak with a value of about 300 meV at around VGS where smallest drain off current was observed, and then decreased with further increase in VGS. These results indicate that the barriers against both electrons and holes exist in the channel. A large potential drop in the CNT channel observed by Kelvin probe force microscopy together with SGM result indicates that the potential barrier with a value of about 300 meV obtained by the Arrhenius plot reflects the barrier due to the defect formed in the m-CNT.

[1] H. Ohnaka et al, *Jpn, J. Appl. Phys,*.**45**, 5485 (2006).
[2] T. Mizutani et al, *J. Appl. Phys.*, **106**, 073705 (2009).

Time-Dependent Gray-Body Thermal Emission from Pulsed Laser Irradiated Vertically Aligned Carbon Nanotube Arrays

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Vertically aligned carbon nanotube arrays (VCNTs) have been reported to be the “blackest” material fabricated to date [1]. They also have a thermal conductivity parallel to the VCNT axis that is very much larger than their thermal conductivity perpendicular to the axis [2,3]. Even so, because of their large length/radius ratio, they can be assumed to have the same temperature in any cross section perpendicular to the tube axis. Consequently, a pulsed laser irradiated VCNT array is a candidate to produce fast thermal emission from the face of a VCNT array grown on a high thermal conductivity substrate. This is essentially a one-dimensional thermal conductivity problem [4,5], where the proximal end of the CNTs jumps in temperature when irradiated with a pulsed laser, and the tube then cools by thermal conduction down its axis to its distal end on a substrate where the temperature is fixed. We have measured and calculated analytically the time dependent infrared emission from a range of VCNT arrays with different tube lengths grown on both AlN and Si substrates. We have also measured the effective absorptivity and emissivity of these arrays to evaluate how close to an ideal black body they are. Shorter CNTs exhibit faster cooling than longer nanotubes and the effective axial conductivity can be estimated by comparison between infrared signatures and theoretical temperature distributions.

[1] Z. Yang, L. Ci, J. A. Bur, S. Y. Lin and P. M. Ajayan, *Nano Lett.* **8**,446–451, (2008)
[2] S. Berber, Y-K Kwon, D. Tománek, *Phys. Rev. Lett.* **84**, 4613-4616, (2000).
[3] H. Xie, A. Cai, and X. Wang, 2007, *Phys. Lett. A,* **369**, 120-123, (2007)
[4] J.V. Beck, K.D. Cole, A. Haji-Sheikh, and B. Litkouhi, Heat Conduction Using Green's Functions, Hemisphere Publishing, London, (1992).
[5] H.S. Carslaw and J.C. Jaeger, Conduction of Heat in Solids, 2nd. Edition, Oxford University Press, (1959).

Optimizing Carbon Nanotube Network Morphology for Thin Film Transistors

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The realization of electronic devices based on random carbon nanotube networks (CNNs) largely depends on the CNT synthesis and deposition methods used. Different strategies are now available to deposit relatively large area networks on a variety of substrates using simple, low temperature and cost-effective techniques. However, the various deposition techniques yield a range of CNN morphologies which largely define the overall performance of the device. In our study single-walled CNTs were synthesized using aerosol (floating catalyst) chemical vapor deposition process and deposited onto the substrate in the form of a random network directly after gas-phase synthesis. Four different deposition techniques were used: electrostatic precipitation [1], thermophoretic precipitation [2], filtration through a membrane filter and further press transferring [3] or dissolving the filter [4]. CNNs were synthesized under the same conditions but collected using various methods with the same deposition time of 5 seconds. The morphology of the CNNs, i.e. nanotube orientation, average area of CNT junctions, junction density and device area fill factor, was analyzed using scanning electron microscopy and atomic force microscopy, aided by image analysis software [5]. We find that mobilities and on/off ratios of bottom-gated thin film CNN transistors with the channel of 50x50 μm^2 vary with the CNT deposition method. The highest mobility was provided by the network deposited using thermophoretic precipitator or transferred by dissolving the filter, and the lowest by using electrostatic precipitator. The difference in the electrical characteristics of thin film transistors was explained by analyzing the morphological properties of the CNNs. The results suggest that engineering the CNN morphology allows to control the device performance via the deposition technique. The study contributes to the ongoing efforts directed towards the improvement of network conductivity with respect to the network morphology for device applications.

[1] M.Y. Zavodchikova, T. Kulmala, A.G. Nasibulin, V. Ermolov, S. Franssila, K. Grigoras, E. I. Kauppinen, *Nanotechnology*, **20**, 085201, (2009)
[2] D. Gonzalez, A.G. Nasibulin, A.M. Baklanov, S.D. Shandkov, D.P. Brown, P. Queipo, E.I. Kauppinen, *Aerosol Science and Technology*, **39**, 1064, (2005)
[3] A. Kaskela, A.G. Nasibulin, M.Y. Timmermans, B. Aitchison, A. Papadimitratos, Y. Tian, Z. Zhu, H. Jiang, D.P. Brown, A. Zakhidov, E.I. Kauppinen, *Nano Lett.*, **10**, 4349-4355, (2010)
[4] D. Sun, M.Y. Timmermans, Y. Tian, A.G. Nasibulin, E.I. Kauppinen, S. Kishimoto, T. Mizutani, Y. Ohno, *Nature Nanotechnology*, **6**, 156-161, (2011)
[5] D. Estrada, E. Pop, *Appl. Phys. Lett.*, **98**, 073102, (2011)

Photoemission Study of Energy Band Alignment of CNT/SiC Heterostructure Formed by Surface Decomposition

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Carbon nanotubes (CNTs)/semiconductor heterojunctions have been an important subject of research in nanoelectronics. However, CNT/semiconductor heterojunctions reported earlier were formed by either laying down or growing CNTs on semiconductor substrates, where either interface layers or native oxides were present at the interface [1]. Recently, we have been investigating CNT growth by surface decomposition of SiC [2]. By this method, aligned zigzag-type CNTs with fairly uniform tube diameters can be selectively produced normal to the SiC surface. In addition, carbon atoms of the CNTs are directly bonded to SiC at the interface without any interlayers, indicating that CNT/SiC heterojunction is a self-formed [3]. In this study, to clarify the electronic structure at the CNT/SiC interface, we performed photoemission spectroscopy (PES) experiments. CNT/SiC heterojunctions were formed by surface decomposition using n-type 6H-SiC single crystals with well-polished (000-1) faces. PES measurements were carried out at BL-6U of UVSOR-II at the Institute for Molecular Science (IMS) using synchrotron radiation. All PES spectra were measured at normal emission with the incident photon energy of 60 and 350 eV. The overall energy resolution was below 100 meV at room temperature (~300K). PES spectra near valence band maximum (VBM)of CNT films showed the existence of Fermi edge, indicating that they were metallic tubes. By measuring C 1s core levels at the CNT/SiC interfaces and energy separations between the VBMand the core levels in both CNT(~400nm)/SiC and SiC substrate samples, we determined the energy band alignment of the CNT/SiC heterostructure. Our results indicate that the band bending occurred at the interface and that the Schottky barrier height is 1.4 eV.

[1] Teng-Fang Kuo et al., *Appl. Phys. Lett.* **92** (2000) 212107.
[2] T. Maruyamaet al., *Chem. Phys. Lett.* **423** (2006) 317.
[3] M. Kusunoki et al., *Chem. Phys. Lett.* **366** (2002) 458.

Direct Conversion Neutron Detection with Nanotubes

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Detection of special nuclear materials (SNM) involves identification of neutron signature with high precision. Solid state neutron detection with ***indirect*** conversion involves two distinct materials – a neutron sensitive material for capture reactions (such as boron) and a semiconducting material for electron–hole pair generation (such as silicon). Advancements in the recent years have focused on optimization of indirect conversion geometries, transport and modern processing techniques for conventional semiconductors such as silicon and germanium. In contrast, neutron capture and charge generation are facilitated by the same material in a ***direct*** conversion neutron detector. Traditional choices for the detector material such as B5C, and uranium and gadolinium rich materials are not optimal for neutron capture, as well as generation, separation and collection of charge carriers. The limiting factor thus far originates from the rather poor semiconducting properties of direct conversion materials.

Functionalized nanotubes provide an exciting alternative where the electronic properties can be enhanced by several orders in magnitude through appropriate doping while maximizing the neutron capture reactions. One of the nanostructured materials which is relevant to neutron detection is the boron nitride (BN) nanotube which has several interesting properties including high neutron capture cross–section, ion radiation stability, thermal stability, and chemical inertness. However, BN nanotube is practically an electrical insulator with a rather large bandgap of 4 eV, approximately. Recent experiments and simulations however, have indicated the possibility of band gap tuning through doping with silicon and transition metals.

Our work explores doped BN nanotubes as a direct conversion detector material that can potentially improve the spatial, temporal and energy resolution of neutron detectors. Using density functional theory (DFT) simulations we have investigated the electronic structure of BN nanotubes doped with group-IV elements and transition metals. Our results show that the band gap can be tuned by varying the doping element and concentration. Our approach thus can potentially lead to the development of a new class of solid–state neutron detectors using nanostructures for improved sensitivity and range.

Electronic and Optical Properties of Carbon Nanotubes Films

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Single Wall Carbon Nanotubes (SWCNT) films are very attractive for optoelectronic applications since they combine the unique properties of SWCNT, and can be treated from a technological point of view as thin films, and not as individual nanostructures. Thus we have developed technological building blocks (film deposition, and etching as well as electrical contacting) for the realization of large uniform and reproducible matrix of micrometric devices. We obtained [1] state of the art results for electrical characteristics (specific contact resistance, and dispersion). Electrical transport and noise properties of such films based on purified SWCNT and sorted SWCNT (i.e. metallic or semiconductors) will be discussed since their characterization and understanding are crucial for optoelectronic applications [2]. We also characterize the IR and THz properties of free standing SWCNT-films by combining FTIR (Fourier Transform Infrared) spectroscopy and TDS (Time Domain Spectroscopy) measurements. We derive their complex optical index, which can be described using Drude, and Drude-Lorentz models. Eventually these properties will be used to design and realize anIR and THz bolometer based on SWCNT.

[1] Charlie Koechlin, Sylvain Maine, Riad Haidar, Brigitte Trétout, Annick Loiseau, and Jean-Luc Pelouard, *Applied Physics Letters*, **96**, 103501, (2010).
[2] Charlie Koechlin, Sylvain Maine, Stéphanie Rennesson, Riad Haidar, Julien Jaeck, Nicolas Péré-Laperne, and Jean-Luc Pelouard, *SPIE Proceeding*, **7945**, (2011).

Effect Of Design Architecture On The Performance Of CNT Supercapacitors

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Carbon based high surface area electrodes are desirable for higher density energy storage. Multiple properties of CNTs make them ideal as electrode materials for supercapacitors; namely their large surface area, their high electrical conductivity and their chemical stability. However, thus far their use in supercapacitors has been limited to laboratory devices due to several factors including material cost and quality, deposition methods and performance. For CNT based electrodes, the growth method, the deposition method, the type/quality/purity of material and the resulting physical arrangement have a large effect in performance. Here we report on the fabrication of two-electrode electric double-layer capacitor (EDLC) cells, and study their performance as a function of several types of CNTs architectured in multiple ways. We compare the merits of each architecture and propose a recipe for an ideal CNT based supercapacitor. Electrodes consisting of flat, random, conducting networks of SWNTs or MWNTs can be produced by vacuum filtration. This low temperature process can be used to deposit CNTs on a large variety of substrates, and films can be made transparent and conducting by controlling the thickness. These electrodes provide multiple possibilities including mechanical flexibility and transparent devices. Alternatively, forests of MWNTs, ~10s of µms in length can be grown onto Si substrates and transferred via a simple rolling mechanism onto the desired electrode or used as self standing films. These result in dense, aligned films with high conductivity, thus removing the requirement for a metallic current collector and maintaining flexibility without the use of a binder. Finally, oriented CNT forests can be grown directly onto the desired charge collector foil. Although the resulting quality of the tubes is somewhat lower due to the temperature constraints of foil growth, the resulting electrode is an excellent template and can be optimized to have a low contact resistance with the charge collector. Overall, CNTs are shown to be a suitable candidate for constructing supercapacitors, however strategic optimization is needed to optimize the architecture in order to exploit the full potential of the material. CNT arrangement has a large effect on capacitance (ranging from ~5 to 35 F/g), on equivalent series resistance (20-160 Ω) and on the resulting power densities.

Low Cost Roll To Roll Fabrication Of Flexible Carbon Nanotube Based Field Effect Devices

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The continued expansion of printing as a manufacturing process for low cost electronics is dependant on the ability to print suitable transistor devices. The technical challenges are considerable; with printing of novel materials required at high speed and with accurate patterning and registration. There has been considerable effort in the development of printable organic semiconductor materials. These have met with some success but may suffer from limited mobility, environmental sensitivity, the need for solvent orthogonality in TFT devices and cost. CNTs can potentially overcome these limitations. Although CNT based transistors have been produced using ink jet printing in a batch processing environment, to date no devices have been produced using high speed roll to roll techniques. CNTs were used as the semiconducting layer in the production of a top gate thin film transistor. This layer was printed onto a polyester substrate using flexographic techniques. Flexography allows for thin films to be patterned with feature sizes below 50μm and with controllable layer thicknesses. A CNT ink was specifically formulated for this process, which when printed forms a network of nanotubes between the source and drain electrode. Industrial grade multi walled CNTs were used to investigate the realities of volume production. The nanotube concentration was varied to tune the device characteristics. The output and transfer characteristics of the devices were studied and field effect behavior was observed. As expected, CNT concentration and source drain gap was critical to tune the on/off ratio and mobility. High CNT concentrations showed high mobility but poor on/off ratio due to the metallic component of the percolating network. Functional field effect devices have been produced using CNT based semiconducting layers. The devices have been produced using flexographic techniques thus making them suitable for high volume roll to roll production.

Single-Walled Carbon Nanotube Based Schottky Device as a Highly Sensitive Biosensor

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Single walled carbon nanotubes (SWNTs) have been widely studied due to its potential applications in various fields, such as field-effect transistor, flexible transparent electrode, chemical sensor and probe tip.[1, 2, 3, 4] Especially, SWNT based biosensor has attractive advantages, such as label-free detection, higher sensitivity and miniaturized device. [5] However, for the application of SWNTs, it is required to develop an effective method to control density, location and orientation of the SWNTs as a large dimension film. Herein, we demonstrate a high sensitive detection of biomolecules using well -aligned SWNT film based device, in which Langmuir-Blodgett (LB) technique was employed to control the density and orientation of SWNT film. Schottky barrier (SB) formed between center gold electrode and SWNT monolayer LB film was modulated by the immobilization or interaction of biomolecules. Plenty of probe molecules are easily and directly linked with thiolated molecules on gold surface in a large area, which helps the sensitivity enhancement and rapid detection of target molecules. Detection limit of our device is 100pM in streptavidin detection experiment. Real clinical serum based human immunodeficiency virus (HIV) was also detected using our device in PBS buffer solution (pH 7.4). The current was gradually decreased with increasing the concentration of HIV antibody solutions.

[1] R. Martel, T. Schmidt, H. R. Shea, T. Hertel, and Ph. Avouris, *Appl. Phys. Lett.* **73**, 2447 (1998)
[2] Daihua Zhang, Koungmin Ryu, Xiaolei Liu, Evgueni Polikarpov, James Ly, Mark E. Tompson, and Chongwu Zhou, *Nano Lett.*, **6** (9), 1880–1886 (2006)
[3] E. S. Snow, F. K. Perkins, E. J. Houser, S. C. Badescu and T. L. Reinecke, *Science*, **307**, 1942-1945 (2005)
[4] Hidehiro Nishijima, Satsuki Kamo, Seiji Akita, Yoshikazu Nakayama, Ken I. Hohmura, Shige H. Yoshimura, and Kunio Takeyasu, *Appl. Phys. Lett.* **74**, 4061 (1999)
[5] Kenzo Maehashi, Taiji Katsura, Kagan Kerman, Yuzuru Takamura, Kazuhiko Matsumoto, and Eiichi Tamiya, *Anal. Chem.*, **79** (2), 782–787 (2007)

Origin of Capacitance Change in Semiconducting and Metallic Carbon Nanotubes

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We report different mechanisms for the capacitance changes from metallic (m-) and semiconducting (s-) single walled carbon nanotubes (SWCNTs) upon gas adsorption. The sensitivity, the change of capacitance, is high and reaches ~ 2500% in the aligned s-SWCNT network, whereas the sensitivity is found to be low in the m-SWCNT network. The charge transfer/Fermi level shift and quantum capacitance related to the localized electronic density of states near the Fermi level are essential causes of the sensitivity changes upon gas adsorption, although the polarization effect also plays a role to invoke capacitance changes particularly in the aligned CNTs under strong electric field.

Oxygen-Free Fabrication and Characterization of n-Type SWNT-FETs with Al Contacts

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Both n- and p-type SWNT-FETs are required for the device application such as the complementary circuits. The conduction types of the SWNT-FETs are expected to be controlled by the work function of the contact metal. The p-type SWNT-FETs were already achieved by using high-work-function metal such as Pd. On the other hand, n-type devices with small-work-function metals such as Ca [1] and Sc [2] are not stable in air atmosphere. In the case of Al contact with relatively high stability, there are contradictory results which report n-type [3] and p-type [4] behavior. In this study, in order to clarify the electrical properties of the SWNT-FETs with Al contacts, SWNT-FETs with Al contacts were fabricated and characterized using an oxygen-free system. The SWNT-FETs with a back- gate insulator of 100-nm-thick SiO_2 were fabricated. Both a cold-wall CVD chamber for the SWNT growth and an electron-beam deposition chamber for the contact metal deposition were connected through a nitrogen-filled glove box. The concentrations of oxygen and water molecule inside the glovebox were less than 0.5 ppm and 0.029 ppm, respectively. Electrical properties of the fabricated SWNT-FETs were measured inside the glove box, and thus the completely oxygen-free process was realized throughout the experiment. The n-type SWNT- FETs with Al contacts were successfully fabricated by the oxygen-free technique without any passivation. Among fabricated eighteen devices, seven devices exhibited n-type properties, and the remaining eleven devices showed n-type-dominant ambipolar behavior. A small subthresshold swing S of 283 meV/decade was obtained with a I_{on}/I_{off} ratio more than 10^3. When the devices were exposed to the air, conduction type changed to p-type or p-type- dominant ambipolar behavior. It seems that the oxygen is responsible for the conduction type change and inhibition of n-type properties in the SWNT-FET.

[1] Y. Nosho et al., *Appl. Phys. Lett.*, **86**,073105 (2005).
[2] Z. Zhang et al., *Nano Lett.*,**7**, 3603 (2007).
[3] M. H. Yanget al., *Appl. Phys. Lett.*,**87**, 253116 (2005).
[4] Z. Chen et al., *Nano Lett.*, **5**, 1497 (2005).

Single-Walled Carbon Nanotubes/Polymer Composite Electrodes Patterned Directly from Solution

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The development of solution-processible single-walled carbon nanotube (SWNT)/polymer composites for electronic devices is essential for applying to organic electronics technology such as flexible flat-panel display devices, batteries, energy harvesting and new optoelectronic devices, and thin film transistors.[1, 2] To obtain good electrical properties, the resulting SWNT pattern films must be composed of clean, aligned, and undamaged tubes with controlled surface coverage. However, the development of SWNT/polymer composite patterns without degradation of SWNT properties and construction technique that relies on solution-based processing plays an important role in its practical applications. In particular, the controlled design of such patterns with good ordered nanostructures for desired applications is a key challenge in micro/nano electromechanical systems. In here, this work describes a simple technique for direct patterning of single-walled carbon nanotube (SWNT)/poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonate)(PEDOT-PSS) composite electrodes in a large area on a substrate based on solution transfer process by microcontact printing using poly(dimethyl siloxane) (PDMS) stamps. Various shapes of SWNT/PEDOT-PSS composite patterns, such as line, circle and square, can be easily fabricated with high pattern fidelity and structural integrity. The single parallel line pattern device exhibits high electrical conductivity (0.75×10^5 S/m) and electronic stability because of alignment of nanotubes and large-size SWNT bundles (~5 nm). Our approach provides a facile, low-cost method to pattern transparent conductive SWNT/polymer composite electrodes and demonstrates a novel platform for future integration of conducting SWNT/polymer composite patterns for electronic applications.

[1] T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata and T. Someya, *Nature Mater.*, **8**, 494 –499 (2009).
[2] S. L. Hellstrom, R. Z. Jin, R. M. Stoltenberg and Z. Bao, *Adv. Mater.*, **22**, 4204–4208 (2010).

Electrical Stability of Carbon Nanotube Thin-Film Transistor

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The effects of bias stress gate stress on carbon nanotube Thin-Film transistor(CNT-TFT) stability were investigated as a function of stress bias and stress time. The p-channel CNT-FETs used a SiO_2 and HfO_2 gate insulator, and each device made using a solution process.[1] The devices also exhibited significant change when apply gate bias. These results in a positive shift of the transfer characteristics, while negative stress results in a negative shift. Higher biases and longer stress times cause degradation of on current of the CNT-TFT. The threshold voltage(V_{th}) variations observed upon successive bias sweeps for devices following gate stress on SiO_2 gate insulator were larger than the V_{th} variation of device using on HfO_2 gate insulator. The devices also demonstrate a logarithmic time-dependent threshold voltage shift suggestive of charge trapping within the band gap and the band tails responsible for the deterioration of device parameters.[2] The CNT device using SiO_2 gate insulator only recover to near-original characteristics after stressed at room temperature without the need for any thermal and bias annealing.

[1] S.Y. Lee, S. W. Lee, S. M. Kim, W. J. Yu, Y. W. Jo and Y. H. Lee, *ACS Nano*, **5**(3)., 2369-2375, (2011).
[2] F.R. Libsch and J. Kanicki, *Appl. Phys. Lett.*, **62**(11)., 1286-1288, (1993).

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Diffusion vs Sub-diffusion of Excitons in HiPCO and CoMoCAT Carbon Nanotubes

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By studying the decay of excitons photogenerated on single-walled semiconducting carbon nanotubes (SWNTs), we show that excitons in HiPCOSWNTs exhibit classic diffusion while excitons in CoMoCAT SWNTs undergo sub-diffusive transport. We correlate this behavior to a higher defect density in the CoMoCAT samples, and show theoretically that the decay dynamics are consistent with hindered diffusion in a fluctuating potential landscape. Hence we have differentiated between intrinsic and extrinsic characteristics of exciton transport on carbon nanotubes. DNA-wrapped HiPCO SWNTs [1] and CoMoCAT tubes dissolved in sodium cholate were studied. Raman spectroscopy and XPS both indicated a significantly higher defect concentration in the CoMoCAT sample, e.g. the intensity ratio of D band to G band was a factor of two higher in the CoMoCAT nanotubes [2].

Excitation with an intense <100 fs laser pulse generated many excitons per nanotube, which decayed rapidly by exciton-exciton reactions according to a power law $n \propto t^{-|\alpha|}$ We determined the slowly-varying exponent α by numerical differentiation. At times exceeding a few ps both samples exhibit anomalous $\alpha \neq 1$ decay characteristic of diffusion-limited processes in one dimension. For the HiPCO nanotubes the exponent is $\alpha = 0.498 \pm 0.004$, consistent with the value $\alpha \equiv ½$ expected for classic Einstein-Smoluchowski diffusion, i.e. the mean-square displacement varying as $\langle z^2 \rangle \propto t^{\gamma}$ with $\gamma = 1$.

Subdiffusion is characteristic of random motion with barriers or trapping [3]. For the CoMoCAT samples we found $\alpha = 0.329 \pm 0.003$ which corresponds to subdiffusion with $\gamma<1$. We attribute this to the higher defect density.We performed Monte Carlo simulations of thermally-activated exciton diffusion and annihilation on a 1D lattice with randomly distributed energy barriers, and showed a subdiffusive decay where α depends on the nature of the energy barriers. We therefore conclude that our HiPCO samples exhibit $t^{-1/2}$ decay at long times due to intrinsic behaviour of excitons, while the CoMoCAT samples exhibit $t^{-|\alpha|}$ decay with $\alpha<0.5$ due to diffusion hindered by defects. This may explain earlier reports of Russo et al. [4] who reported diffusion-limited reactions with $\alpha = 0.5$ in HiPCO samples, and Zhu et al. [5] who reported weakly subdiffusive behavior with $\alpha = 0.45 \pm 0.03$ in CoMoCAT nanotubes.These results will influence selection of nanotubes for electronic and photonic applications.

[1] Q. Yang et al., *Nanotechnology*, **18**(40), 405706, (2007).
[2] M. Kalbac et al., *Nano Letters*, **10**(11), 4619, (2010).
[3] S. B. Yuste et al., *Physical Review E*, 80, 051114, (2009).
[4] R. Russo et al., *Physical Review B*, **74**(4), 041405, (2006).

[5] Z. Zhu et al., *The Journal of Physical Chemistry C*, **111**(10), 3831, (2007).

Large Hyperfine Enhancement At Lattice Defects In Single-Walled Carbon Nanotubes

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We present a first principles study of the hyperfine interaction in 13 C enriched achiral single-walled carbon nanotubes (SWCNTs). We show that while the hyperfine constant is extremely small in pristine nanotubes, it is significantly enhanced near lattice defects such as vacancies and Stone-Wales pairs. We argue that this hyperfine enhancement is due to electron localization around the defect sites. Using this argument we give a qualitative explanation of recent measurements on the hyperfine coupling in SWCNT-based double quantum dots which showed a larger than expected hyperfine coupling.

Growth Mechanisms Of Single Wall Carbon Nananotube From Tight Binding Computer Simulations

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Selectively growing single wall carbon nanotubes is quite a challenging task and a number of papers recently reported significant steps forward in this direction. An atomic scale understanding of the nanotube – catalyst particle interface and of the way carbon atoms get incorporated in the tube, under the conditions of the experiments is then highly desirable. Using a carefully parameterized order N tight binding model [1], we could identify the temperature and carbon chemical potential conditions for the nucleation of a tube cap on nickel particles. We could show that the nucleation takes place after the outer Ni layer(s) are saturated with carbon [2, 3]. We also discussed the role of Ni in the healing of defected carbon structures [4]. Recent technical improvements [5] of the algorithm of our tight binding Monte Carlo code made it significantly faster and make it now possible to address the tube growth by varying the growth parameters. Working in the Grand Canonical ensemble enables one to control the carbon incorporation in the open system made of an initial tube butt located on a Ni particle. The chirality of the initial tube structure and the diameter of the Ni particle are varied, as well as the growth conditions (temperature, carbon chemical potential, "feeding rate" characterized by the number of relaxation steps performed between two successful C insertions or destructions). In this parameter space, we identify two growth termination mechanisms, either by encapsulation of the catalyst particle by a graphitic layer, or by detachment of the growing tube from the catalyst. We also evidence the need for a correct matching between the tube and catalyst particle diameter. Finally, we characterize the conditions to grow tubes and focus on keeping the chirality of the initial tube butt during the growth (i.e. : growing a defectless tube). In agreement with other computer simulation studies [6] our calculations emphasize the role of short carbon (polyyne) chains that are attached to the tube lip and lead to the formation of ring structures.

[1] H. Amara et al., *Phys. Rev. Lett.*, **100**, 056105, (2008).
[2] H. Amara et al., *Phys. Rev. B* **79**, 014109 (2009).
[3] M. Moors et al., *ACS Nano*, 3 (3), 511-516, (2009).
[4] S. Karoui et al., *ACS Nano*, **4**, -10-, 6114-20 (2010).
[5] J. H. Los et al., submitted
[6] A. Page et al., *J. Phys. Chem. C* **114**, 18, 8206-11 (2010).

Stacking Dependent Electronic Structure and Transport in Bilayer Graphene Nanoribbons

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The stacking-dependent electronic structure and transport properties of bilayer graphene nanoribbons suspended between gold electrodes are investigated using density functional theory coupled with non-equilibrium Green's functional method. Two different stacking arrangements, namely the AA and Bernal (AB) of monolayer graphene nanoribbons are considered. In the AA stacking, all carbon atoms of the hexagonal rings sit atop each other, whereas only half of the atoms sit atop each other in the AB-stacked bilayer configuration. For monolayer and bilayer nanoribbon configurations, the current (I)-voltage (V) characteristics show a linear behaviour in the bias range from 0 to 1 V. Our calculations show substantially enhanced electron transmission as well as tunnelling currents in the AA stacking of bilayer nanoribbons compared to the single-layer graphene nanoribbon. Interlayer separation between the nanoribbons appears to have a profound impact on the conducting features of the bilayer nanoribbons, which is found to be closely related to the topology and overlap between the edge-localized π orbitals. This feature of the bilayer graphene nanoribbons can be used to develop practical nanoscale electronic devices.

In situ NEXAFS study of Initial Growth Process of Carbon Nanotube by Surface Decomposition of SiC

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Carbon nanotube (CNT) growth by thermal decomposition of SiC is a unique technique because CNTs grow only by heating SiC substrates above 1200 ºC in a vacuum. By this method, aligned zigzag-type CNTs with fairly uniform tube diameters can be produced without any catalysts. So far, it has been reported that nanosized cap structures (“carbon nanocap”) are initially formed and that these nanocaps determine the CNT structures. However, formation process of carbon nanocaps has never been clarified, although elucidation of growth mechanism would lead to control of structural parameters of CNTs. In this study, we carried out in situnear edge X-ray absorption fine structure (NEXAFS)spectroscopy measurement for the initial stage of CNT growth by surface decomposition of SiC. 6H-SiC single wafers with well-polished (000-1) carbon-face were used as samples. After HF treatments, the samples were transferred into a UHV chamber and heated up to an intended temperature under a H_2 ambient atmosphere. The sample temperature was monitored with a pyrometer. Above 1000 ºC, the heating rate was kept less than 1 º C/min to form carbon nanocaps. In situ C *K*NEXAFS measurements were carried out in the UHV chamber at BL-7A in the Photon Factory of KEK. The NEXAFS spectra were measured in Auger electron yield detection mode, keeping the sample at the heating temperature. Below 1000 ºC, the C *K* NEXAFS spectra were similar to those of 6H-SiC. At 1110 ºC, a weak C-C π^* resonance peak appeared at 285 eV in the spectrum, suggesting the beginning of decomposition of SiC surface. When the sample temperature was 1360 ºC, the NEXAFS spectrum was almost the same as that of graphite, indicting the carbon nanocap formation. Polarization dependence of the NEXAFS spectra indicated that direction of C-C bonds changed during the carbon nanocap formation. Based on these results, we propose a formation model for carbon nanocaps by surface decomposition of SiC.

[1] M. Kusunoki et al., *Appl. Phys. Lett.* **77** 531 (2000).
[2] T. Maruyama et al. *Chem. Phys. Lett.* **423** 317 (2006).

Tip Enhanced Raman Scattering & Multiprobe Scanned Probe Imaging & NanoLithography of Carbon Nanotubes & Graphene

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Research will be described that has focused on optimizing the essential components of instrumentation and probes for carbon nantubes and Graphene functional imaging. One important such probe isfor tip enhanced Raman scattering (TERS) and associated techniques based on full integration of scanned probe microscopy with microRaman spectroscopy. The results of this research effort have allowed for a general TERS solution that can be applied for both opaque and transparent samples and employing exciting developments of multiprobe scanned probe microscopy. It also permits for integration with all upright, inverted and dual 4 Pi microscope solutions. The probes that have worked best have been those that are based on single gold nanoparticles at the exposed tip of a low dielectric glass probe (see diagrammatic representation below). These probes were originally designed for use in tip enhanced non-linear optical microscopy (TEN)1. Such probes will be compared to other solutions in the literature especially those based on etched wires of gold or silver or coated silicon probes. The data indicate that single gold nanoparticle probes provide artifact free TERS results As part of this researchit has been necessary to define samples which have specific properties to demonstrate the nature of the TERS effect. This aspect of the research has identified the factors that maximize enhancement and minimize the optical interference that can be parasitic to the TERS signal. In addition it will be shown that these TERS developments are compatible with exciting new directions in multiprobe scanned probe microscopy measurements (see above) with probes that include not only those for TERS but also those that can be applied to multiprobe electrical, thermal and Kelvin probe scanned probe microscopy. The results indicate that these developments together with their full integration with Raman spectroscopy are powerful techniques for such carbon based fundamental and applied developments.

[1] Barsegova et al, *Applied Physics Letters* **81**, 3461-63 (2002)

High-Resolution Photocurrent Microscopy of Carbon Nanotube Film Photodiodes

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Semiconducting carbon nanotubes (CNT) are a promising material for photovoltaic applications [1]. Within a photovoltaic element CNTs can take up various functionalities, e.g. as a light absorbing layer, conducting channel material or (transparent) electrode. Here we present CNT thin film photodiodes in which CNTs act as the light absorbing layer and simultaneously promote the carrier separation and transport to the electrodes. The CNTs used in this study are highly separated (99%) semiconducting single-wall carbon nanotubes [2] that are self-assembled on a transparent substrate by an evaporation-driven process [3]. CNT thin film photodiodes are fabricated with two different contact metals, i.e. Palladium and Aluminum. The work function difference creates a built-in electric field in the device channel that transforms electron-hole pairs into free carriers at opposite contacts [4]. We use scanning oil-immersion laser microscopy in order to acquire short-circuit photocurrent and open-circuit photovoltage images of the CNT thin film photodiodes. A maximum optical resolution below 300nm is demonstrated by comparative measurements of the local potential landscape in the same device, with and without the use of immersion oil at different excitation wavelengths. The possibility to study the underside of the device contacts provides unique insight into the coupling mechanisms at the CNT-metal interface.

[1] Avouris et al., *Nature Photonics* **2** (6) 341-350 (2008)
[2] Arnold et al., *Nature Nanotechnology* **1** (1) 60-65 (2006)
[3] Engel et al., *ACS Nano* vol. **2** (12) 2445-2452 (2008)
[4] Chen et al., *Small* **4** (9) 1313-1318 (2008)

In Situ TEM Investigations Of Electronic And Mechanical Properties Of Nanotube Architectures

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Nanotubes have attracted great research interest due to their unique structure, novel properties and potential applications. However, it is important to have them connected via suitable interfaces for achieving specific functions and applications. While many studies have been conducted on the individual nanotube level, there are still only a few investigations on the complex architectures and the influence of interfaces on the device performance. In this contribution, we applied an *in situ* transmission electron microscopy (TEM) technique to investigate the electronic and mechanical properties of nanotube architectures. With the aid of atomically-resolved TEM imaging the interface structure and nanotube architecture properties were correlated. The first example is the electronic properties of fabricated carbon nanotube (CNT)-clamped metal atomic chains (MAC) [1]. This hybrid nanostructure was prepared by *in situ* machining a metal-filled CNT, which included peeling off carbon shells by a spatially positioned and energy selective electron beam and further elongating the exposed metal nanorod. First-principles calculations indicated that strong covalent bonds had been formed between the CNT and MAC. The electrical transport properties of the CNT-clamped MAC were experimentally measured, and quantized conductance was observed. The second example is the effects of a homogeneous interface on the mechanical properties of boron nitride (BN) nanobamboos, an assembly of short BN nanotubes [2]. By combining *in situ* TEM mechanical tests and molecular dynamics simulations, it was demonstrated that the interface geometry had an important influence on the mechanical properties. Under a geometry strengthening effect, the BN nanobamboos showed fracture strength and Young' modulus up to 8.0 GPa and 223 GPa, respectively.

[1] D.-M. Tang, L.-C. Yin, F. Li, C. Liu, W.-J. Yu, P.-X. Hou, B. Wu, Y.-H. Lee, X.-L. Ma, H.-M. Cheng, *Proceedings of the National Academy of Sciences* **107**, 9055 (2010).
[2] D.-M. Tang, C.-L. Ren, X. Wei, M.-S. Wang, C. Liu, Y. Bando, D. Golberg, *Submitted*, (2011).

Quantification of the Metallic/Semiconducting Ratio of Bulk SWCNT Samples by Cobalt Porphyrin Probe EPR Spectroscopy

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A simple, quantitative, and self-calibrating spectroscopic technique for the determination of the ratio of metallic (M) to semiconducting (SC) single-wall carbon nanotubes (SWCNTs) in a bulk sample is presented. The technique is based on the measurement of the electron paramagnetic resonance (EPR) spectrum of the SWCNTs to which Cobalt(II)octaethylporphyrin (CoOEP) probe molecules have been added.[1] This yields signals from both CoOEP molecules on M and on SC tubes, which are easily distinguished and accurately characterized in this work. The EPR intensities can be directly related to the mass fraction of M and SC tubes respectively.[2] By applying this technique to a variety of SWCNT samples produced by different synthesis methods, it is shown that these EPR signals for porphyrins adsorbed on M and SC tubes are independent of other factors such as tube length, defect density, and diameter.[2] CoOEP adsorption is checked to be unbiased towards M or SC tubes.

[1] S. Cambré, W. Wenseleers, J. Čulin, S. Van Doorslaer, A. Fonseca, J. B.Nagy, E. Goovaerts, *ChemPhysChem* **9**, 1930 (2008).
[2] S. Cambré, W. Wenseleers, E. Goovaerts, D.E. Resasco, *ACS Nano* **4**, 6717 (2010)

Micro-Dielectric Environment Effect on the Band Gaps of (n,m)Single-Walled Carbon Nanotubes

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The electronic states of carbon nanotubes are one of the most fundamental properties of the nanotubes. We report the finding that the band gaps of (*n*,*m*)SWNTs are strongly affected by the change in micro-dielectric environments around the isolated nanotubes[1]. In situ photoluminescence (PL) spectroelectrochemistry of the films containing fifteen isolated (*n*,*m*)single-walled carbon nanotubes (SWNTs) cast on ITO electrodes in organic solvents including DMSO, acetonitirile, DMF, THF and chloroform was completed and then the oxidation and reduction potentials, and band gaps (ΔE_{electr}) of the (*n*,*m*)SWNTs in the solvents were determined. We have discovered that the ΔE_{electr} of the (*n*,*m*)SWNTs become greater as the solvent dielectric constants decreased, which is in sharp contrast to the optical band gaps (ΔE_{opt}) that show virtually no solvent dependence. Such a strong solvent dependence of the electrochemical band gaps is due to the difference in the solvation energy of the charged SWNTs produced during the electrochemical processes.

[1] Y. Hirana, Y. Tanaka, Y. Niidome, N. Nakashima, *J. Am. Chem. Soc.*, **132**, 13072–13077 (2010).

Evaluation of Intrinsic Exciton Diffusion Length in Long Single-Walled Carbon Nanotubes

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Optical processes in single-walled carbon nanotubes (SWNTs) are mainly dominated by the dynamics of excitons which were confined in one dimension with large binding energy on the order of several hundred meV. It has established that excitons in SWNTs are mobile and, the exciton diffusion length that characterizes the average distance over which an exciton can diffuse within its lifetime is critical for SWNT photoluminescence (PL) efficiency. Previous experimental studies for evaluating the diffusion length of excitons in SWNT were mostly carried out with ensemble and surfactant or DNA wrapped SWNT samples, presenting an averaging and perturbed results. We here perform a directly measurement of the intrinsic diffusion length of excitons in a long individual-SWNT by using single-SWNT PL microscope. Long SWNT samples are prepared by gas flow-guided chemical vapor deposition on trench-patterned quartz substrates. The trenches with widths of 80-1000 nm were patterned periodically to get suspended SWNT with varying length. PL spectroscopy is performed to identify the chirality and the PL emission intensity of the individual long nanotubes. The performance of PL intensity depends on the length of the suspended SWNTs in air environment. The exciton diffusion length is extracted from the dependence of PL emission intensity on nanotube length from a single-SWNT. We show that the room temperature diffusion length in these clean and pristine SWNTs is on the order of 10^2 nanometers, which is significantly larger than those measured from surfactant [1, 2] or DNA [3] wrapped SWNT samples and on the same size scale for other suspended SWNT samples [4, 5].

[1] L. Cognet, et al., *Science* **316**, 1465-1468 (2007).
[2] L. Lüer, et al., *Nat. Phys.* **5**, 54-58 (2009).
[3] Y. Miyauchi, et al., *J. Phys. Chem. C* **114**, 12905-12908 (2010).
[4] K. Yoshikawa, et al., *J. Phys. Chem. C* **114**, 4353-4356 (2010).
[5] S. Moritsubo, et al.,*Phys. Rev. Lett.* **104**, 247402-1-247402-4 (2010).

How to Improve Interference Substrates for the Exploration of Graphene and Nanotubes

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Progress on single layer graphene can be attributed to making graphene visible using optical microscopes. Using interference colour changes on oxidized Si surfaces makes single layer graphene visible [1]. This can be explained using a Fresnel law based model. We use the transfer matrix method to calculate the local filed across the oxidized Si substrate showing that the maximum of optical surface standing waves fall at the surface of the substrate. This means that the interference substrate acts as a half cavity. We have calculated the broadening of the interference maximum due to the numerical aperture of the illumination optics. Adding a highly reflecting metal layer improves the performance of the half cavity and one can enlarge the amplitude of the surface standing wave increasing optical contrast. The fact that the maximum of the surface standing wave falls on the surface makes that the Raman signal is enhanced [2]. The maximum amplitude at the substrate surface corresponds to four times the amplitude in vacuum. We show how plasmon coupling combined with the enhanced field at the surface of the substrate contributes to the observed enhancement in graphene enhanced Raman spectroscopy [3].

[1]. P. Blake, W. Hill, A.H. Castro Netoet al., *App. Phys. Lett,*. **91**, 063124,(2007)
[2]. W.S. Bacsa, J. Lannin, *Appl. Phys. Lett.*, **61**, 19-21, (1992)
[3]. X. Ling, L. Xie, H. Xu, H. Zhang, J. Kong, M.S. Dresselhaus, J. Zhnag, Z. Liu, *Nano Letters*,**10**, 553-561, (2010)

Interfaces in Carbon Nanotube FETs Studied by Kelvin Probe Force Microscopy

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Carbon nanotubes are one of promising materials for CMOS devices because of their high carrier mobility. In the previous study, we have realized air-stable, high-performance, Si-process compatible, n-type carbon nanotube field-effect transistors (CNFETs) and CMOS inverters, utilizing fixed charges introduced in the gate insulator deposited by atomic layer deposition (ALD) [1, 2]. In this study, we studied interface dipole and charge distribution near the interfaces of the gate insulator layer by Kelvin probe force microscopy (KFM). First, we studied the interface between the contact electrode and the gate insulator. The HfO_2 dielectric films were deposited on a Au electrode by ALD technique, followed by post-deposition annealing at 300˚C in vacuum. The surface potential of the HfO_2 layer measured by KFM increased with the thickness of HfO_2,and saturated with a value of about 1 V at a thickness of about 10 nm, showing that positive charges distribute near the interface. The interface charge density was evaluated to be 4.5×10^{13} cm^{-2}. We also studied the interface between the HfO_2 gate insulator and a SiO_2 substrate. The interface charge density was evaluated to be 6.1×10^{13} cm^{-2}. In addition, we found that a monolayer deposition of HfO_2 caused an abrupt change in surface potential by 0.4 V. This suggests an existence of the interface dipole layer between the SiO2 and the HfO2. We discuss the effect of these interfaces on characteristics of CNFETs.

[1] N. Moriyama et al., *Nanotechnology* **21**, 165201 (2010).
[2] N. Moriyama et al., *Appl. Phys. Exp.* **3**, 105102 (2010).

Combining Independent Measurements on Individual Carbon Nanotubes

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We have studied the individual properties of freely suspended carbon nanotubes (CNTs) using three different measurement techniques: electronic transport measurements, Raman spectroscopy and electron diffraction measurements in a transmission electron microscope. The two latter techniques give two independent methods to determine the chirality of the nanotube [1,2]. CNTs with determined chiral indices are then studied, allowing us to tie the optical and electronic response to a known lattice structure. We have e.g. recently performed the first time-resolved (femtosecond) four-wave-mixing (FWM) measurements on individual (8, 4), (24, 14) and (28, 14) CNTs [3], directly probing both exitonic and vibrational dynamics. We will present those measurement, as well as transport and Raman measurements of known individual CNTs down to cryogenic temperatures.

[1] J. Rintala et al., *J. Phys. Chem. C*, **113**, 15398, (2009)
[2] H. Jiang et al., *Carbon*, **45**,662, (2007)
[3] P. Myllyperkiö, et al., *ACS Nano*, **4**, 6780, (2010)

Interaction Between Carbon Nanotubes And Plasmonic Surfaces

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We investigated the interaction of plasmonic surfaces with carbon nanotubes. Therefore we use surface enhanced Raman scattering on nanopatterned surfaces to gain a better understanding of the influence of high evanescent fields on macromolecules such as carbon nanotubes. We investigated the plasmonic resonance over several excitation wavelengths (532 nm, 633 nm and 756 nm) in and around the plasmonic resonance region. The plasmonic surface consisted of golden bowtie antennas in an hexagonal arrangement. These nanopatterned surfaces were obtained by shadow nanosphere lithography. This technique uses latex nanospheres as a shadow mask for metal evaporation. We prepared areas of 100 µm x 100 µm using this technique, thus giving homogeneous plasmonic areas for our Raman investigations. CoMoCat carbon nanotubes were deposited onto this substrate. Raman Spectroscopy was used to measure the properties of the nanotube plasmonic system. Plasmonic enhancement was observed for the G-Peak at 1590 cm-1 by at least one magnitude on Sapphire at the resonance wavelength at 633 nm. For wavelengths around the plasmonic resonance, no enhancement could be observed. Additionally, we found that the highest enhancement could be found at a power density around 25 kW/cm² for the plasmonic surface used.

Single-Molecule and Bulk Spectroscopy of the Electronic Transitions for Empty and Water-Filled Carbon Nanotubes

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We study the effect of water-filling on the first and second optical transitions of semiconducting single-walled carbon nanotubes by single-molecule and bulk photoluminescence-excitation (PL-EX) spectroscopy. Previously it was found by Raman spectroscopy that empty and water-filled SWCNTs coexist in aqueous surfactant solutions.[1,2] This complicates the characterization by 2D PL-EX spectroscopy in bulk solutions (as electronic transitions of empty and filled tubes are shifted, but strongly overlap). The macroscopic separation of empty from filled tubes by density gradient ultracentrifugation[3] clearly helps in this perspective, and combining this with single- molecule spectroscopy yields very detailed information on the electronic shifts and broadening effects. Statistics are obtained for SWCNTs with different diameters showing red- shifts in the order of 10-20 meV and both homogeneous and inhomogeneous contributions for the broadening. Single molecule spectroscopy furthermore allows for studying the red- shifts and broadenings in a spatially resolved way along the length of the tube. Also the effect of filling on the exciton dynamics of single empty and filled (6,4) SWCNTs is presented. Typical biexponential decays are found both for empty and filled tubes, originating from the specific exciton fine structure with a dark exciton a few meV below the bright exciton.[4] While the long time component (~1-2ns, related to the lifetime of the dark exciton state) is not influenced by the filling, the short decay times are reduced.

[1] W. Wenseleers et al., *Adv. Mater.* **19**, 2274-2278, (2007)
[2] S. Cambré et al., *Phys. Rev. Lett.* **104**, 207401, (2010)
[3] S. Cambré et al., *Angew. Chem. Int. Ed.* **50**, 2764-2768, (2011)
[4] S. Berciaud et al., *Phys. Rev. Lett.* **101**, 077402, (2008)

55 cm long semiconducting super-strong CNTs: fabrication, optical visualization, macroscopical manipulation and their capacity for the storage of mechanical energy

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Ultralong carbon nanotubes (CNTs) have received extensive attention due to their easy fabrication of massive FET devices with nearly identical properties and potential for direct spinning into super strong fibres. However, the fabrication of centimetre-long CNTs is still restricted by many factors and the highest length is 20 cm in the published reports [1]. Besides, manipulation of individual ultralong CNTs is not an easy task due to their nanoscale diameters while macroscale lengths. In this contribution, we report the fabrication of 55 cm long semiconducting carbon nanotubes (CNTs) as well as their optical visualization, macroscopical manipulation, and huge capacity for the storage of mechanical energy. These CNTs were synthesized by water-assisted chemical vapor deposition (CVD) with a growth rate up to 80-90 μm/s. They were selectively semiconducting tubes with a mixture of 49% of double-walled carbon nanotubes (DWNTs), 40% of triple-walled carbon nanotubes (TWNTs), and 11% of single-walled carbon nanotubes (SWNTs). These CNTs also have perfect structures and identical chiralities along the tubes at least for several centimetres [2]. By deposition of TiO_2 particles onto the tubes, the individual CNTs could be visualized under optical microscope due to the strong brightness and reflectivity of TiO_2 particles to visible light. With the optical visualization of individual CNTs, they could be easily manipulated on the macro scale, such as stretching, blowing, vibrating, etc. We measured the mechanical properties of as-synthesized CNTs through a special designed device. The CNTs with perfect structures have tensile strength of 200 GPa, Young's modulus of 1.34 TPa, and breaking strain of 17.5% [3]. Meanwhile, a signal generator linked with a loudspeaker was used to measure the acoustic vibration of the suspended CNTs. They could endure the vibration of hundreds million times without breaking, showing excellent strain-relaxation reversibility and high fatigue resistance capability. The high stiffness and ability of the CNTs to keep high strain endow their extraordinary performance on mechanical energy storage. They have an energy density as high as 1125 Wh/kg and a power density of 144 MW/kg. The superb mechanical property proves the potential of ultralong CNTs not only as a super strong fibre in the future, but also as an effective storage medium with mechanical energy for nano- electromechanical system, flexible device, sensors, actuator, antenna, and so on.

[1] Q. Wen, R. F. Zhang, W. Z. Qian, Y. R. Wang, P. H. Tan, J. Q. Nie, F. Wei, *Chem. Mater.* **22**, 1294-1296, (2010).
[2] Q. Wen, W. Z. Qian, J. Q. Nie, A. Y. Cao, G. Q. Ning, Y. Wang, L. Hu, Q. Zhang, J. Q. Huang, F. Wei, *Adv. Mater.* **22**, 1867-1871,(2010).
[3] R. F. Zhang, Q. Wen, W.Z. Qian, D. S. Su, Q. Zhang, F. Wei, Adv. Mater. DOI: 10.1002/adma. 201100344, (2011).

Surface Modification of Directly Spun Carbon Nanotube Films

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Carbon nanotubes (CNTs) have revealed unparalleled properties in many areas of science; however the employment of as-made CNTs is still in need of fine tuning. The chemical vapor deposition direct spinning process of CNT films affords specimens adulterated with extraneous disordered carbon material. That, in turn, has an unfavorable effect on their compatibility with polymer matrices in composite applications. The most common strategy to obviate this problem has been hazardous acid pre-treatment, the disadvantage of which is the need for subsequent neutralization as well as drying steps. In this study, we explored the possibility of using cheap, widely available and environmentally friendly hot air treatment. This method was found successful to improve the purity of the material as confirmed by Raman spectroscopy and electron microscopy. Moreover, it enabled gentle tailoring of the film surface chemistry, which improved its wettability. The water contact angle of a carbon nanotube film could be adjusted to mimic that of a substance it can be combined with and thus possibly enhance their interaction.

Ingress of Liquid into a CNT Assembly

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The subject of this paper is a study of liquid ingress into a high performance carbon nanotube (CNT) assembly. The fact that the CNT assembly consist of a network of carbon nanotubes allows it to provide highly accessible porosity and surface area for foreign molecules to penetrate into its structure. This also has an effect on the electrical properties of the material, which indicates that the CNT assembly could be used as a sensor for liquid detection.

Electromechanical Properties Of Carbon Nanotube Fibre Under Strain

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Individual carbon nanotubes (CNTs) were found to show piezoresistivity with gauge factors up to thousands. The magnitude of the tensile force evoked resistivity change was found to strongly depend on chirality of the strained CNTs and the effect was attributed mostly to change in their bandgap [1]. It was also demonstrated that larger assemblies of carbon nanotubes are showing piezoresistivity but with much smaller gauge factors than individual nanotubes. CNT fibres i.e. long assemblies of axially aligned CNTs which are particularly interesting for many sensing applications were investigated by several research groups [2-4]. The CNT fibres showed changes to the electrical resistivity due to tensile forces applied in the direction of the main fibre axis. This phenomenon was again associated with the change in the bandgap of the constituent individual CNTs. The thorough investigation of the electrical resistance of the fibre response to axial forces show, however, that in such assemblies the network interaction in the fibres is likely to be equally important to the changes in the bandgap. Electromechanical measurements of the CNT fibre soaked with polyethylene glycol showed the influence of the interbundle and nanotube-nanotube spacings on the resistivity and stiffness of the fibre. Furthermore, due to the stress relaxation, realignment of the CNT network within the fibre was observed by X-ray diffraction and also revealed through the improvement of electrical conductivity.

[1] J. Cao, Q. Wang, H. Dai, *Phys Rev Lett*, **90**, 157601, (2003).
[2] H. Zhao, Y. Zhang, P.D. Bradford, Q. Zhou, Q. Jia, F.-G.Yuan, Y. Zhu, *Nanotechnology*, **21**, 305502, (2010).
[3] F.A. Hill, T.F. Havel, A.J. Hart, C. Livermore, *J. Micromech. Microeng.* **20**, 104012, (2010).
[4] N. Mallik, M.J. Schulz, V.N. Shanov, D. Hurd, S. Chakraborty, Ch. Jayasinghe, J. Abot, A. Song, *Adv. Mat. Res.*, **67**, 155-160, (2009).

Magnetic Behavior of Pure and N-doped MWNT Nanostructures with Controlled Morphologies

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In this work we describe a method to produce multi-walled carbon nanotubes (MWNTs) and nitrogen doped multi-walled carbon nanotubes (CN_xMWNTs) with controlled morphologies. The samples were synthesized by chemical vapor deposition method (CVD) using ferrocene ($FeCp_2$) and toluene (C_7H_8) for MWNT, or benzylamine (C_7H_9N) and ferrocene ($FeCp_2$) for CNX- MWNTs. Both nanotubes types (pure and N-doped) were grown on SiO_2/Si substrates (2 cm x 1 cm). The morphology modifications resulted from the adjustment of the hydrostatic pressure in the downstream liquid trap. All nanotube samples were characterized by scanning electron microscopy (SEM), powder X-ray diffraction analysis, and their magnetic properties were studied using aphysical properties measurement system (PPMS). The X-ray diffraction studies show the presence of graphitic carbon and metallic phases caused by the introduction of iron and iron carbides inside the nanotube cores. The analysis of the magnetic properties exhibits a possible path to enhance the coercive fields, remanence and saturation values for both MWNTs and CN_xMWNTs by modifying the synthesis conditions.

Effect of Carbon Sources on the Diameter of SWCNTs Synthesized by DIPS Method

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Properties of single-walled carbon nanotubes (SWCNTs) vary significantly with the structures (wraping vectors, lengths) as well as the dispersion state within a given sample. Many efforts have been focusing on the controlled synthesis of SWCNTs with a certain structure. Previously, we reported that the diameter of SWCNTs synthesized by direct- injection-pyrolytic-synthesis (DIPS) method [1] could be controlled by changing the amount of C_2H_4 addition; increasing the amount of C_2H_4 resulted in the decrease in diameter of SWCNTs [2], with the high G/D ratios measured from Raman scattering (generally >100). In the present study, we have investigated the effect of CH_4 addition on the synthesis of SWCNTs at 1200 °C by DIPS method. Toluene was used as the primary carbon source and CH_4 as the secondary carbon source. The mixture of hydrogen-argon gases was used as the carrier gas, instead of pure hydrogen for C_2H_4 addition. The characterization of SWCNTs were performed by electron microscopy observations (SEM and TEM), resonant Raman Scattering and optical absorption spectroscopies. It was found that the yield of SWCNTs was affected by the composition of catalyst precursor and the promotor added to toluene. The addition of CH_4 increased the yield of SWCNTs up to about 200 mg/h at a certain condition. Different from the case of C_2H_4 addition, on the other hand, the diameter range of synthesized SWCNTs was almost constant (2.2-2.4 nm), even if the added amount of CH4 was changed. The G/D ratios were somewhat lower than that in the case of C_2H_4 addition, but kept between 50-120, according to the reaction conditions.

[1] T. Saito, et al., *J. Phys. Chem. B*, **110**, 5849, (2006).
[2] T. Saito, et al., *J. Nanosci. Nanotech.*, **8**, 6153, (2008).

Hetero-junctions of Carbon Nanotubes and Boron Nitride Nanotubes

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Heterojunctions of boron nitride nanotubes (BNNTs) and carbon nanotubes (CNTs) are predicted to have appealing properties that are not available from pure BNNTs and CNTs. These BNNT/CNT junctions are expected to have tuneable electronic, photonic, magnetic, and spintronic properties. Here we report on the first success of growing two types of BNNT/CNT junctions and their properties.

Theory predicts that BNNT/CNT junctions [1, 2] and BN sheet/graphene junctions [3, 4] are energetically stable. Various configurations of such BNNT/CNT nanotubular junctions have been evaluated and concluded as follows:1) BNNT/CNT junctions are energetically stable either in the armchair or the zigzag configurations. 2) Zigzag BNNT/CNT junctions posses flat band structures with tuneable direct band gaps (~0.5 to 2.0 eV). Thus these BNNT/CNT junctions are promising ferromagnetic, spintronic, electronic, and photonicmaterials. 3) Armchair BNNT/CNT junctions will have direct band gap and can form Schottky barrier devices, diodes, and quantum dots etc.

Experimentally, the growth of BNNT/CNT junctions was hindered by the absent of a common growth techniques for both BNNTs and CNTs. Based on our recent capabilities in growing CNTs [5-7] and BNNTs [8-11], we have succeeded in producing BNNT/CNT junctions using a series of common catalysts. Results indicated that two types of new nanotubular structures were realized 1) branching, and 2) co-axial BNNT/CNT junctions. The details of the synthesis methodology, the growth model, and properties of these junctions as realized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS), Raman spectroscopy, Fourier-transformed IR (FTIR), and scanning probe microscopy (SPM) will be discussed in the conference

[1]. X. Blase, J.-C. Charlier, A. De Vita, R. Car, *Appl. Phys. Lett.***70**, 197 (1997).
[2]. J. Choi, Y-H Kim, K. J. Chang, D. Tománek, *Phys. Rev. B* **67**, 125421 (2003).
[3]. S. Okada, M. Igami, K. Nakada, A. Oshiyama, *Phy. Rev. B* **62**, 9896 (2000).
[4]. S. Okada, A. Oshiyama, *Phy. Rev. Lett.* **87**, 146803 (2001).
[5]. V. Kayastha, Y. K.Yap, S. Dimovski, and Y. Gogotsi, *Appl. Phys. Lett.* **85**, 3265 (2004).
[6]. V. K. Kayastha, et al, *Appl. Phys. Lett.* **86**, 253105 (2005).
[7]. V. K. Kayastha, S. Wu, J. Moscatello, Y. K. Yap, *J. Phys. Chem. C* **111**, 10158 (2007).
[8]. J. Wang, et al, *Nano Letters.* **5**, 2528 (2005).
[9]. C. H. Lee, et al, *Nanotechnology* **19**, 455605 (2008).
[10]. C. H. Lee, M. Xie, V. K. Kayastha, J. Wang, Y. K. Yap, *Chem. Mater.* **22**, 1782 (2010).
[11]. J. Wang, C. H. Lee and Yoke Khin Yap, *Nanoscale* **2**, 2028 (2010).

The Synthesis of Vertically-aligned Carbon Nanotubes on an Aluminum Foil Laminated on Stainless Steel

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Aligned carbon nanotubes (CNTs) were grown on an aluminum foil laminated on a flexible stainless steel (SS) substrate [1]. Lamination was carried out under a pressure of 10 MPa with simultaneously heating at 400 ºC. The laminated Al foil was spray-coated with an iron chloride catalyst precursor solution and the CNTs were grown using water-assisted chemical vapor deposition at 810 ºC. The CNTs grew as vertically aligned forests, approximately 600 µm in height, within 600 s without crumpling of the Al foil. The Al foil acts as a sacrificial barrier layer to grow the CNTs. The CNTs had 2-30 walls with an inner diameter of 3-8 nm. Thermogravimetric and field emission analysis of the CNTs revealed a degradation temperature and turn-on field of 643.5 ºC and 0.46 V/µm, respectively. Transmission electron microscopy and x-ray photoelectron spectroscopy were used to analyze the Al-SS interface and chemical states. After removing the CNTs, the flexible SS substrate could be cleaned, recoated with Al and reused for CNT growth. Overall, this process is a repeatable and continuous roll-to-roll processable method that can be scaled up for industrial production.

[1] S. P. Patole, H. I. Kim, J. H. Jung, A. S. Patole, H. J. Kim, I. T. Han, V. N. Bhoraskar and J. B. Yoo, *Carbon*, (In press DOI: 10.1016/j.carbon.2011.04.051).

Changing Chirality During SWNT Growth: A Reactive Molecular Dynamics / Monte Carlo Study

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One of the major obstacles in making SWNTs applicable in everyday electronic applications on the large scale, is our current inability to control the exact properties, and specifically the chirality of the tube. On a fundamental level, the mechanism of chirality determination is indeed not yet known. While many researchers have worked on the growth of SWNTs using atomistic simulation techniques, these works have always resulted in highly defected structures, due to the neglect of long time scale effects. These simulations therefore do not allow to study the chirality determination during growth. Recently, we have demonstrated the importance of taking these long time scale effects into account, in generating a SWNT with – for the first time – a definable (12,4) chirality [1]. In the present work, we focus on the growth mechanism as well as on the exact mechanism of chirality formation during the growth using this novel simulation methodology. The observed SWNT growth process was found to proceed through a number of distinct steps, viz. the dissolution of carbon in the metallic particle, the surface segregation of carbon with the formation of aggregated carbon clusters on the surface, the formation of graphitic islands that grow into SWNT caps, a restructuring process of the carbon network in which many topological defects are healed, and finally continued growth of the SWNT. Usually, it is assumed that the chirality is determined during the initial cap formation, and that this chirality subsequently remains invariant. However, we here demonstrate that it is possible that the chirality still changes after the initial cap formation, through a metal-mediated restructuring process. Specifically, we observe the SWNT chirality to change from (11,0) (i.e., zigzag type) to finally (7,7) (i.e., armchair type). These calculations demonstrate for the first the simulated growth of an armchair SWNT with a definite chirality on a surface-bound catalyst.

[1] Neyts et al., *ACS Nano* **4** (2010) 6665

Simulated PECVD Growth Of Aligned Single Walled Carbon Nanotubes

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Traditionally, carbon nanotubes (CNTs) are grown in arc discharges, laser ablation sources or in catalytic chemical vapor deposition (CCVD). Since about 10 years, CNTs are also grown by means of plasma-enhanced chemical vapor deposition (PECVD). PECVD allows the formation process to occur at lower temperatures, which is beneficial for e.g. deposition on temperature sensitive polymeric substrates. Very recently, it has also become possible to generate SWNTs in a PECVD process. Besides the lower growth temperature, PECVD for SWNT growth has additional advantages over thermal CVD such as alignment of the SWNTs during the growth (instead of forming spaghetti as in thermal CVD). Furthermore, using PECVD, freestanding SWNTs can be produced, and most importantly, it offers perspective on controlling the chirality of the growing SWNTs. Because these are very recent developments, until now there has been very little fundamental research on the precise PECVD-based SWNT growth process. Here, we investigate the fundamental mechanisms of SWNT growth in a PECVD- setup using state-of-the-art atomistic simulations. The simulation technique that we use is a hybrid molecular dynamics / force biased Monte Carlo (MD/fbMC) model. Recently, we have demonstrated its effectiveness by simulating a chiral (12,4) SWNTs [1]. Using small, surface bound nickel nanoparticles as catalysts, we demonstrate in this work how the electric field can enhance the phase separation between the carbon and the nickel. When applying weak electric fields, phase separation is barely enhanced and typical thermal CVD growth results emerge. Applying higher electric fields, however, does enhance phase separation and forces the nucleation of the SWNT cap to occur in alignment with the field, resulting in aligned SWNT growth. Finally, when applying very strong electric fields, SWNT caps can no longer nucleate, and amorphous carbon is formed instead.

[1] E. C. Neyts, Y. Shibuta, A. C. T. van Duin, A. Bogaerts, *ACS Nano* 4 (2010) 6665

Ethanol Assisted Floated CCVD Synthesis of Few Walled Carbon Nanotubes

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The effect of growth conditions and catalyst lifetime on the vertically aligned few walled carbon nanotubes "VA-FWCNTs" production in macroscopic form through the EtOH- assisted floated-catalytic chemical vapour deposition (EtOH-CCVD) technique has been investigated. The EtOH concentration in toluene-ferrocene solution was found to strongly influence the catalyst activity, the growth rate of the VA-FWCNTs as well as the walls number in the final products. The CNTs arrays grown by EtOH-assisted CCVD were systematically investigated using XRD, low and high magnification "TEM and FESEM" electron microscopy, thermal analysis "TGA", XPS and Raman spectroscopies in order to determine the VA-CNTs structure, morphology, selectivity, density, purity and yield.

Single-Walled Carbon Nanotube Growth at Low Pressure from Pt catalyst using Alcohol Gas Source Method

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Carbon nanotubes (CNTs) have been anticipated for application in a lot of future nanodevices. To fabricate CNT devices in a conventional LSI process, it is desirable to grow CNTs under high vacuum. Recently, using alcohol gas source method, we achieved single-walled carbon nanotube (SWNT) growth under an ethanol pressure of 1×10^{-4} Pausing Co catalyst [1, 2]. However, the yield of grown SWNTs was too low to fabricate CNT devices. In this study, using Pt catalyst, we attempted to increase the SWNT yield in the low pressure growth. SiO_2 layers formed on Si were used as substrates and Pt was deposited on them by either an e-beam evaporator or a pulsed arc plasma gun. The nominal thickness of Pt catalysts were varied between 0.025~0.5 nm. SWNT growth was carried out at 700 ºC using the alcohol gas source method in a ultra high vacuum (UHV) chamber. The ambient ethanol pressures during the growth were set between 1.0×10^{-4} ~ 1.0×10^{-2} Pa. The grown SWNTs were characterized by SEM and Raman spectroscopy, and the size distribution of catalysts was analyzed using TEM observation. SEM results showed that web-like CNTs were grown overall substrates, irrespective of the ethanol pressure. In the Raman spectra, both G band and RBM peaks were observed, indicating growth of SWNTs using Pt catalysts. The G band intensity increased as the ethanol pressure decreased, and it reached its maximum at 1.0×10^{-4} Pa. Compared with the growth using Co catalyst, the SWNT yield was more than 10 times larger at an ethanol pressure of 10^{-4} Pa. Also, the average diameter of SWNTs was smaller in the growth with Pt catalyst. TEM results suggest that the reduction of SWNT diameter was caused by the suppression of surface migration of catalysts during the growth. The growth mechanism on Pt catalyst will be discussed based on the decomposition of ethanol and diffusion of carbon atoms on the catalyst surface.

[1] K. Tanioku et al., *Diamond Relat. Mater.* **17** 589 (2008).
[2] T. Maruyama et al. *J. Nanosci. Nanotechnol.* **10** 4095 (2010).

Towards Chirality-controlled Growth of Single-walled Carbon Nanotubes

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In this contribution, we present a series of our efforts aiming at structure-controlled synthesis of single-walled carbon nanotubes (SWNTs). Firstly [1], we have developed a novel catalyst system where SiO_2-supported cobalt (Co) catalyst is partially reduced and anchored by unreduced Co ions in a carbon monoxide (CO) CVD process. The resulting sub-nanometer metallic Co clusters catalyze growth of small diameter SWNTs with a narrow diameter distribution. The chiral selectivity of SWNTs has also been largely improved with only a few SWNT species, such as (6,4), (6,5), (7,5), (8,3), (8,4) and (7,6) observed in the products grown at 600 ºC. Secondly [2], we show that high quality small diameter SWNTs with a narrow diameter distribution can also be grown on a silica-supported monometallic nickel (Ni/SiO_2) catalyst at temperatures as low as 500 °C. By comparing the properties of SWNTs grown on Ni with those grown on the above-mentioned Co catalysts, it is indicated that chiral-selective growth of SWNTs can be achieved by tuning the catalyst compositions. Thirdly [3], a unique MgO-supported bimetallic FeCu catalyst system has been developed which facilitates a predominant growth of (6,5) SWNTs at 600 ºC in a CO atmosphere at ambient pressure. The (*n,m*) distribution is significantly narrower than that of CoMoCat tubes. It was shown that the chirality selectivity can be further increased by adjusting the ratio of Fe and Cu. Both the MgO support and the Cu promoter can be easily removed after the growth. In the end [4], in contrast to all the above endeavors where SWNTs were produced at low growth temperature which restricts the tubes to a relatively thin diameter, we established a new approach based on an aerosol floating-catalyst CVD process in an effort to produce nanotubes with a narrow chirality distribution, while maintaining the large diameter of high- temperature routes. It is found that introducing 500 ppm of ammonia resulted in SWNTs with the majority having chirality around (13,12). Above 90% of the nanotubes made using the ammonia route have a chiral angle in the range 20–30°, and 50% between 27° and 29°. The average tube diameter is 1.67 nm. In order to avoid the optical limitation usually for detecting large-diameter nanotubes, electron diffraction technique was employed for faithful chirality determination.

[1] He, M. S. et al., *Chem. Commun.* **47**, 1219-1221, (2011).
[2] He, M. S. et al., *Nano Res.* **4**, 334-342, (2011).
[3] He, M. S. et al., *J. Am. Chem. Soc.* **132**, 13994–13996, (2010).
[4] Zhu, Z. et al., *J. Am. Chem. Soc.*, **133**, 1224–1227, (2011).

Laser-Induced Growth Of Carbon Nanotubes

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For almost two decades the electronic and optical properties of carbon nanotubes (CNTs) have suggested their application in fields from nano-electronics to nano-optics. Despite intense research on the syntheses of CNTs, however, in most cases the utilization of CNTs is still inhibited by lack of control over the CNT growth. On the other hand the characterisation of CNTs by optical means has been well established and allows distinguishing individual single-walled CNTs of different chirality.

In this study we investigate a novel approach for controlling the growth of CNTs, namely by focused laser light. Light reaching the catalyst covered sample creates local heating corresponding to the substrates and catalysts optical properties, thereby inducing catalytic chemical vapour deposition (CVD) of CNTs. The advantage of this technique over standard CVD is the high and, in particular, fast control over the growth conditions via the laser parameters, combined with in-situ optical characterisation of the grown structures.

Reversible Laser-Induced Modification Of The Optical Properties Of SWCNTs

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Currently a wide range of applications for CNTs, particularly for SWCNTs, are hampered by the lack of direct control over the growth. In response post-growth selection methods have been developed alongside novel growth techniques, both of which require precise characterisation of the growth output. For in-situ growth characterisation the optical characteristics of CNTs are often exploited due to their non-disruptive nature for the growth process, producing well-defined Raman modes, fluorescence spectra (of semiconducting CNTS), and distinct scattering peaks of individual SWNTs. However, high light intensities are often required for fast real-time measurements, which by themselves can change the spectral response of the sample.

The present study investigates the influence of laser irradiation on the optical properties of SWCNTs in tightly grown forests. We observe significant changes in reflectivity during exposure, which are reversible after termination of the laser irradiation. The dependence of this effect on laser power and exposure time and ambient pressure has been studied and indicate novel optical responses to previously assumed ones. Reflection spectrum, Rayleigh scattering, and Raman signals during, and post-irradiation, have been studied to give a detailed analysis of this phenomenon which originates in thermo-structural flexing within the CNT forest.

Healing Mechanisms During The Growth Of Carbon Nanotubes

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Despite considerable progress in synthesis processes, the detailed microscopic mechanisms involved in the growth of carbon nanostructures are still lacking. In situ experimental atomic scale investigations are very difficult, whereas computer simulations allow such investigations. Nevertheless, whether the employed method is empirical or semi-empirical, all final configurations are plagued by a high concentration of atomic-scale defects. These include, but are not limited to, heptagon-pentagon topological defects, adatoms, and atomic vacancies. In the present work, we investigate the healing processes of defective carbon nanotubes at atomic scale. We have developed a tight binding (TB) model for nickel and carbon that uses Monte Carlo simulations in the grand canonical ensemble to study the formation of carbon structures (graphene and nanotubes) from a metallic substrate[1,2]. In particular, we have recently discussed the key role played by metallic atoms in the reconstruction of a defected graphene sheet by annealing defects [3]. We use our TB model to study the evolution at finite temperatures of defected nanotubes. Different lengths and diameters of nanotubes have been investigated at various temperatures ranging from 500 to 3000 K. We have also investigated the role played by the metal catalyst and a vapor of carbon atoms in the healing process. The building up of the tube chirality is analyzed and discussed through electron diffraction patterns. The approach proposed here could help identify individual healing mechanisms during growth that produces perfect tube structures and those favoring a definite chirality [4].

[1] H. Amara, C. Bichara, and F. Ducastelle, *Phys. Rev. Lett.*, **100**, 056105, (2008).
[2] H. Amara, J.-M. Roussel, C. Bichara, J.-P. Gaspard and F. Ducastelle, *Phys. Rev. B* **79**, 014109 (2009).
[3] S. Karoui, H. Amara, C. Bichara, and F. Ducastelle, *ACS Nano*, **4**, 6114 (2010).
[4] M. Diarra, H. Amara, C. Bichara, and F. Ducastelle,(in preparation)

Synthesis and Characterization of Diameter-Controlled Single-Walled Carbon Nanotubes by Arc Discharge

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We demonstrated the synthesis and characterization of diameter-controlled single-walled carbon nanotubes (SWCNTs) according to catalyst species using an arc-discharge method. The SWCNTs synthesized by Ni-Y catalyst showed a small diameter about 1.2nm, and the SWCNTs by Fe catalyst indicated a medium diameter about 1.5 nm. On the other hand, the SWCNTs by Fe-Bi catalyst showed a large diameter about 2.0nm. The Raman spectrum and the UV-Vis-NIR analysis showed that the small diameter SWCNTs are mainly semiconductor-rich but the large diameter SWCNTs are metal-rich. In detail, the SWCNTs by the Ni-Y catalyst mainly consisted of semiconducting SWCNTs while the SWCNTs by the Fe-Bi catalyst revealed almost metallic SWCNTs. By the way, the SWCNTs by the Fe catalyst showed a mixture of semiconducting and metallic materials. To understand the electrical behavior of SWCNTs, we fabricated SWCNT films using a filtration transfer method from three kinds of SWCNT materials and measured the sheet resistance of SWCNT films using the four probe method. Our results showed that the electrical conductivity of the SWCNT films is strongly dependent on the diameter of SWCNTs and well agreed with the proportion of semiconducting and metallic SWCNTs.

Repeated Purification of Semiconducting and Metallic Carbon Nanotubes by Electric-field induced Layer Formation method

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Separating high purity semiconducting (sc-) or metallic (m-) singlewalled carbon nanotubes (CNTs) is essential for the electronic device application of CNTs such as carbon nanotube thin-film transistors (CNT-TFTs). Recently, we proposed a separation method of "Electric-field induced LayerFormation (ELF)" as an ion-free, simple, and scalable method. Here, we report the repeated application of ELF separationto obtain highpurity sc- and m-CNTs. CNTs were dispersed into D2O with 1 wt% of polyoxyethylene stearyl ether (Brij 700, Aldrich) by sonication and ultracentrifugation. Afterthe dispersing process, the concentration of Brij 700 in thesolution was adjusted by adding Brij 700-D2O solution. The adjustedsolution was introduced into a vertical cell attached with a pair of electrodes, which was used for applying electric field to the solution by a DC powersupply. For the separation, a constant voltage of 30 V was appliedbetween the lower (anode) and upper (cathode) electrodes, leading to thelayer formation of sc- and m-CNTs near the anode and cathode, respectively. Both layers were fractionated and their purities wereestimated from optical absorbance spectra and Raman spectra. First, we investigated the dependence of the voltage applicationperiod on the purities of sc- and m-CNTs. It was found that both puritiessaturated after 24 hours of application, possibly due to the formation ofa transparent layer between the upper (m-CNT) and lower (sc-CNT) layers. Repeated layer formation wassuccessfully confirmed for the separatedsamples under the condition that the concentration of the surfactant was relevantly adjusted. With the repeated 24-hour separation,the purities of s- (m-) SWCNTs were obtained to be 90% (58%), 97%(74%), and 99% (85%) for one, two, and three repetitions, respectively. It is worth to note that the purity depends on the repetition count with a power law. To demonstrate the advantages of this separation method, we fabricatedCNT-TFTs made with sc-CNTs (97%) and compared device performances withpristine (67%) one. The devices were fabricated on heavily dopedsilicon substrates covered by SiO2 gate dielectric with its surface functionalized byaminopropyltriethoxysilaneto accommodate CNT random networks. Devices made from sc- and pristine CNTs showed completely different on/off current ratios, 4.4×10^5 and 25, respectively. These results suggest that this repeated ELF separation would be a suitable method to obtain high-performance electronic devices.

Electrical Properties of Carbon Nanotube Thin Film Transistor Dependent on Alignment of Carbon Nanotube Channel Network

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We fabricated the back-gate CNT-TFTs using arc single-walled CNT (SWCNT) on silicon (Si) substrate and also investigated the electrical properties of the CNT-TFTs dependent on alignment of CNT network used to channel. The carbon nanotube thin film transistors (CNT-TFTs) typically have the trade-off relationship between the on/off current ratio and mobility when metallic (m-)/semiconducting (s-) mixed CNTs are used for a channel of TFT devices. The trade-off relationship is mainly dependent on the density and the alignment of the CNT network. In this work, the aligned SWCNT network was formed by dropping the SWCNT in 1,2-Dichloroethane solution with AC dielectrophoresis. The source/drain electrodes and the gate electrode were made of Au film by e-beam evaporation. The alignment control of SWCNT network was performed by varying the gap between the electrodes (channel length). The results showed that the on-current level, mobility were decreased as the channel length increased while the on/off current ratio was increased. It is attributed to decreased alignment level of the SWCNT network at lower electric field. We also observed significant changes of the gate-sweep curves as the channel length increased, which are mainly contributed by current flow via the s-SWCNT network. The CNT-TFT showed I_{on}/I_{off} of 10^5, maximum on- current of 1μA and mobility about 6.7 cm2/V•s.

A Thickness Dependant Response Mechanism for Gas Sensors Based on Sorted Semi-Conducting SWCNT Films

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Gas sensors based on single walled carbon nanotubes (SWCNT) films have attracted so far a lot of attention because of their high sensitivity and low power consumption. However, the development of SWCNT based selective gas sensors currently remains a challenge because the origin of the sensing mechanisms remains 1unclear. Theoretical work based on ab-initio calculations [1] claimed that charge transfer between the adsorbed gas molecules and the carbon nanotubes was consistent with a variation of the global sensor resistance during gas exposure. On the contrary, Peng et al. [2] have mainly attributed the sensor response to the modulation of the Schottky barrier between semiconducting SWCNTs and metallic electrodes. This effect was recently used to elaborate a selective gas sensor by changing the electrode metal [3]. In this communication, we propose to elucidate this discrepancy by investigating the influence of the film density on the sensing mechanism. Semi-conducting SWCNTs enriched solutions (90%) were obtained by density gradient ultracentrifugation [4]. Several gas sensors with various film thicknesses ranging from a few nanometers to 150 nanometers were fabricated either by spray coating on platinum electrodes or by filtration of the SWCNT solution on a nitrocellulose membrane and transfer on platinum electrodes. Two pollutant gases were considered for gas detection: NH_3 and NO_2. The SWCNT film resistance and the Schottky barrier at the interface between the SWCNT film and the metallic electrodeswerediscriminated from the I(V) characteristicsby using a theoretical analytical conduction model [5]. A comparative study of different SWCNT film thickness devices allowed us to demonstrate that the percolation of metallic SWCNTs in the SWCNT network plays a crucial role on the gas detection mechanism. Indeed, in the case of thick films, the percolation of metallic SWCNTs minimizes the influence of the Schottky barrier in the response to gas. Although the sensing mechanism of a sensor based on SWCNT thin film is clearly attributed to the variation of the Schottky barrier height, the adsorption of gas molecules on SWCNTs is mainly responsible for the response to gas in the case of thick SWCNT films. The gas sensitivity of SWCNT-based sensors is enhanced in the case of thin films, but the resolution is lowered by low level current. This study allows us to propose an optimal sensor architecture based on sorted semiconducting SWCNT films, combining increased current intensity by thicker films, with Schottky barrier modulation at the interface during the gas exposure.

[1] W.-L. Yim, X. G. Gong, Z.-F. Liu, *J. Phys. Chem. B*, **107**, 35, 9363–9369 (2003).
[2] N. Peng, Q. Zhang, C. L. Chow, O. K. Tan, N. Marzari, *Nano Lett.*, **9**, 1626–1630, (2009).
[3] P.Bondavalli, P.Legagneux, D.Pribat, *Sensors and Actuators B,* **140**, 304-318 (2009)
[4] J. Posseckardt, Y. Battie, R. Fleurier, J. S. Lauret, A. Loiseau, O. Jost, M. Mertig, *Physica*

Status Solidi (B), **247**, 2687–2690 (2010).
[5] Y. M. Wong, W. P. Kang, J. L. Davidson, A. Wisitsora, K. L. Soh, *Sensors and Actuators B*, 9, 327-332 (2003).

Carbon Nanotube Based Flexible Transparent Thin Film Transistor

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Carbon nanotubes (CNTs) have been considered as promising material for flexible electronics due to their unique electrical and mechanical properties. We demonstrated fabrication and electrical properties of all-CNT based flexible transparent thin film transistor (TFT) on a PET substrate. The CNT-TFT consists of a channel, source/drain electrodes and a gate electrode made by single-walled CNTs (SWCNTs). The semiconductor-rich (s-) SWCNTs were used for the channel of the CNT-TFT and the metal-rich (m-) SWCNTs were used for the source/drain electrodes and the gate electrode. The SU-8 was used for a gate insulating layer. Here, we separated the s-SWCNTs by a density gradient method to obtain high purity s-SWCNTs for the TFT channel. The m-SWCNT films for the source/drain electrodes and the gate electrode indicated low sheet resistance of 120 Ω/□ at 85 %T. The SWCNT films were fabricated by a vacuum filtration method with an alumina oxide membrane, and then transferred onto the PET substrate. After transfer, the SWCNT films were patterned for the channel or the electrodes using a photolithography method followed by either a lift-off or a reactive ion etching processes. The SU-8 for the gate insulating layer was deposited by a spin coating process. The all CNT based flexible transparent CNT-TFT exhibited the I_{on}/I_{off} value up to 10^4, the maximum on-current of 1 nA and mobility of 0.26 $cm^2/V\bullet s$ at 80%T.

Carbon Nanotube Based Flexible Field Emitters

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Carbon nanotubes (CNTs) have been studied as an ideal material for field emitters due to the high aspect ratio, excellent electrical property and good mechanical strength. There have been many reports on CNT field emitters fabricated on rigid substrates such as Si or glass substrates, but rare reports on flexible substrates. Due to high Young's modulus and elasticity of CNT, it is considered as a good candidate for a flexible field emitter material. In this work, we demonstrated fabrication of CNT flexible field emitters on a flexible substrate by using a filtration-transfer method and also investigated their field emission properties. We formed the CNT film on a filter membrane by vacuum filtration then transferred the film onto a conductive adhesive tape which is fixed on a flexible substrate.This method is a simple and effective way to fabricate flexible field emitters, and all the processes are performed at room temperature. The CNT flexible field emitters showed the low threshold electric field, the high emission current density and good stability. Emission patterns of the CNT flexible field emitters exhibited very stable and uniform emission performance regardless of their bending curvatures. We consider that the CNT flexible field emitters can be applicable to flexible field emission lamp or devices in the future.

Carbon Nanotube Based Humidity Sensor

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This work aims to investigate the potentialities of using carbon nanotube field effect transistors (CNTFET) as humidity sensors. A CNTFET device consists in a CNT channel connecting two metal electrodes and separated by an insulating material from a back or top gate. The CNT channel is either made up of an individual or of a low density network of semiconducting single-walled carbon nanotubes (SWCNT). The transistor effect is attributed to the Schottky barriers between the CNT and the metal electrodes. As Schottky barriers are very sensitive to the environment, the CNTFET characteristics (subthreshold slope, on/off ratio, hysteresis) are found to strongly depend on the type and the relative concentration of surrounding gas, especially in case of water vapor [1]. The overall goal of this study is to prove that one can exploit the sensitivity of CNTFET devices to water vapor for humidity sensing. Due to the devices small size, their low cost and high sensitivity, there is a large applicative potential for such devices, among others in civil engineering [2]. We considered various CNTFET designs and fabrication processes, CNT doping with different materials as well as CNT decoration with metal nanoparticles. We studied how these different factors influence the CNTFET sensitivity to humidity. CNTFET devices were fabricated using two technics: in-place, diameter-controlled, CVD growth of SWCNT networks consisting mostly of semiconducting specimens [3] and spraying of a solution of dispersed SWCNTs [4]. A conventional photolithographic process is used to create metal electrodes (Pd, Pt, Au, and Ti) on a doped silicon substrate with a 100 nm layer of thermal silicon oxide. The devices have a typical 1mm gate channel width and differentchannel length ranging from 1 µm to 10 µm. For all metal electrodes but Ti, we observea strong and reproducible dependence of the electrical characteristics on the relative humidity from 60% RH to 100% RH. We also investigated the influence of CNT coating with organic materials (e.g. polyethyleneimine [5]). Whereas the initial CNTFET devices (before coating) feature p-type behavior and are very sensitive to high relative humidity, the final devices display n-type behavior and appear highly sensitive to low relative humidity from 0% RH to 30% RH. This result is to be attributed to the strong cationic nature of the investigated covering materials. Finally, we investigated the CNTFET resilience in time and we evidenced that CNTFET devices may feature a significant degradation of current level in time with the degradation speed depending on the device design.

[1] P. Na, H. Kim, H.M. So, K.J. Kong, H. Chang, B. Ryu, Y. Choi, J.O. Lee, B.K. Kim, J.J. Kim, J. Kim, *Appl. Phys. Lett.* **87** 093101,(2005).

[2] L. Basheer, J. Kropp , D. J. Cleland D., *Construction and building materials*, **15**, 93-103, (2001).
[3] F. Z. Bouanis, L. Baraton, V. Huc, D. Pribat and C. S. Cojocaru, *Thin Solid Films*, doi:10.1016/j.tsf.2011.01.326, (2011).

[4] L. Gorintin, P. Bondavalli, P. Legagneux, and M. Chatelet, *MRS*, (2010).
[5] M. Shim, A. Javey, N. Wong Shi Kam, and H. Dai, *Science*, **290**, 1552-1655, (2000).

Very Stable Electron Emission from Carbon Nanotube Matrices

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Tremendous efforts were evidenced on the study of electron field emission from carbon nanotubes (CNTs) for more than a decade. However, commercial field emission products based on CNTs is still not available. Apparently, emission stability is one of the major issues and the understanding on this is still lacking. Based on theoretical simulation, we have designed a series of novel carbon nanotube matrices that will have enhanced field emission stability. Experimentally, stable emission was recorded for continuous operation of thirty thousand minutes (30,000 min). We have focused our efforts in understanding the basic factors that contribute towards stable field emission from CNTs. Apparently field emission from CNTs is not just the quantum tunnelling process but involve Joule heating when electrons are flowing from the base to the tips of CNTs. We previously reported that fieldemission stability depends on many factors including the Joule heating on vertically-aligned multiwalled carbon nanotubes (VA- MWCNTs) [1, 2]. Later, we demonstrated that Joule heating can be suppressed by reducing the screening effect on self-assembled conical bundles of opened-tip CNTs [3]. These nanotubes bundles are stable field emitter as Joule heating is reduced. Later, we describe a lithography free process to increase the long term emission stability of VA-MWCNTs. We found that the emission threshold of VA-MWCNTs was reduced by more than two-fold when VA-MWCNTs were embedded in PMMA [4]. These PMMA-CNT matrices were tested for continuous emission at a current density 1.2mA/cm2 for 40 hours with 96% stability and emission density. Multiple theoretical models and simulation were conducted to support these observations [4]. Based on these results, we created new CNT matrices that have excellent emission properties with low emission threshold, enhanced emission site density and outstanding stability. Results indicate that the threshold electric field as low as 0.7 V/mm can be obtained. Excellent emission stability was obtained when tested matrices for continuous emission > 20 days (30,000 mins). Details of these results will be discussed in the meeting.

[1] B. Ulmen, et al, *Diamond & Related Materials* **15**, 212 (2006).
[2] V. K. Kayastha, et al, *Nanotechnology* **18**, 035206 (2007).
[3] Pandey et al, *Carbon* **48**, 287 (2010) + cover image in the 48/3 issue (2010).
[4] Pandey et al, *ACS Nano* **4**, 6760 (2010).

Schottky Solar Cells Based On Graphene And Silicon

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Graphene has been widely used for composites, nanoelectronics and transparent electrodes owing to its unique 2D nanostructure and conductibility. For example, solution-processed graphene dispersed into polymers such as P3OT or P3HT was used as the acceptor material. Graphene films were used as conductive and transparent electrodes to replace ITO in organic and dye-sensitized solar cells. Here we directly deposited highly conductive, semi-transparent graphene films on n-type silicon (n-Si) wafer to form Schottky junction solar cells. Our results show that Graphene serves multiple functions as transparent electrode, active junction layer and charge transport path in the solar cells. The power conversion efficiencies of the graphene/n-Si solar cells are up to 1.6% at AM 1.5 [1], which can be further optimized to 2.5%.Our results show that thechemical doping of graphene films with $SOCl_2$, led to anobvious enhancement of Schottky junction, which is attributedto the drop of the sheet resistance of graphemefilm.The solar energy conversion efficiency was improvedto 3.7~3.9%, which are about 2~3.7 times higher than those for the cells without chemical doping [2]. Though these efficiencies are still lower than those for the cells based on pure silicon, this photovoltaic model provides a new trend to develop a new type solar cell which has the relatively low cost and easy fabrication. Furtherimprovement of G/Si solar cells may be envisioned viafurther optimization of the graphene films and chemicaltreatments.

[1] Li XM, Zhu HW, Wang KL, et al, *Advanced Materials*, 22, 2743–2748,2010.
[2] Li XM, Zhu HW, Wang KL, et al.http://arxiv.org/abs/1012.5730, *Proceedings of the Conference on China Technological Development of Renewable Energy Source*, Vol. I, 387-390,2010.

Nitrogen Doped Single Walled Carbon Nanotube films : New strategy for Ammonia Gas Sensing Selectivity

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The major issue of CNT-based gas sensors resides on their lack of selectivity. To address this issue, many SWCNT functionalization strategies have been developed so far, such as metallic nanoparticles [1], nanotube sorting [2] and conductive polymers [3]. This work aims at the development and evaluation of new time-stable, temperature-stable, and efficient functionalization strategies by taking advantage of intrinsic SWCNT properties such as chirality and doping. In this communication, we report the development of a selective differential sensor architecture based on the comparative interrogation of two sub-sensors based on respectively pristine SWCNT and nitrogen-doped SWCNT (N-SWCNT) films. Three pollutants were investigated: NH_3, NO_2 and H_2O. The nanotube films were synthesized by a floating catalyst chemical vapour deposition method as reported in [4]. The sensors consist of a thick (100-150 nm) (N-)SWCNT film deposited on platinum electrodes. The sensor interrogation principle is a resistivity measurement based on the transfer length method (TLM) to separate the SWCNT film sheet resistance from the contact resistance. We show that for both pristine and N-doped films, a large variation of the sheet resistance of the sensors could be measured while no variation of the contact resistance was experienced. This result is attributed to the percolation of metallic nanotubes in the case of thick films, yielding ohmic contacts. As a consequence, the sensing mechanism is mainly attributed in our sensors to the adsorption of gas molecules on the SWCNT film, which induces a charge transfer between the gas molecules and the nanotubes. In the case of NO_2 or H_2O gas exposure, we demonstrate that the sensitivity of N-SWCNT sensors is similar to the sensitivity of pristine SWCNT based sensors. However, the sensitivity to NH_3 is improved 3 times in the case of the N-SWCNTs. We suggest that this result is attributed to the presence of pyridinic nitrogen dopant groups. Finally, the temperature dependence of the sheet resistance of both N-doped and pristine nanotube films was also studied and was found to be comparable. An architecture for a differential NH_3 sensor is then proposed, and its sensitivity to temperature, humidity and NO_2 will be discussed and compared to standard non differential SWCNT based sensors.

[1] A. Star, V. Joshi, S. Skarupo, D. Thomas, and J-C. P. Gabriel, *Journal of Phys. Chem. B* **110**, 42 (2006).
[2] Yann Battie, Olivier Ducloux, Philippe Thobois, Yannick Coffinier, Annick Loiseau, *C. R. Physique* **11** 397–404 (2010),

[3] P. Qi, O. Vermesh, M. Grecu, A. Javey, Q. Wang, H. Dai, S. Peng, and K. J. Cho, *Nano Letters* **3**, 3 (2003).
[4] T. Susi, A. Kaskela, Z. Zhu, P. Ayala, R. Arenal, Y. Tian, P. Laiho, J. Mali, A.G. Nasibulin, H. Jiang, G. Lanzani, O. Stephan, K. Laasonen, T. Pichler, A. Loiseau, and E. I.

Kauppinen, *Chemistry of Materials*, in press (2011), doi: 10.1021/cm200111b.

Polarization Switching And Ferroelectric Field Effect In Devices Combining Carbon Nanotubes With Epitaxial Pb(Zr0.2Ti0.8)O3 Thin Films

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Combining carbon nanotubes (CNTs), with their exceptional electronic properties, and ferroelectric materials, presenting a switchable remanent polarization opens new possibilities for multifunctional devices. As recently reported in such device, ferroelectric field effect doping can modulate CNT charge carrier density [1,2], while the CNT can act as a local electric field source for nanoscale polarization switching [3]. The important question it the minimum size of the ferroelectric domains which can be stabilized, a key parameter for possible memory applications. Recent studies [4] have suggested a minimum domain size strongly limited by the film thickness. To fabricate CNT-ferroelectric devices, we deposited single-walled CNT from aqueous suspension onto epitaxial $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films patterned with electrode arrays. In such devices, we demonstrate directly repeated, reversible polarization switching with voltage pulse application via the CNT, exploring the effects of the voltage pulse duration and magnitude on the size of the resulting ferroelectric domain. For the shortest voltage pulses, we could switch nanodomains with widths lower than 10% of the film thickness. Although the size of these nanodomains initially decreases on a timescale of several weeks, stabilization occurs after about 3 months. We also report a clockwise hysteresis in transconductance measurements, characteristic of a ferroelectric field effect, and explore the electronic properties of the device over the 4K to ambient temperature range.

[1]T. Sakurai et al., Jap. *J. of Appl. Phys.*,**45**, L1036, (2006).
[2] W. Y. Fu et al., *Nanotechnology*,**20**, 475305, (2009).
[3] P. Paruch et al., *Appl. Phys. Lett.*, **93**, 132901, (2008).
[4] N. Tayebi et al., *Appl. Phys. Lett.*, **96**, 023103, (2010).

Carbon Nanotubes As Local Probes For Ferroelectric And Multiferroic Thin Films

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The extremely small diameter, high aspect ratio, and mechanical robustness of carbon nanotubes (CNTs) have made them very attractive, when attached to Atomic Force Microscopy (AFM) tips, as local probes for a range of different systems. CNT tips provide superior resolution [1], and can act as local electric field source for nanolithography [2] and ferroelectric polarization switching [3]. Separately, magnetic functionalization for Magnetic Force Microscopy measurements [4] and SiO2 rigidification for contact measurements, including Piezoresponse Force Microscopy [5] have been recently implemented. Our goal is to combine these different advances to develop a high resolution, conductive, magnetic and rigidified CNT-AFM tip for the full spectrum of measurements on ferroelectric and multiferroic thin films. Here, we report on the fabrication of such a probe by direct CVD growth of CNT on AFM tips with subsequent shortening, magnetic metal coating and rigidification. A comparison of these tips with standard commercial probes on topography, Electrostatic-, Magnetic and Piezoresponse Force Microscopies will be presented.

[1] J.H. Hafner, C.-L. Cheung, and C.M. Lieber, *J. Am. Chem. Soc.*, **121**, 9750-9751 (1999)
[2] H. Dai and N. Franklin, *Appl. Phys. Lett.*, **73**, 1508-1510 (1998)
[3] P. Paruch,T. Tybell, and J.-M. Triscone, *Proc CIMTEC D*, 675, (2002)
[4] H. Kuramochi et al, *Jap. J. Appl. Phys.*, **44**,2077-2080 (2005)
[5] N. Tayebi et al, *Appl. Phys. Lett.*, **96**,023103 (2010)

Gate Tuning of Optical Fabry-Perot Cavities with Suspended Multilayer Graphene Mirrors

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Graphene based membranes provide ideal materials to implement semi transparent mirrors. These can be electrostatically actuated [1, 2] and their motion optically detected [1]. We fabricate micron-scaled optical cavities composed of multi-layer (MLG) graphene cantilevers which are free-standing over an oxidized silicon wafer. Reflectometry and Micro-Raman characterizations are performed by scanning a laser probe over the cantilever. Thickness variations within the MLG/Silica gap induce equal spacing interference fringes in both the reflected and Raman scattered waves. Spatial variations within interference patterns allow spatial splitting of all Raman modes emitted by both the MLG and Silicon substrate. The cavity finesse of the resulting Fabry-Pérot-like interferometer can reach about 6 and is in agreement with simulation involving graphite based semi-reflecting membrane of similar geometry. The MLG membrane is connected to a gold gate electrode that allows applying an electric field within the cavity and tuning the cavity thickness with nanometer scale precision. Intensity of the reflected light and Raman lines exhibit quadratic dependence upon the applied gate voltage while G and 2D Raman modes show a softening in frequency as well. We discuss the use of such graphene-based nano-electromechanical devices for implementing adjustable cavities and high resolution Raman spectroscopy.

[1] J. Bunch, A. van der Zande, S. Verbridge, I. Frank, D. Tanenbaum, J. Parpia, H. Craighead, and P. McEuen, *Science*, **15**, 490, (2007).
[2] C. Chen, S. Rosenblatt, K. Bolotin, W. Kalb, P. Kim, I; Kymissis, H. Stormer, T. Heinz, and J. Hone, *Nature Nanotech*, **4**, 861–867, (2009).

Hydrogen Sensing With Diameter And Chirality Sorted Carbon Nanotubes

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The work function of palladium is known to be sensitive to hydrogenbythe formation of a surface dipole layer or Pd hydride. Oneapproach to detect such a change in the work function can be based on the formation of a Schottky barrier between the Palladium metal and a semiconductor. Here, we present the hydrogen sensitivity of Schottky-barrier field effect transistors made for the first time fromdiameter-and chirality-sorted semiconducting single-walled carbon nanotubes (s-SWNT) in contact with Pd electrodes[1]. We observe an unrivaled 100-fold change in the on-state conductance at 100ppm H_2 compared to air, for devices withs-SWNT and diametersbetween 1 to 1.6 nm. Hydrogen sensing is not observed for devices of Pd-contacted few-layer graphene (FLG), as expected due to the absence of a significant Schottky barrier. Unexpectedly we observe also a vanishing sensitivity for small-diameter SWNTs. We explain this observation by changes in the nanotube work function caused by spillover and chemisorption of atomic hydrogen onto small diameter nanotubes. We also observe that long-term sensing stability is only achieved if the gate voltage is invertedperiodically. Under constant gate bias, the sensitivity reduces with time, which we relate to gate screening by accumulated charges in the substrate.

[1] M. Ganzhorn et al., *ACS Nano* **5** (2011) 1670

Low Bias Operation & Individual Charge Detection of Carbon Nanotube Quantum Nano Memory

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10 times lower writing bias and individual charge transfer from nanotube channel to memory node was observed in the carbon nanotube (CNT) quantum nanomemory, in which the CNT with narrow diameter of ~1nm was used as a channel surrounded by the SiN/SiO_2 double layer insulaters with the gold nano particle that works as a memory node. Top gate electrode was formed over the double layer insulaters. Because of the narrow CNT channel, the high-electric field concentration was generated even at the low applied gate bias, and charge in the nanotube is easily extracted by the Fowler-Nordheim tunneling through the insulater to the gold nano particle, and is trapped there. Thus, even at low applied gate bias of 2V, CNT quantum nanomemory shows the enough hysteresis though the conventional memory with flat channel structure needs more than 20~25V for the writing bias. Thus, 10 times lower writing bias was realized using the CNT channel memory. The threshold voltage of CNT quantum nanomemory showed the step like shift, i.e., at the applied gate bias lower than 300 mV, the threshold voltage stayed constant value, and shifted suddenly around 260 mV when the applied gate bias exceeds more than
300 mV. This is attributed to the Coulomb blockade effect. The diameter of the gold nano particle that works as a memory node was measured by AFM and found to be ~2.5 nm. The charging energy for the 2.5 nm gold nano particle in the present device structure is calculated to be 300 meV. Therefore, the step like shift of the threshold voltage is due to the single charge injection from the CNT channel to gold nano particle. When the top gate bias comes back to 0 V after the enough writing bias was applied, the step like jump of the drain current attributed by the single hole discharge was observed.

Enhancement of high-frequency characteristics of carbon nanotube FETs by chemical doping

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Carbon nanotube field-effect transistors (CNFETs) are expected to operate at the frequency higher than conventional semiconductor transistors because of the high carrier velocity due to the ballistic conduction. In order to realize the high frequency operation in practical CNFETs, it is important to eliminate parasitic delay due to capacitances belonging to the electrodes by increasing the current driving ability. For this purpose, aligned carbon nanotube arrays grown on a quartz substrate [1] and dense semiconductor-enriched carbon nanotube thin film deposited by dielectrophoresis [2] have been used as the channel for high- frequency CNFETs. However, the cut-off frequency (fT) is still much lower than that expected for CNFETs. One of the reasons for the low fT can be attributed to the carbon nanotubes that does not significantly contribute to the driving current in the carbon nanotube array. In fact, the driving current per a carbon nanotube channel of CNFETs with aligned carbon nanotube array [3] is about one-fifth of that of high-performance single-channel CNFETs [4] in our case. This is probably because a part of carbon nanotube array does not flow current enough due to high contact resistance. Then, the transconductance and high-frequency characteristics can be degraded even if the density of carbon nanotube array is high. In the previous study, we have shown that the contact resistance can be reduced by chemical doping near the contact and is effective to improve the transconductance of top-gate CNFETs [5]. The doping molecules form dipoles at the edge of the contact where carriers are injected into a carbon nanotube [6], so that, the Schottky barrier formed at the contact can be reduced. Here, we have studied the effect of chemical doping on the high-frequency characteristics of CNFETs with aligned carbon nanotube array. CNFETs with an 80-nm mushroom gate were fabricated by the self-aligned process. F4TCNQ (tetrafluorotetracyano- p-quinodimethane) is doped onto the access regions between the drain/source and the gate, which results in an enhancement of fT by a factor of two. Based on the equivalent circuit analysis, we show the enhancement in fT can be attributed to an increase in the intrinsic transconductance as well as a reduction of contact resistances. Finally, fT of the semiconductor part of the array channel is extracted to be 91 GHz.

[1] C. Kocabaset al.,*Nano Lett.* **9**, 1937 (2009).
[2] L. Nougaret et al., *Appl. Phys. Lett.* **94** 243505 (2009).
[3] D. Phokharatkul et al., *Appl. Phys. Lett.* **93**, 053112 (2008).
[4] N. Moriyamaet al., *Appl. Phys. Exp.* **30** 53112 (2010).
[5] Y. Noshoet al., *Nanotechnol.* **18**, 415202 (2007).
[6] Y. Noshoet al., *Jpn. J. Appl. Phys.* **46**, L474 (2007).

Molecular Nanostructures with Carbon Nanotube-Molecule Heterojunctions

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Single-wall carbon nanotubes (SWCNT) are attracting building blocks for quantum nanodevices, such as single electron devices and quantum computing devices [1,2]. The present device processing techniques combined with conventional top-down technique are not suitable for the purpose, because 1) they cannot take full advantage of the extremely small diameter of the SWCNT, and 2) the devices fabricated with the techniques are not always reproducible and reliable. To overcome the problems, we fabricate extremely small nanostructures with SWCNT-molecule heterojunctions. As examples, we show chemically bonded SWCNT ring structures, and a SWCNT with both endsterminated with molecules. The structures are characterized by the scanning tunnelling microscopy (STM) with simultaneous optical spectroscopy. We have observed standing wave patterns in the ring, and a ground state and excited states of electrons confined in the parabolic potential in the SWCNT terminated by the molecules. A SWCNT single quantum-well structure is also fabricated with molecule barriers. The developed techniques may open a path to realize molecular-scale nanostructures for quantum device applications.

[1] S. Moriyama, T. Fuse, M. Suzuki, Y. Aoyagi, K. Ishibashi , *Phys. Rev. Lett.* **94**, 186806 (2005).
[2] K. Ishibashi, S. Moriyama, D. Tsuya, T. Fuse, M. Suzuki, *J. Vac. Sci. Technol. A* **24** (4), 1349 (2006)

Functionalization of Single-Walled Carbon Nanotubes with Ribonucleic Acids

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Optical properties of single-walled carbon nanotubes (SWCNTs) dispersed in ribonucleic acids (RNA), purified from Escherichia coli, were studied using photoluminescence (PL), Raman, and absorption spectroscopy. Isolated SWCNT-RNA hybrids were successfully synthesized. Two distinct PL peaks at 1.248eV and 1.392eV were observed originating from (6,5) and (6,4) SWCNT, respectively. Atomic force microscopy (AFM) images and height profile also showed the evidence of isolated SWCNT-RNA hybrids.

Possible CVD Synthesis Region of Single-walled Carbon Nanotube in the Bachmann Diagram

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Considering the massive-scale synthesis of single-walled carbon nanotube (SWCNT), chemical vapor deposition (CVD) has become a standard process for synthesizing CNTs, because it is an economical and a fast process. In most of these processes, oxygen and hydrogen atoms were included originally or added later; these atoms were expected to have important roles such that they helped in the removal of amorphous carbon from catalysts and prevented SWCNTs from containing metal particles. However, whole perspectives for suitable carbon source or ideal balance among carbon, hydrogen, and oxygen have not been reported. Therefore, we performed experiments from the point of view of determining the appropriate C-H-O components ratio in raw materials could be used to synthesize CNTs by CVD processes. In this study, we employed a C-H-O ternary diagram, which was known as the Bachmann diagram for diamond synthesis, to clearly understand the most important relationship among the components of each raw material. We examined a variety of raw materials in our newly developed round-trip-type vacuum furnace in order to determine whether they could be used to synthesize a carbon nanotube. We used Raman spectroscopy to identify the developed carbon nanotube, and we plotted the component ratios of effective and ineffective materials on a C-H-O ternary diagram. In this study, we employed two kinds of catalyst supporters such as aluminum oxide and zeolite (USY type). We confirmed a kind of affinity between catalyst supporters and carbon sources, but this affinity did not lead to inconsistency in the tendency on the C-H-O ternary diagram. Some carbon sources are shown in the same position on this diagram; for example, ethanol and DME (C_2H_5OH and CH_3OCH_3) or hydrocarbon gases and hydrocarbon gases with hydrogen (C_2H_6 and $C_2H_4 + H_2$), there is no contradiction. As a result, in this diagram, the growth region became highly apparent. It should be noted that for the growth of the carbon nanotube, this region should satisfy the equation $O < C < (H + O)$ in molar ratio. Furthermore, it was observed that adjusting the component ratios by mixing raw materials did not cause an inconsistency in the growth region.

Molecular Orbital Calculations of Small Graphene-Like Species to Interpret Their Site-Dependent EELS

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Electron energy -loss spectroscopy of coronene ($C_{24}H_{12}$), perchlorocoronene ($C_{24}Cl_{12}$), and graphene was compared with the theoretical calculation of those derivatives. The contributions of individual carbon atoms to the carbon K-edge spectrum is evaluated, which roughly approximates the site-dependent electronic properties. The first principle calculations provide information of a specific carbon site that is mainly influenced by surrounding chemical environment. Real -space molecular orbital (MO) calculations, based on the density functional theory (DFT), can determine both the energy levels and the density of states after self-consistent field (SCF) calculations. Some results of theoretical calculations will be shown based on the model structures of coronene, perchlorocoronene [1] and other graphene-like derivatives that assumingly possess zigzag- edge ($C_{150}H_{30}$), armchair- edge ($C_{114}H_{30}$), and Klein- edge ($C_{120}H_{24}$) structures [2]. When focusing on the π^* peak of peripheral carbon sites, the chlorine-terminated carbon site relatively shift to higher energy level compared to hydrogen- terminated carbon. The chlorine atom pulls the valence electron from the carbon site which is positively charged and accordingly binds the inner 1s energy level of carbon atom much deeper (lower) energy level. The hydrogen- terminated peripheral carbon atoms of coronene do not show significant energy shift compared with other carbon atoms inside the coronene molecule. In graphene derivatives with zigzag- edge, armchair- edge, and Klein- edge structures, the peripheral hydrogen-terminated carbon atoms do not show significant energy shift compared to the observed experimental energy shift of graphene edge. The distribution of unoccupied 2p orbitals on the peripheral edge of carbon, however change drastically to show the characteristic fine structures Indeed, there are numbers of parameters that must be considered in the calculations, for instance, the precise structure of the materials of interest (whether the termination should be hydrogen, other elements, or perhaps no termination should be applied), valency (or charge) of carbon atoms, size effect of model structures (cluster size), etc. As the building block comparison is not suitable to predict the electronic properties of new materials like a graphene edge, the theoretical calculation still plays an important role to interpret or explain what we experimentally see.

[1] M. Koshino, H. Kurata, S. Isoda, *Ultramicroscopy,* **110**, 1465-1475, (2010).
[2] Kazu Suenaga & M. Koshino, *Nature,* **468**, 1088-1090, (2010).

Birth-Death Markov Modeling for Single Molecule Counting using Single- Walled Carbon Nanotube Fluorescent Sensor Arrays

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Functionalized SWNTs could be used as local concentration sensors for the biological community. In recent work we have shown that d(AT)$_{15}$ DNA-wrapped single-walled carbon nanotubes (SWNT) are able to detect the adsorption and desorption of single molecules of nitric oxide (NO) from their surfaces by quenching of the near-infrared fluorescence [1]. This work employs an exact solution to the Birth-Death Markov model to estimate the local concentration from the stochastic dynamics. Analytical expressions are derived for the intrinsic variance displayed by identical sensor elements, and the homogeneity of the environment is assessed by comparing experimental sensor-to-sensor variance with this limit. d(AT)$_{15}$ DNA-wrapped SWNTs are found to demonstrate variances that are close to the idealized limit at relatively high NO concentrations (19.4 μM). At 780 nM, the sensor-to-sensor variance is double the idealized value, which indicates marginal variation in the SWNT array. We outline how to predict the

ocal analyte concentration from sensor dynamics, and identify an NO adsorption rate coefficient 2.6×10^{-4} s^{-1} μM^{-1}.

[1] Zhang, J.; Boghossian, A.A.; Barone, P.W.; Rwei, A.; Kim, J.-H.; Lin, D.; Heller, D.A.; Hilmer, A.J.; Nair, N.; Reuel, N.F.; Strano, M.S. *J. Am. Chem. Soc.* **133**(3), 567–581 (2010).

Spin-Related Novel Optical Phenomena in Single-Walled Carbon Nanotubes

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The interplay between conduction electrons and localized spins is one of fundamental and important problems in modern condensed matter physics giving us unexpected phenomena: It is well known that they induce resistivity minimum phenomena, known as the Kondo effect. Besides the conducting electrons, the fundamental question arises whether the interplay between photo-excited electrons and localized spins leads novel phenomena. In this regard, semiconducting single-walled carbon nanotubes (CNTs) provide us an interesting research field of spin-related optical phenomena. Because of their quasi-one- dimensional structure, photo-excited electrons and holes in CNTs are strongly correlated and form a bound electron-hole pair, called an exciton, which has large binding energy, leading to remarkable stability up to room temperatures. Therefore, when there are localized spins in CNTs, optical phenomena are expected to exhibit wide variety. In this paper, we demonstrate two interesting examples of novel optical properties of CNTs that are induced by localized spins based on the theoretical investigations:(1) Recent experiments have shown the evidence in which the excitons correlate with localized spin induced by the defects in CNTs those are essential in the bipartite lattice of CNTs. However, unfortunately, the fundamental theory for this problem has not been addressed yet. We thus propose a theory that expresses the interaction between excitons and localized spins in CNT system[1]. Our theory solves one of the most important issues regarding the optically activated triplet dark excitons and first successfully provides a unified explanation for all the experimental conditions [2,3,4].(2) It has bee pointed out that ultrathin magnetic nanowires encapsulated in carbon nanotubes are potential candidates for constituent elements in the next-generation spintronics and electronics devices with nanometer scale [5]. For the device application, the evaluation methods for detecting the magnetic state of the nano-wires are essential and important. For such methods, we theoretically propose a non-contacted optical probing method based on the optical response from such magnetic nanomaterials encapsulated in carbon nanotubes. Due to the exchange interaction between excitons and polarized spins inferromagnets, triplet excitons acquire finite oscillator strength and can thus be excited by light [6]. This mechanism certainly detects magnetic ordering of nano-materials encapsulated in carbon nanotubes.

[1] S. Konabe and S. Okada, submitted.
[2] H. Harutyunyan et al. *Nano Lett.* **9** 2010 (2009).
[3] R. Matsunaga et al. *Phys. Rev. B* **81**, 033401 (2010).
[4] K. Nagatsu, S. Chiashi, S. Konabe, Y. Homma, *Phys. Rev. Lett.* **105** 157403 (2010).
[5] R. Kitaura et al. *Angew. Chem. Int. Ed.* **48**, 8298 (2009).
[6] S. Konabe and S. Okada, *Appl. Phys. Lett.*, **98** 073109 (2011).

Stretching A Bilayer Graphene

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In the present work, bilayer graphene flakes have been subjected to a uniaxial tension using the polymer cantilever beam technique. In all cases the mechanical response was monitored by simultaneous Raman measurements using different excitation wavelengths, mainly 514 nm (2.41 eV), 633 nm (1.96 eV) and 785 nm (1.58 eV). The flakes were either laid bare on a polymer substrate or covered by another polymer layer to minimize a possible slippage during loading. For comparison, monolayer graphene flakes close to the studied bilayers were monitored during the same experiment. In all cases, when both the mono- and bilayer are a part of the same flake, they show the same behavior under tension, with shift rates of approx. 31 and 10 $cm^{-1}/\%$ for G^- and G^+, resp. The G^-/G^+ relative intensities of such samples remain the same too, confirming the integrity of the respective layers. The behavior of the G band is the same when studied with different wavelengths. On the contrary, the 2D band evolution under tension differs upon the used laser line. The most pronounced changes can be observed with 1.58 eV excitation, mainly in the evolution of the highest-frequency component ($2D_{11}$), which originates from the double resonance process involving the "original" π_1 and π_1* bands belonging to the single layer. For the fitting procedure with Lorentzian line shapes the FWHMs were set as equal for all components and otherwise left unconstrained. The shift rates of the three lower frequency components involving the π_2 and π_2* electronic bands are all similar - close to 50 $cm^{-1}/\%$. However, the $2D_{11}$ shifts at a rate of only 30 $cm^{-1}/\%$. The relative intensities of the components evolve differently. The $2D_{12}$ experiences a twofold intensity increase in the observed strain range, mainly at the cost of the $2D_{11}$. The evolution of $2D_{11}$ and $2D_{12}$ closely resembles the splitting behavior of the 2D band in a monolayer when excited with the same wavelength [1].

[1] O. Frank, M. Mohr, J. Maultzsch, C. Thomsen, I. Riaz, R. Jalil, K.S. Novoselov, G. Tsoukleri, J. Parthenios, K. Papagelis, L. Kavan, C. Galiotis, *ACS Nano* **5**, 2231–2239 (2011).

Graphene xylophone

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We studied a mechanical resonance properties of graphene sheets and their applications. Rectangular shape of graphene sheet was prepared using O_2 plasma and suspended structure was made on the pre-patterned trench by the micro contact transfer printing method. Xylophone like structure was prepared for studying length and thickness dependance of mechanical properties of graphene resonator. Single layer graphene sheet shows nonlinear and bistable behaviors the actuation voltage was increased. The resonance frequency of graphene sheet can be tuned by applied DC bias voltage. Based on our results, we will suggest the potential application of the graphene resonator to the broadband tunable RF components.

Ultrafast Non-Thermal Electron Dynamics In Single Layer Graphene

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The dynamics of elementary excitations in graphene has been the object of a great deal of studies, aimed at understanding the fundamental relaxation mechanisms[1,2]. Following ultrafast photoexcitation, a strongly non-equilibrium (athermal) distribution of electrons in the conduction band (and holes in the valence band) is established. This then rapidly thermalizes due to electro-electron interaction, giving rise to an electron distribution with a well defined temperature, which in turn reaches thermal equilibrium with the colder lattice via electron-phonon scattering [3]. These equilibration processes change the transient absorption spectrum over a broad range of energies and an ultrafast timescale. Their time- domain observation calls therefore for the combination of very short pulsewidths with wide spectral tunability. Here we perform pump-probe spectroscopy on graphene using two-color few-optical-cycle pulses, thus combining high time resolution with broad spectral coverage [4]. Differential transmission experiments are carried out on graphene deposited on a fused silica substrate. We impulsively excite optical transitions with an ultra-broadband 6-fs pulse centered at 2.3 eV (2-2.5 eV bandwidth) and probe with a red-shifted 13-fs pulse covering the 1.4-1.6 eV range. The overall time resolution of our apparatus (width of the pump-probe cross- correlation) is 15 fs. We find that the delay in the formation of the photobleaching signal in the probe spectral window is shorter than our time resolution, suggesting that the early scattering dynamics are extremely fast. The photobleaching signal then relaxes on the 200-fs timescale at all the probe photon energies, that in our system are simultaneously recorded by an optical multichannelanalyzer. By studying the dependence of the dynamics on the pump pulse energy we could observe that at high fluencies the build-up of the photobleaching signal remains “instantaneous”, but a new ultrafast decay channel (around 20 fs time constant) is detected.

[1] Z. Sun et al., *ACS Nano* **4**, 803 - 810, (2010).
[2] F. Bonaccorso et al., *Nature Photonics* **4**, 611 - 622 (2010).
[3] M. Breusing et al., *Phys. Rev. B* **83**, 153410 (2011).[
[4] D. Brida et al., *J. Opt.* **12** 013001 (2010).

Characterization of Carbon Nanotubes with a Confocal Raman Microscope

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Raman spectroscopy is one of the techniques commonly used to study the properties of carbon nanotubes. Single walled carbon nanotubes (SWCNT) have typical diameters in the nanometer range and can exceed a length of several micrometer. Thus they represent unique systems for the study of Raman spectra in one-dimensional systems. The one-dimensional confinement of electronic and photonic states, leads to resonant enhancement of the corresponding photophysical process which is reflected in unique optical and spectroscopic properties. Characteristic for SWCNT`s are the radial breathing modes, providing information about the diameter of the tube. The G band is used for diameter characterization, to distinguish between metallic and semiconducting SWCNT's and to probe the charge transfer arising from doping a SWCNT. The G* band, characteristic for interlayer coupling in graphite, arises from photon resonance in SWCNT's. By combining the chemical sensitive Raman spectroscopy with high resolution confocal microscopy into a confocal Raman microscope, it is possible to characterize carbon nanotubes also in terms of orientation and distribution either on flat substrates or within a solid matrix. In confocal Raman microscopy, a complete Raman spectrum is recorded at every image pixel, leading to a 2D array of Raman spectra. By extracting spectral properties from the recorded 2D array of spectra such as peak intensity, position or width, various different Raman images can be extracted from one 2D array, giving insight not only to the properties of the carbon nanotubes, but also about the matrix around the carbon nanotubes.

Imaging & Tracking Single-Walled Carbon Nanotube Dynamics in Rock-Like Porous Media

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Single-Walled Carbon Nanotubes (SWNTs) have unique electronic and mechanical properties that have led to an increased interest for their use in a wide range of applications (i.e. composite materials, drug delivery, and electronics). Because of their extremely high aspect ratio and slenderness (~1 nm diameter), SWNTs can increase the electrical conductivity of fluids more effectively than other particles. Moreover, under appropriate conditions, SWNTs precipitate into highly conducting chains that can span macroscopic length scales.[1] Finally, because of their slenderness, SWNTs are expected to penetrate much tighter pores than isotropic particles of equivalent volume. Therefore, SWNTs can be useful in oil reservoirs as tools for sensing, targeting and as contrast agents. Recently, we have used direct imaging of SWNTs by tagging with fluorescent dyes [2] and semiconducting SWNTs by near-infrared (NIR) fluorescence [3,4] to directly measure bending dynamics and stiffness in aqueous media. We have also studied SWNT dynamics in agarose gels, a special case of porous media mimicking biological tissues and cells.[5] In this poster, we present current work studying the dynamics of single SWNTs within a rock-like porous media as a model for oil reservoirs. Rock-like porous media was produced by packing concentrated colloidal silica particles between clean glass coverslips where the thickness of the packed layer is equal to a few particle diameters thus allowing for optical imaging without index matching. Using an amphiphilic fluorescent molecule (PKH26, emission 567 nm) to tag surfactant stabilized SWNTs, we show that fluorescence at visible wavelengths can be used to directly image SWNT mobility within this porous media. Results are presented for SWNTs experiencing Brownian motion and under externally induced flow. In the no-flow case, reptation dynamics within the packed silica are measured and compared to that previously observed in agarose gels. [5] We find that, qualitatively, the lower porosity, large and fixed obstacles present in the silica pack versus that of agarose gels lead to slower and highly path dependent dynamics for SWNT motion. Silica particles have also been packed within microfluidic channels similar to column based electrophoresis techniques for fluorescent imaging and length separation of DNA and other macromolecules.[6] We show that, in similar devices, fluorescently tagged SWNTs can be imaged while flow is used to transport SWNTs through rock-like porous media with small pores (<1micron) and low porosity. Ongoing work is focused on investigating the effects of SWNT surface functionalization toward forming conductive SWNT networks for signaling, as well as, specific targeting of oil-water interfaces within porous media.

[1] P.V. Kamat, K.G. Thomas, S. Barazzouk, G. Girishkumar, K. Vinodgopal, D. Meisel, *Journal of the American Chemical Society*, **126**, 10757-62, (2004).
[2] R. Duggal, M. Pasquali, *Physical Review Letters*, **96**, 246104-1-4, (2006).
[3] R.B. Weisman, S.M. Bachilo, D. Tsyboulski, *Applied Physics a-Materials Science & Processing*, **78**, 1111-6, (2004).
[4] N. Fakhri, D.A. Tsyboulski, L. Cognet, R.B. Weisman, M. Pasquali, *Proceedings of the National Academy of Sciences of the United States of America*, **106**, 14219-23, (2009).

[5] N. Fakhri, F.C. MacKintosh, B. Lounis, L. Cognet, M. Pasquali, *Science*, **330**, 1804-7, (2010).
[6] Y. Zeng, D.J. Harrison, *Analytical Chemistry*, **79**, 2289-95, (2007).

Direct Measurements Of Bending Stiffness And Rippling Phenomena In Free-Standing Carbon Nanotubes

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Carbon nanotubes (CNTs) have a low mass and a high stiffness, which makes them suitable for future nano-electromechanical systems (NEMS), especially in high- frequency switching applications. In relays, the CNTs are bent during operation and a high bending stiffness is important throughout the bending sequence. Deformation modes will appear at large deflections, leading to a lower bending stiffness which in turn will influence the device performance. At relatively low bending curvatures there can be a wave-like rippling of the walls, while at higher bending curvatures there can additionally be a local collapse, buckling, of the walls. Buckling [1] and severe rippling [2] have both been observed using transmission electron microscopy (TEM). TEM imaging is not particularly useful though for detecting the very onset of the rippling, as there are only minute distortions of the CNT-walls [3]. Various theoretical modelling [3,4] have indicated at which strain levels the rippling would emerge, and how the bending stiffness would be affected. There has been very little experimental data to compare with though, thus far. Here we present direct measurements of the force response in freestanding carbon nanotubes. The measurements have been performed using a custom-built atomic force microscope (AFM) inside a scanning electron microscope (SEM). We have been able to detect the very onset of the rippling mode [5], which is manifested through an abrupt change in the bending stiffness of the CNTs. The stiffness drops by about a factor of two and the force response continues to be linear in the rippling phase. Critical strains for the rippling onset have been measured in nanotubes of 7-18 nm in diameter, and the obtained strain values compare well with theoretical modelling predictions. We have additionally found an indication that defects in the nanotubes will increase the critical strain value and give a reduction in Young's modulus. The present findings will have implications for the design of CNT-based NEMS, where exceeding the critical strain will influence the device performance.

[1] S. Ijima, C. Brabec, A. Maiti, and J. Bernholc, *J. Chem. Phys.* **104**, 2089 (1996)
[2] P. Poncharal, Z. L. Wang, D. Ugarte, and W. A. de Heer, *Science* **283**, 1513 (1999)
[3] M. Arroyo and I. Arias, *J. Mech. Phys. Sol.* **56**, 1224 (2008)
[4] I. Nikiforov, D.-B. Zhang, R. D. James, and T. Dumitrica, *Appl. Phys. Lett.* **96**, 123107 (2010)
[5] H. Jackman, P. Krakhmalev, and K. Svensson, Accepted for publication in *Appl. Phys. Lett.* (2011)

In Situ Raman Spectroscopy Of Carbon Nanotubes During Growth By A Local Heating Technique

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Most carbon nanotube synthesis methods require temperatures that are higher than what can be used for integration of nanotubes into electronics. In this study, a local heating technique is used to grow nanotubes in a CMOS-compatible process. High temperatures are generated locally on the sample by sending a current through a small molybdenum wire/heater which is deposited on the substrate. Nanotubes are grown from catalysts deposited on top of the heater whereas the temperature rapidly decreases to room temperature outside it. Since no furnace is required in this technique a small chamber that fits under a Raman microscope is used. This allows in situ Raman spectroscopy of the growing nanotubes. It is found that the heater is carbonised before any growth occurs and that the growth can be well described by the model used in refs. [1-3]. The kinetics show that the process is limited by mass transport of the carbon precursor. Fast growth rates are recorded despite the use of a cold carbon precursor, which has been shown to decrease the growth rate significantly [4]. We find that the molybdenum heater creates an additional pathway for the carbon cycle from gas to nanotube formation.

[1] E. Einarsson, et al., *Carbon*, **46**(6): p. 923-930 (2008).
[2] D.N. Futaba, et al., *Physical Review Letters*, **95**(5): p. 056104 (2005).
[3] M. Picher, et al., *Nano Letters*, **9**(2): p. 542-547 (2009).
[4] A.J. Hart, et al., *Small*, **3**(5): p. 772-777 (2007).

Effect of Laser Power on Raman Spectrum of Single-Walled Nanotubes

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Raman spectroscopy is now firmly established as a standard characterisation method for carbon nanotubes. While it is able to reveal many physical properties of the nanotubes, the most widespread application is to obtain a qualitative measure of the defect density of the nanotubes. This is measured by the relative intensity of the G- peak (~1580cm^{-1}) and the D-peak (~1350cm^{-1}), referred to as the G/D ratio. Although typically the wavelength of the laser used is reported, the power of the laser is rarely stated. In this work, we show briefly that the laser power can have a strong effect on the G/D ratio obtained from a nanotube sample. We discuss possible reasons for this, as well the effect this has on comparisons between samples tested under different conditions. We also recommend that the laser power be routinely quoted when reporting G/D ratios of carbon nanotubes.

Doping Single-Walled Carbon Nanotubes With Nitrogen: A STM And STS Investigation

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Prior to the integration of carbon nanotubes (CNTs) into nanoelectronic and C-based devices, large batches of nanotubes with reproducible and controlled properties are necessary. Because of the strong dependency of the electronic structure of carbon nanotubes with respect to geometrical parameters such as the diameter and the helicity, many efforts have been directed towards controlling the chiral indices of the tubes during synthesis or towards sorting nanotubes according to theses chiral indices. Another method to tune the nanotubes' electronic structure is to use doping, which may lead to properties that are more controlled by the chemistry than by the structure of the tubes. One of the most promising candidates for doping carbon nanotubes is nitrogen, thanks to its suitable atomic radius. Nitrogen atoms can however adopt different local environments (graphitic-like, pyridinic-like) which can have various effects on the nanotube's electronic structure. To investigate this impact, Scanning Tunnelling Microscopy(STM) and Spectroscopy (STS), appears as a unique tool since it can provide local information regarding both the structural and electronic properties of carbon nanotubes. For instance, this technique has given experimental evidence of the correlation between the chiral indices of single-walled CNTs and their electronic structure [1-2]. Here, we present the results of a STM/STS study of nitrogen doped single-walled carbon nanotubes, prepared by two different techniques: the vaporization with a continuous laser of a C:Ni/Y target under a nitrogen atmosphere [3]and a CVD floating catalyst reactor using a hot iron wire/CO/ammonia system[4]. These techniques lead to single-walled nanotubes with a nitrogen content ranging from 0.3 to 4%, as determined by EELS. For both synthesis methods, the STM images of nitrogen-doped CNTs reveal the presence of defects which can be assigned to the presence of N atoms since they are not observed in pure single-walled CNTs prepared in a similar way. These defects appear as large protusions (1 to 3 nm wide) at the surface of the nitrogen-doped tubes. High resolution STM images of the defects display various patterns, associated with different configurations involving one or several N atoms. Another signature of the incorporation of nitrogen is the presence of interference patterns which can be extended up to a few nanometres away from a defect. On the STS spectra, that measure the local density of states, we observe additional sharp peaks at the N-based defects, as compared to spectra recorded in defect-free area that only display contributions associated with the van-Hove singularities (vHs). These new peaks appear at energies that are different from those of the vHs and correspond to localized states. Based on a comparison between our STM/STS data, other experimental results and theoretical studies, we will discuss the nature of the defects induced by nitrogen doping of carbon nanotubes and their consequences on the tubes' structural and electronic properties.

[1] J.W.G. Wildöer et al., *Nature*, **391**; 59 (1998)
[2] T.W. Odom et al., *Nature*, **391**; 62 (1998)
[3] H. Lin et al., *J. Phys. Chem. C*, **113**, 9509 (2009)

[4] T. Susi et al., *Physica Status Solidi B*, **246**, 2507 (2009)

Anisotropic Optical Absorption Of Individual Carbon Nanotubes

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We first studied polarization-dependent Raman spectra of individual single- (SWNTs) and multi- walled nanotubes (MWNTs). Main goal was to investigate the Raman signal intensity and energy of G band as a function of the angle between the nanotube axis and the vector of the incident light (for two polarization configuration: VV and VH). We show that for the incident light polarized perpendicularly to nanotube axis the Raman peak intensity is fully diminished (to zero!). To our knowledge this has been never shown for individual multi-walled tubes. The interpretation of this behavior in case of MWNTs is based mainly on the depolarization effect and for SWNTs more significant are the available optical transition. Finally, we observed an extremely anomalous behavior: the dependence of energy of the G peak on the polarization direction of incoming light (not related with the symmetry of the G band). We propose that this behavior is related with anisotropy of the optical absorption of carbon tubes. The absorption anisotropy induced the change in local temperature of the tubes, what causes the shift of Raman peak.

Effect of Variations in Carbon-Carbon Bond Lengths on the Optical Absorption Properties of Different Carbon Nanotubes

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The electronic and optical properties of carbon nanotubes are known to be highly dependent on their diameters. For small-diameter nanotubes, the curvature of the nanotube sidewall has shown to significantly influence their electronic structures. One effect of this curvature is the change in the carbon-carbon bond length after geometry relaxation. In this theoretical work, we show the importance of geometry optimization in the prediction of the band structure and optical absorption spectra of nanotubes. We first study the effect of geometry relaxation on the carbon-carbon bond length along and perpendicular to the nanotube axis. For this purpose, we simulate three zigzag nanotubes with considerably different diameters ((4,0), (8,0) and (16,0) nanotubes with diameters of ~0.34, ~0.63, and ~1.27 nm, respectively) and calculate the bond length change resulting from the geometry optimization with different density functional theory (DFT) and hybrid methods. For example, after geometry optimization with the hybrid method of HSEH1PBE/6-31G,the carbon-carbon bond length along the nanotube circumference increases by about 4.37%, 0.92% and 0.27% from the original value of 1.42 nm in graphene for the (4,0), (8,0) and (16,0) nanotubes, respectively. In the next step, we show how this bond length change can affect the band structure and consequently the optical absorption spectra of carbon nanotubes. For instance, the first optical transition energy of the (4,0) nanotube decreases by %50 after geometry optimization (0.8 eV for a non- relaxed and 0.4 eV for a relaxed structure). For an (8,0) nanotube the first optical transition energy increases by 14% and for a (16,0) nanotube it decreases by 9%. We also perform a systematic study to separate the effects of the perpendicular bond length and the parallel bond length on the electronic bands and absorption spectra of nanotubes.

Optical And Electrical Properties Of Single-Walled Carbon Nanotubes Arrays

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In this work horizontally-aligned single-walled carbon nanotubes (h-al-SWNTs) were grown by chemical vapor deposition (CVD) on a (ST)-cut single crystal quartz substrate using ethanol as a carbon feedstock. High density SWNTs were obtained over a large area with variable tube densities depending on the catalyst concentration and the CVD duration time. They were then characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), UV-Vis and Raman spectroscopy and four-probe technique.SEM analysis showed that a nearly perfect alignment was achieved on large areas with a good homogeneity and high coverage of the substrate. AFM images confirmed that the tubes are mostly single-walled individuals and allowed for the determination of an average tube diameter. The found tube density is consistent with SEM observations. To further characterize the h-al-SWNTs, polarized micro-Raman spectroscopy was performed. Orientation-dependent measurements in parallel-polarized configuration revealed an angular dependence of the intensity which can be described with a $I(\theta) \propto \cos^2(\theta)$ law; Raman intensity of all major vibrational modes is thus maximum when the tubes are aligned parallel to the incident laser light polarization and minimum when perpendicular. In addition the diameter of the tubes was deduced from the radial breathing mode (RBM) and is in good agreement with AFM results. The strong anisotropy of the tubes is also evidenced by electrical conductivity measurements performed on a four probe station. These results demonstrate that h-al-SWNTs arrays are promising coatings for transparent and anisotropic conducting layers which in turn can be used as a replacement material of conventional ITO electrodes.

Electrochemical Decoration Of Carbon Nanotube Interconnects For Improvement Of The Electrothermal Properties

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Carbon nanotubes (CNTs) are attracting considerable interest for electronic interconnect applicationsdue to their unique electrical and thermal properties, all included in a nanometer scale object [1]: ballistic conduction of electrical current [2], capability to transport current densities up to 10^9 A/cm^2 [3] and thermal conductivities in the range of thousands W/mK [4]. CNTs produced by arcdischarge combine the above excellent properties, while CNTs grown by chemical vapor deposition (CVD) have poorer electrical and thermal properties. On the other hand, CVD grown CNTs are more suitable for practical applications as they can be integratedinto electronic circuits by placing the catalyst at specific locations. Here, we show that the electrothermal properties of CNT interconnects grown by CVD can be improved by electrochemically decoratingthe CNT interconnects with metal particles [5]. The CNTs are grown by CVD from Ni catalyst particles that are attached by electrochemical deposition (ECD) on one titanium nitride (TiN) electrode [6-8]. As-grown CNTs contact the opposing TiN electrode and can be electrically probed without any need of further post- growth contacting [6-8]. First, we demonstrate that a single as-grown CNT is able to carry a power up to 0.6 mW before breaking down under vacuum, with a corresponding maximum current density as high as $8\cdot107$ A cm^{-2}. Next, we demonstrate that the decoration with ECD Ni particles allows to protect the CNT interconnects from oxidation and to improve the heat release through the surrounding environment. Note that the particles deposited by ECD preferably nucleate at the defect sites where the breakdown of CNTs grown by CVD is initiated [9]. When decorated with Ni particles,a CNT can carry a much higher power on the order of 1.5 mW before breaking down under vacuum, with a corresponding maximum current density as high as $1.2\cdot10^8$ Acm^{-2}.Finally, we demonstrate that the Joule heat produced along the current carrying CNT interconnects is able to melt the Ni particles. The high temperature promotes the formation of titanium carbon nitride that, in combination with an electrostatic motion of the CNTs towards the metal electrodes, improves the electrical contact between CNTs and TiN electrodes before breakdown of the CNT interconnects. Our study provides new insight into the breakdown of the CNT interconnects and indicates that our growth method can produce CNTs with appropriate properties for electronic interconnect applicationsand that these properties can be further improved by ECD decoration of the CNT interconnects.

[1] M. S. Dresselhaus, G. Dresselhaus, Ph. Avouris, Carbon Nanotubes synthesis, structure, properties and applications, Springer, (2001).
[2] H. J. Li, W. G. Lu, J. J. Li, X. D. Bai, C. Z. Gu, *Physical Review Letters*,**95**, 1-4, (2005).
[3] Z.Yao, C. L.Kane, C. Dekker, *Physical Review Letters*,**84**, 2941-2944, (2000).
[4] P.Kim, L. Shi, A.Majumdar, P. L.McEuen, *Physical Review Letters,* 8721, 1-4, (2001).
[5] C. A.Santini, P. M.Vereecken, A. Volodin, S.De Gendt, G.Groeseneken, C. Van Haesendonck, Submitted to *Advanced Functional Materials*.

[6] C. A. Santini, D. J. Cott, A. Romo-Negreira, S. RivaSanseverino,S.De Gendt,P. M. Vereecken, *ECS Transactions*, **18**, 845-850, (2009).
[7] C. A.Santini, D. J.Cott, A.Romo-Negreira, B. D.Capraro, S. Riva Sanseverino, S.De Gendt, G.Groeseneken, P. M.Vereecken, *Nanotechnology*, **21**, 1-9, (2010).
[8] C. A. Santini, A. Volodin, C. Van Haesendonck, S. De Gendt, G. Groeseneken, P. M. Vereecken, Submitted to *Carbon*.
[9] K.Molhave, S. B.Gudnason, A. T.Pedersen,C. H.Clausen, A.Horsewell, P.Boggild, *Nano Letters*, **6**, 1663-1668, (2006).

Boron Doped Single Wall Carbon Nanotubes Grown by High Vacuum CVD Using a New Precursor

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Boron doped Carbon nanotubes are very important due to new discoveries about superconductivity [1], and improved field emission properties when compared with pure and nitrogen doped Carbon nanotubes [2]. They also behave as better transparent conductors than pure tubes since they reduce the sheet resistance at the same transparency[3].
In this work we propose a new Boron precursor, Triethyl Borate, to be used on the production of the doped Carbon nanotubes in a high vacuum CVD.As catalyst, we use a powder of Iron Nitrate III and Magnesium Oxide that was reduced at 700 °C with a Hydrogen flow. The tubes were
Synthesized between 750 °C and 900 °C. We characterize our samples by electron microscopy, SEM and TEM. The microscopy images clearly show the presence of bundles of SWNT. Raman spectroscopy can be related to boron doping, since the G band of the Raman spectra is up shifted when compared with SWNT grown using ethanol in similar experimental conditions[4]. The Raman spectrum also has a low ID/IG feature, indicating the high quality of the tubes, even if they are B-doped. We use XPS analysis to determine the total amount of Boron in the samples and the chemical environment of these atoms. The spectra reveal the presence of boron atoms bonded to carbon. We also compare these results with those obtained from tubes prepared with Ethanol and with Triisopropyl borate which is known to produce B-doped tubes [5]. Our results suggested that high-vacuum CVD with temperatures around 820 °C using Triethyl Borate as precursor is a reliable route to obtain boron-doped single wall carbon nanotubes.

[1] N. Murata et al., *Phys. Rev. Lett.*,**101**, 027002, (2008)
[2] R.B. Sharma et al., *Chem. Phys. Lett.*, **428**, 102-108, (2006)
[3] X. M. Liu et at., *Nano Lett.*, **8**, 2613-2619, (2008)
[4] Anindya Das et at., *Phys. Rev. Lett.*, **99**, 136803, (2007)
[5] P.Ayala et al., *Phys. Stat. Sol. (b)*, **245**, 1935-1938, (2008)

The World of CNT Forests

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Since the discovery of the carbon nanotube (CNT), extensive effort has been made to harness their exceptional intrinsic properties, such as electrical and thermal conductivity, mechanical strength, etc. In addition, this obstacle has been further limited by the ability to process the CNTs, either by wet (dispersion) or dry (sheets, yarns, etc), into functional forms. Moreover, CNT forests, a highly efficient growth of CNTs into vertical arrays, have shown great progress toward industrial production. Therefore, to promote the industrial use CNTs further fundamental understanding on the relationship between the CNT forest structure, e.g. height, density, etc, and the intrinsic and processing properties is needed. Therefore, the structure of CNT forests could be tuned to possess the set of optimum properties for a given application. Here, I will present our roadmap and current progress on developing our understanding of the relationship between forest structure and properties. I will discuss our development of a set of standardized evaluation techniques. Then, our progress on controlled growth, and finally some understanding we have at the present.

Low Temperature Synthesis of Metal-Catalyst-Free CNTs Using a Modified Chemical Vapour Deposition System.

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Carbon nanotubes (CNTs) possess unique structural, electronic, mechanical, magnetic, thermal and optical properties. Most carbon nanotubes synthesis techniques require the introduction of metal catalyst in the form of gas particulates or as a solid support. However, the main problem of using metal nanoparticles for CNT's growth is presence of impurities and thus usually requires further CNT purification. The most effective chemical purification methods, such as oxidation by heating, acids and oxidizing agents separate the synthesis products based on their reactivity which normally introduce unavoidable defects along the tubes and the pentagonal structure at the tube ends, causing considerable damage to the structure and morphology of the CNTs. To avoid the need for CNT purification and to clarify the role of catalysts, several research groups are exploring metal-catalyst-free methods to grow CNTs [1-5]. It has been suggested [3,6] that metal-catalyst-free growth of CNTs on SiO_2 substrates can be achieved by making nanostructures such as nano-curvatures or holes on their surfaces by sputtering or scratching of the SiO_2 substrate surface [2]. However in the previous studies metal-free growth of CNTs has only been achieved by using higher temperature (over 800 ºC) [2-5] CVD methods. Also annealing at 950 – 1000 ºC has found to be essential for CNT's growth [2]. Since almost exiting developed electronics devices have electrical interconnections, almost of which are formed of aluminium having a melting point of 660 ºC, it is very important to develop the method of low temperature CVD synthesis of metal-catalyst-free CNTs. In our research we demonstrate successful growth of CNTs at 500 ºC without high temperature pre-treatment. CNTs were synthesised in a modified dual furnace CVD system using oxidised Si wafer as a substrate and ethanol as a carbon source. It was found that the chemical pre-treatment of the Si-substrate in liquid ethanol is critical for defect generation on a Si/SO_2 surface which were found to be responsible for carbon precipitation and formation of the metal-catalyst-free CNTs. The role of separating ethanol vapour pyrolysis from the CNT formation in the two-zone CVD and the role of ethanol pre-treatment of the Si/SO_2 surface are discussed.

[1] D., Takagi; Y., Kobayashi; Y., Homma *J. Am. Chem. Soc.* **131**, 6922, (2009).
[2] H., Liu; D., Takagi; S., Chiashi; Y., Homma, *Carbon* **48**, 114, (2010)
[3] B., Liu; W., Ren; L., Gao; S., Li; S., Pei; C., Liu; C., Jiang; H. M., Cheng, *J. Am. Chem. Soc.*, **131**, 2082, (2009).
[4] J.-H., Lin; C.-S., Chen; H.-L., Ma; C.-W., Chang; C.-Y., Hsu; H.-W., Chen, *Carbon* **46**,1619, (2008).
[5] D., Takagi; H., Hibino; S., Suzuki; Y., Kobayashi; Y., Homma, *Nano Letters*, **7**, 2272, (2007).
[6] S., Huang; Q., Cai; J., Chen; Y., Qian; L., Zhang, *J. Am. Chem. Soc.*, **131**, 2094, (2009).

Effect Of Thin Film Catalyst Pattern Size On Carbon Nanotube Forest Growth

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We grow vertically aligned carbon nanotube forests from patterned thin film catalyst and investigate the effect of the size of these regions on the kinetics and morphology of the resulting forests. In our chemical vapor deposition process, the catalyst is cobalt on alumina, patterned at the 100 μm scale, and the carbon source is acetylene with water vapor as an enhancer. In situ kinetics of the growing forests are extracted using optical microscopy and scanning electron microscopy is used ex situ to analyze the morphology of the forests. We observe that the kinetics and morphology of the forests, especially the initial growth rate, termination time, final height, and synchronized periodic rippling pattern, depend on the size of the patterned catalyst region. These variations indicate that the local concentration of gas available for forest growth varies as well. The resulting variations in the growth rate can lead to a build up of strain, whichcan have profound effects on the termination of growth and the forest morphology, including the concavity of the top surface. The conclusion is that size matters when it comes to patterned thin film catalyst.

Chemical Vapor Deposition Growth Of CNTs And Other Nanocarbons From C_{60}

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Recent studies have reported the use of C_{60} as a seed material for the chemical vapor deposition (CVD) growth of carbon nanotubes (CNTs), instead of commonly used metal catalysts. [1,2] Since C_{60} molecules are identical, they have a uniform size distribution and might be used to grow CNTs with improved diameter and type control when compared to metal nanoparticles. In this work, the hot-walled CVD growth of graphitic carbon, carbon nanofibers, and CNTs is obtained from C_{60} using ethanol as the precursor. Samples are characterized by in situ and ex situ Raman spectroscopy, global Raman imaging, and ex situ scanning electron microscopy. We confirm that, as reported by Yu et al. [1], a pre-growth oxidation step performed at a minimum temperature yields small quantities of single-walled or thin multi-walled CNTs. By varying sample preparation, oxidation, and CVD conditions, we observe substantial changes to nanocarbon yield and relative abundance.

[1] X. Yu et al.,*Nano Lett.*,**10**, 3343-3349, (2010).
[2] F. Rao et al., *Carbon*, **47**, 3580-3589. (2009).

Directly Drawing Self-Assembly, Porous And Continuous Graphene Fibres From CVD-Grown Graphene Films

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The integration of nanoscale graphene into macroscopic structures has been proved to realize applications of graphene. We report a novel and simple approach to controllably fabricate graphene fiber, a porous and continuous macrostructure based on two-dimensional (2D) CVD-grown films [1]. The graphene film could be self- assembled from a 2D film to a 1D fiber-like structure in the ethanol solvent and a drying process was needed to confirm the porous and creased structure. The method developed here is scalable, continuous, controlled and low cost. The forming of the fibers and the size of the pores can be affected by the surface tension and solvent evaporation, respectively. The diameter of the obtained fiber is about 20~50 μm and the length is about 1~2 cm. The high electrical conductivity of this graphene fiber was determined to be ~10 S/cm. Its structure facilitated chemical doping, energy storage, electrochemistry and optoelectronics, which could be utilized in super capacitors, sensors, batteries and so on. This work provides a novel method to control the self-assembly behavior of the porous graphene fiber and to develop the graphene-based nanomaterials for macroscopic application.

[1] Li XM, Zhu HW, Wang KL, et al, In preparation.

Optimization and Understanding of Spin-capable CNT Growth using Water-assisted Chemical Vapor Deposition

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The spin-capable carbon nanotube (CNT) forest is a prerequisite for the production of CNT sheets and yarn. Spin-capable CNT forest was grown using water-assisted chemical vapor deposition (WA-CVD). The initial heating rate, growth temperature, gas flow rates, substrate preparation, buffer layer thickness and catalyst thickness affects the spin-capability of CNT forest. A growth model for spin-capable CNT forest is proposed. Our systematic approach revealed that the initial heating rate around 6 min, with growth temperature of 700 ºC, buffer layer (Al) thickness around 6 nm and catalyst (Fe) thickness more than 2 nm is essential to grow the spin-capable CNT forest. At these particular conditions, the catalyst film breaks into higher density catalyst particles and contribute to the spin-capable CNT growth. The spin-capable CNT forest consists of CNTs network in which neighboring CNTs shares some part of their outer wall. In some cases, two CNTs show tip-tip or bottom-bottom attachment. The spin-capable CNT forest can withdraw into a sheet or yarn. We believe that our rational approach for optimizing the spin-capable CNT forest may help to the other groups to grow spin-capable CNT forest more efficiently.

The Effect of Buffer Layer Deposition on Diameter and Alignment of Carbon Nanotubes in Water-assisted Chemical Vapor Deposition

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The buffer layer (Al) deposition plays important role in controlling the surface morphology of the substrate, which ultimately affects the growth of vertically aligned carbon nanotubes (CNTs) in water-assisted chemical vapor deposition [1]. In our previous studies, we have shown the effect of catalyst thickness on the diameter and alignment of CNTs [2]. The catalyst particles can also diffuse through the buffer layer and affects the morphology of CNT forest [3]. In the present study, we examined the effect of buffer layer deposition on the height, alignment and diameter of CNTs. Scanning electron microscopy, atomic force microscopy and tunneling electron microscopy were used to study these effects. The higher deposition rate makes the substrate rougher, which can grow more aligned, thin diameter CNTs with more height. In contrast, the slow deposition makes the smooth surface, which can grow misaligned, large diameter CNTs with less height. The details about the studies are presented.

[1] Patole SP, Alegaonkar PS, Lee HC, Yoo JB. *Carbon* **46**:1987-93 (2008)
[2] Patole SP, Alegaonkar PS, Shin HC, Yoo JB. *J Phys D: Appl Phys* **41** 155311-1-6 (2008).
[3] Patole SP, Yu SM, Shin DW, Kim HJ, Han IT, Kwon KW, Yoo JB. *J Phys D: Appl Phys* **43**:95304-1-7 (2010).

Nitrogen-induced CNT Catalyst Stabilisation For Chirality Control

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The addition of certain aromatic nitrogen containing molecules during the chemical vapour deposition synthesis of carbon nanotubes results in selective chiral angle MWNTs [1]. This has been traced to the structural order and templating effect of the catalyst particles that produce these CNTs [2], but it remains unclear exactly how these molecules are able to modify the catalyst in this way. We investigate the chemistry of the synthesis process and how certain nitrogen containing molecules are able to induce structural order in the catalyst during CNT growth.

[1] K. Koziol, M. Shaffer & A.H. Windle, *Advanced Materials*,**17**, 760–763 (2005).
[2] K. Koziol, C. Ducati, A. Windle, *Chemistry of Materials*, **22**, 4904–4911(2010).

Water-Free Chemical Vapor Deposition of Tall Multiwalled Carbon Nanotube Forests

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Despite the many potential applications of carbon nanotubes (CNTs), the controlled synthesis of CNTs remains a major challenge on the way toward the commercialization of the material. Water-assisted synthesis of millimeter-long arrays of aligned CNTs(so-called nanotube forests) has been demonstrated by Hata et al.[1] using an ethylene-based chemical vapor deposition (CVD) system and referred to as super growth. It has been revealed that the addition of oxygen plays a key role in balancing the various processes involved during CNT synthesis and leads to a higher yield [2][3].Subsequent work [4][5] has shown that millimeter-long nanotube forests can also be obtained without the supplement of oxidizing agents. However, this type of synthesis appears to have a relatively narrow window for the growth parameters. In this work, we present a systematic study of the synthesis of vertically-aligned CNT forests from ethylene without any oxidizing agent. Thermal CVD of nanotube forests on silicon substrates, patterned with 1.5/30 nm of Fe/Al thin films, and using $C_2H_4/H_2/Ar$ as gases was carried out at atmospheric pressure. The nanotube forest height was observed to be proportional to the ethylene flow rate in a relatively wide range of flow rates. Although hydrogen also plays a partial role as a carrier gas (in addition to its role as reducing agent), variations in the hydrogen and argon flow rates lead to very different trends in the yield, indicating diverse roles for the reducing and carrier gases: changing the proportions of hydrogen and argon for a given total flow rate had a drastic impact. The gas flow profile was optimal at an ethylene-to-total flow ratio of 8% and ethylene-to- hydrogen ratio of 25%, yielding multiwalled nanotube forests with a height of over 100 µm at 750 °C growth temperature. We also observed a very strong temperature dependence: while the growth was similarly successful at 675 °C and 725 °C, a temperature of 650 °C led to severely suppressed growth. Further optimization of the growth parameters allowed us to grow CNT forests approximately 1 mm in height. Characterization using energy-dispersive X-ray spectroscopy and transmission electron microscopy suggested that a tip-growth mechanism is dominant in this synthesis. The resulting multiwalled CNTs typically have less than 10 walls and their inner-shell diameters range from 5 nm to 15 nm.

[1] K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, and S. Iijima, *Science,* **306**, 1362-1364, (2004).
[2] T. Yamada, A. Maigne, M. Yudasaka, K. Mizuno, D. N. Futaba, M. Yumura, S. Iijima, and K. Hata, *Nano Letters,* **8**,4288-4292, (2008).
[3] G. Zhang, D. Mann, L. Zhang, A. Javey, Y. Li, E. Yenilmez,Q. Wang, J. P. McVittie, Y. Nishi, J. Gibbons, and H. Dai,*Proceedings of the National Academy of Sciences,* **102**, 16141-16145, (2005).
[4] A. J. Hart and A. H. Slocum,*Journal of Physical Chemistry B,* **110**, 8250-8257, (2006).
[5] J. Wu, Q. Huang, Y. Ma, Y. Huang, Z. Liu, X. Yang,Y. Chen, and D. Chen,*Colloids and Surfaces A*, **313-314**, 13-17, (2008).

Morphology Control Of CNTs In Continuously Spun Fibres

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Carbon nanotubes (CNT) based macroscopic systems (films, fibres, yarns etc.) have gained significant interest amongst both the academic and industrial communities. For the purposes of scientific study and to gauge the performance of these materials, it is imperative to synthesise such structures consisting of nanotubes with well-defined structural characteristics (number of walls, aspect ratio and chirality distributions). We present approaches towards large-scale continuous production of CNT based macroscopic structures consisting bundles of exclusively single-walled, double-walled or multi-walled CNTs by chemical vapour deposition (CVD). The process involves the pyrolysis of a catalyst and a carbon precursor (ferrocene and methane respectively) in a stream of hydrogen resulting in the in-situ production of catalyst nanoparticles, followed by nucleation and growth of CNTs. A promoter precursor, a sulphur-containing compound, is also incorporated to the reaction feedstock. The presence of sulphur aids in the rapid growth of exceptionally long nanotubes resulting in a smoke of CNTs that can be spun continuously in to a fibre. Here, we report strategies to control the size distribution of the catalyst particles utilising orchestrated thermal degradation of ferrocene and sulphur precursors. The effect of different sulphur precursors, with varied pyrolysis behaviour in terms of the temperature regimes of sulphur availability and its interaction with iron catalyst nanoparticles will be explored. We demonstrate, with extensive characterisation, the consequences of catalyst size control on the number of walls and diameter distributions of the constituent nanotubes in the resulting fibre. In addition, we will make attempts to relate the attributes of the individual nanotubes to the properties (mechanical and electrical) exhibited by the fibre. As a further step, we will also present some preliminary results of our attempts to explore the possibility of optimising the synthesis for production of fibres consisting of preferentially metallic nanotubes.

Selective Synthesis of (9,8) Single Walled Carbon Nanotubes

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Selective synthesis of single walled carbon nanotubes (SWCNTs) with specific (*n*,*m*) structures is desired for many potential applications. Current chirality control growth has only achieved at small diameter (6,5) and (7,5) nanotubes. Each (*n*,*m*) species is a distinct molecule with structure-dependent properties, therefore it is essential to extend chirality control to various (*n*,*m*) species. We demonstrate the highly selective synthesis of (9,8) nanotubes on several new cobalt based catalysts. The reduction and catalyst calcination temperatures were optimized. When catalysts were prereduced in H_2 at the optimized temperature around 500 °C, 59.1 % of semiconducting nanotubes have the (9,8) structure. The uniqueness of these catalysts relies on their low reduction temperature (483 °C), large surface area and strong metal–support interaction, which stabilizes Co clusters responsible for the growth of (9,8) nanotubes. SWCNT thin film field effect transistors fabricated using (9,8) nanotubes from our synthesis process have higher average device mobility and higher fraction of semiconducting devices than those using (6,5) nanotubes. Combining with further post-synthetic sorting techniques, our selective synthesis method brings us closer to the ultimate goal of producing (*n*,*m*) specific nanotube materials.

[1] Wang, H.; Wang, B.; Quek, X. Y.; Wei, L.; Zhao, J. W.; Li, L. J.; Chan-Park, M. B.; Yang, Y. H.; Chen, Y., *Journal of the American Chemical Society*,**132** (47), 16747-16749, (2010)

Ultra-High Vacuum-Assisted Control of Metal Nanoparticles for Horizontally-Aligned Single-Walled Carbon Nanotubes with Uniform Diameter

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Horizontally-aligned array of single-walled carbon nanotubes (SWNTs) on single crystalline substrates has attracted a recent interest for their electronic applications [1,2]. In contrast to many attempts to increase the SWNT density, little has been studied to control the SWNT diameter and chirality. This is mainly because the single crystal substrates cannot stabilize the small metal nanoparticles due to very flat surface and high CVD temperature. Here, we develop a new method to grow uniform diameter, horizontally-aligned SWNTs on sapphire substrate through the control of Fe nanoparticle size by annealing in ultra-high vacuum (UHV) [3]. We find that thermal annealing in UHV reduces the Fe nanoparticle size and significantly narrows their size distribution. These size-controlled Fe nanoparticles enable the catalytic growth of uniform-diameter SWNTs while maintaining their horizontal alignment. Systematic analyses of Raman radial breathing modes with three laser wavelengths indicate that ~76% of the horizontally-aligned SWNTs have diameters in the range of 1.3-1.4 nm under optimized annealing condition. Longer UHV annealing induces the increase in the Fe nanoparticle size, giving large-diameter SWNTs. Precise correlation between the metal nanoparticle size and SWNT diameter is demonstrated. Effects of UHV annealing on the nanoparticle size are discussed in terms of metal evaporation, subsurface diffusion, and surface precipitation of catalyst metals.

[1] N. Ishigami, H. Ago, K. Imamoto, M. Tsuji, K. Iakoubovskii,N. Minami, *J. Am. Chem. Soc.*, **130**, 9918 (2008).
[2] H. Ago, T. Nishi, K. Imamoto, N. Ishigami, M. Tsuji, T. Ikuta, K. Takahashi, *J. Phys. Chem. C*, **114**, 12925 (2010).
[3] H. Ago, T. Ayagaki, Y. Ogawa, M. Tsuji, submitted.

Carbon Nanotubes: Effects of Plasma Protein Binding

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In biomedical applications of carbon nanotubes (CNTs) the CNTs will come into contact with blood and its various components. It has been shown that among the many proteins present in human plasma, only a few bind to various pristine and chemically modified CNTs. We show the binding is highly selective and dependent on the type of nanotubes (single-walled, multi-walled) and the chemical modification, such as dispersant or oxidation. The proteins which bind in largest quantity are human serum albumin and fibrinogen, and also the lipoprotein complex high density lipoprotein (HDL), which contains phospholipids, cholesterol and the apolipoproteins AIV, AI, CIII. Binding most likely occurs at irregularities in the carbon network. In a competition experiment at least two non-overlapping types of binding sites for proteins on carbon nanotubes were identified. Binding of proteins to CNTs was shown to be unstable. Proteins pre-coated onto CNTs can be displaced fairly easily in blood plasma: for example precoated BSA (bovine serum albumin) is replaced by HSA (human serum albumin) when CNTs are incubated in human plasma. Another important group of proteins found to interact with CNTs are innate immune system proteins. The innate immune response plays a key role in protection against pathogens and synthetic particles. By haemolytic assays and western blots we showed CNTs bind C1q, C3 and C4, which are important proteins of the complement classical and alternative pathways. This indicates that the complement system is activated by CNTs and this activation may promote inflammation, granuloma formation and interaction with cells that have receptors for complement proteins. When complement is activated, C3b (the large fragment of activated C3) binds covalently to most targets, via OH or NH_2 groups on the target. The same occurs for C4b. CNTs do not have many available reactive groups of this type, therefore C3b and C4b may bind covalently to other proteins adsorbed to the CNTs; or they may bind by hydrophobic interaction. No evidence was found for covalent binding of C3b to other plasma proteins bound to the CNTs and therefore hydrophobic binding is assumed. We are currently studying interactions of CNTs with red blood cells which may occur by binding of the C3b coated on the CNTs to the receptor CR1 on red blood cells. Furthermore as C3b is a strong opsoniser, a signal for phagocytes to take up C3b-coated particles, we are examining the role of C3 in uptake of CNTs.

Growth and Characterization of TiO_2 Nanotubes for Resistive Switching Memory Applications

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1-dimensional (1D) nanostructures including nanotubes and nanowires have received great attention these days due to their increased technological importance in possible applications to various areas, for example, catalysis, sensors, energy storage/conversion applications, biological/medical applications, and microelectronics. Among the many types of 1D nanomaterials, nanotubes have a high specific surface area that is expected to have many advantages in comparison to their bulk counterparts. The fabrication of nanotubes using nanoporous templates has advantages in controlling the length and/or diameter of the nanotubes to the desired dimension. Active researches have been done on the fabrication and characterization of resistive switching memory devices based on metal-oxide thin-films. For further device scaling, it is highly required to investigate the resistive switching behaviours in 1-dimensional nanostructures. In this study, the resistive switching phenomenon of nanotubular TiO_2 was investigated. The anodized aluminum oxide (AAO) membrane templates were employed to synthesize the nanotubular structure of TiO_2. The diameter of TiO_2 nanotubes was well controlled by the pore-size of the AAO nano-templates. In addition, the wall thicknesses of the TiO_2 nanotubes were controllable by varying the deposition conditions. After removing the AAO templates, TiO_2 nanotube arrays were synthesized on the desired substrates. By using focused ion-beam deposition Pt metal electrodes were precisely deposited on the TiO_2 nanotubes to form memory device structure. The fabricated memory devices showed resistive switching characteristics according to the set and reset processes, showing the programmable memory properties. The fabrication and characterization of AAO nano-templates, controlled TiO_2 nanotubes, and memory devices will be presented in detail. The reported approach offers new opportunities to prepare non-volatile memory devices based on the 1D nanostructures for extending the device scaling limit.

Numerical Study on AC Response of Defective Carbon Nanotubes

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Recent progress in ultrafast electronic devices stresses a need for the understanding on dynamical response of nanoscale materials. However, even for metallic single-walled carbon nanotubes (M-SWNTs), which are promising for the next-generation ultrafast devices, only few theoretical investigations have been reported on their AC response [1,2], though their DC response has been extensively explored thus far. In particular, the influence of defects in M-SWNT on AC response remains to be elucidated. In this work, we have performed numerical analysis of AC response of M-SWNT with a single atomic vacancy by the density functional theory combined with non-equilibrium Green's function method [3]. We found that when the Fermi level is increased (note that experimentally the Fermi level shift can be realized by applying Gate voltages), transitions between inductive and capacitive emittance occur around the defect energy levels. Similar transition between capacitive and inductive responses has already been seen in previous theoretical investigations on M-SWNT without defects [2]. Unexpectedly, we also found features of AC response that are not seen in the previous investigations. That is, when the defect position shifts from the center of nanotube, the emittance behaviors at the defect energy levels change towards inductive response, while DC conductance does not change. This behavior induced by the position of defect is unique to AC response, and can be understood in the light of parity symmetry breaking.

[1] T. Yamamoto, K. Sasaoka, S. Watanabe, and K. Watanabe, *Phys. Rev. B.*, **81**, 115448, (2010).
[2] T. Yamamoto, K. Sasaoka, and S. Watanabe, *Phys. Rev. B*, **82**, 205404 (2010).
[3] D. Hirai, T. Yamamoto, and S. Watanabe, in preparation.

Exciton Crystals and Exciton Reactions in Carbon Nanotubes

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By studying single-walled semiconducting carbon nanotubes (SWNTs) under intense illumination, we show evidence for the existence of a one-dimensional 'exciton crystal', i.e. a spatially-ordered arrangement of excitons with separation comparable to their size. The ordering is deduced from the initial decay dynamics after the illumination is turned off, which deviate from the well-behaved reaction rates followed at longer times, and vary with increasing illumination intensity as the initial population distribution becomes ordered rather than spatially random. The exciton crystal was theoretically predicted by Ivanov and Haug in 1993 [1] and is a distinct state compared to Wigner crystals or Bose-Einstein condensates. Studies were performed on purified DNA-wrapped HiPCO SWNTs [2]. Excitons were photoexcited by illuminating with <100fs laser pulses, and at sufficient intensity a fast decay was observed due to exciton-exciton annihilation [3,4]. By differentiating the decay of the population n, we determine the reaction order β where $-dn/dt \propto n^{\beta}$. We observe crossover between mean-field behavior ($\beta = 2$) at times <3ps and high excitation, and anomalous diffusion-limited behavior ($\beta = 3$) at times >3ps. A further crossover to exponential decay ($\beta = 1$) occurs when there is ≤1 exciton per nanotube remaining, allowing precise calibration of the exciton population. The initial population saturates when excitons are separated by their theoretically-calculated length of 1.3nm. The same result was reported by Lüeret al. [5] and attributed to Pauli repulsionof the excitons.

The dynamics at times <1ps and high excitation deviated from these rate equations. For generic 1D reaction-diffusion systems, this has been attributed to different initial spatial distributions [6]. The diffusion-limited reaction rate coexists with an annihilation-induced partially-ordered state. At low densities, the measured initial decay rate was larger that of the simple rate equation, as randomly-generated excitons may be closer together. However at saturation the initial decay rate was instead smaller, revealing a distinct ordered state at times too early to arise as a result of annihilation. We ascribe this to the exciton crystal statearising from Pauli repulsion predicted by Ivanov and Haug [1]. Monte Carlo calculations of non-overlapping particles reproduce the measured behavior and confirm the Fermionic description of excitons at distances comparable to the Bohr radius.

[1] A. Ivanov and H. Haug, *Physical Review Letters*, **71**(19), 3182, (1993).
[2] Q. Yang et al., *Nanotechnology*, **18**(40), 405706, (2007).
[3] Y. Z. Ma et al., *J. Chem. Phys.*, **120**, 3368, (2004).
[4] R. Russo et al., *Physical Review B*, **74**(4), 041405, (2006).
[5] L. Lüer et al., *Nature Physics*, **5**, 54, (2009).
[6] C. Doering and D. Ben-Avraham, *Physical Review A*, **38**, 3035, (1988).

Field Electron Emission of Carbon Nanotubes Grown on Titanium Substrates by Hot-filament Chemical Vapor Deposition

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We report on direct growth of vertically aligned carbon nanotubes by using hot-filament chemical vapor deposition (hot-filament CVD) via selectively heat pre-treatment of catalyst. Pre-treatment by thermal annealing in air produced dense catalyst nanoparticles, which promoted hundreds-µm-long vertically aligned carbon nanotubes. Scanning electron microscopy and micro-Raman spectroscopy were employed to evaluate the quality and nature of the CNT formed.

We also measured electron emission properties of the 1.5-mm-diameter CNT-Ti structures in a 10^{-7} torr vacuum chamber using a simple diode configuration. The turn-on electric field for a current of 100 nA was 0.51 V/µm, and the threshold electric field corresponding to a current density of 1.00 mA/cm^{2}was only 0.68 V/µm. It is evident from our data that our CNT emitters exhibited excellent field emission and followed Fowler-Nordheim theory.

Contact Geometry Dependent Transport and Hysteresis in Carbon Nanotube Field Effect Transistors

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Contact properties of carbon nanotubes (CNTs) and metal electrodes are important factors in determining the transport properties of the CNT devices. Two different contact geometries, i.e. side-contact and end-contact geometries have been predicted to have different junction properties due to the different chemical bonding between carbon and metal atoms [1]. Most of the CNT devices have been fabricated using side-contact geometry due its easier fabrication processes. Recent calculation results have predicted the superior of end-contact junction with much lower contact resistance [2]. Thus, a development of fabrication method of the end- contact geometry is a challenge. Very recently, an end-contact geometry but having long contact length, called as embed-end-contact geometry, using metallic CNTs has been demonstrated [3]. The transport properties have been found to be similar to those of side-contacted devices since the domination of the transport at the edge of the contacts. Here we demonstrate a realization of end-contacted CNT devices with contact length down to several nanometers. The proposed fabrication method has also been motivated for realization a resist-free process that is important in suppressing the hysteresis usually appears in carbon nanotube field effect transistors (CNT-FETs). The first step was the formation of a passivation layer of HfO_2 by means of atomic layer deposition on the as-grown CNTs. This passivation layer avoids the direct contact of the CNTs to the resist materials and acts as a layer for controlling the contact length. A part of the CNTs of the patterned areas where the source and drain electrodes would be deposited, were removed altogether with the HfO_2 layer and a part of the SiO_2 layer under the CNTs by dry etching. Then, Au-covered Ti electrode was deposited. The transport and hysteresis properties were evaluated using the Si substrate as a backgate. As expected, the fabricated end-contacted CNT-FETs exhibit small hysteresis width compared to conventional side-contacted CNT-FETs passivated with HfO_2 layer. We have also fabricated side- and end-contacted CNT-FETs on the same CNT channel to directly compare the transport properties.

[1] J.J. Palacios et al., *Phys. Rev. B* **77**, 113403, (2008).
[2] Y. Matsuda et al., *J. Phys. Chem. C*, **114**, 17845, (2010).
[5] X. Song et al., *Nanotechnology* **20**, 195202, (2009).

The Ultimate Field Emitter Using Millimeter Long Carbon Nanotubes

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We are reporting the fabrication of a very efficient electron source using long and crystalline carbon nanotubes. These devices start to emit electrons at fields as low as 0.10 V/µm and reach threshold emission at 0.164 V/µm. In addition, these electron sources are very stable and can achieve peak current density of 750 $mAcm^{-2}$ at only 0.25 V/µm. To demonstrate intense electron beam generation, these devices were used to produce visible light by cathodoluminescence. Finally, to rational the measured properties in open carbon nanotubes of different lengths we used density functional theory. The modelling establishes a clear correlation between length and field enhancement factor.

Separation Of Metallic And Semiconducting SWCNTs For Integrated Circuits By Polarized Laser Radiation

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Graphene and Single-Walled Carbon Nanotubes (SWCNT) share properties that make both materials interesting for a high-speed carbon-based electronics of the future: both semiconducting SWCNTs (sc-SWCNTs) and graphene show extremely high electron mobilities roughly 70-100 times the electron mobility of silicon [1]. Metallic SWCNTs (m-SWCNTs) on the other hand show an unprecedented ballistic electron conductivity. Both together could form novel integrated circuits with an all-carbon approach for both the wires (m-SWCNT) and integrated devices (sc-SWCNTs). The drawback for such a nanotube based electronics typically is the spaghetti-like appearance of intermixed m-SWCNTs and sc-SWCNTs which is (i) hard to separate and (ii) hard to orient in a manner that would allow to build electronics circuits from them. However, it seems to be possible to get rid of this double issue.
Thin SWCNT films containing both sc-SWCNTs and m-SWCNTs have been deposited on planar surfaces. By using different lasers it is possible to preferably destroy either semiconducting or metallic nanotubes, simply by using different laser wave-lengths (as derivable from the Kataura-Plot). This is possible despite the tubes being organized in cross-linked bundles. In this way, laser-structured surfaces with different line-widths could be prepared with a strongly suppressed amount of sc-SWCNTs or m-SWCNTs, respectively. Preliminary experiments also show that the use of polarization filters can destroy a part of the remaining (metallic or semiconducting) tubes so that the surviving ones are oriented perpendicular to the polarized laser beam. This might indeed be a major step towards a purely nanotube based high-speed carbon electronics.

[1] T. Dürkop, S. A. Getty, Enrique Cobas, M. S. Fuhrer, *Nano Lett.* **4**, 35-39 (2004) & J.H. Chen, C. Jang, S. Xiao, M. Ishigami, M.S. Fuhrer, *Nature Nanotechnology*, **3**, 206 – 209, (2008).

Carbon Nanotubes as Cooper Pair Beam Splitters

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Producing entangled electron pairs in a solid state device from the splitting of Cooper pairs is a challenging possibility which is starting to generate an intense experimental effort. A basic splitting device is a three terminal system with a central superconducting lead (S) in between two normal (N) ones. The basic mechanism for converting Cooper pairs into quasiparticles is the Andreev reflection in which an originally quantum coherent electron pair in the singlet spin state is produced at an interface between a superconductor and a normal conductor. Conventional Andreev reflections (AR) are local and cannot readily be used to create bipartite states. Theoretical suggestions hint towards the crossed Andreev reflection process. Many theoretical proposals for circumventing this fact have been around for the last decade. It has been suggested to make use of electron-electron interactions, spin filtering or anomalous scattering in graphene to promote Cooper-pair splitting, i.e., the crossed Andreev reflection process. Metallic carbon nanotubes are predicted to exhibit ballistic transport and long spin-flip scattering lengths, both relevant to the coherent transport of Cooper pairs. Hence Cooper pairs are supposed to have a long superconducting coherence length within these quasi-one dimensional conductors. The devices studied here are double quantum dots which can be viewed as artificial molecules connected to one superconducting reservoir (Al) and two normal reservoirs (Pd). Thanks to their tunability, they allow to change in situ the probability of emitting split Cooper pairs. These findings open an avenue for more complex quantum optics like experiments with electronics sates which should allow, among other things, to test the coherence of the emitted split Cooper pairs.

[1] L. G. Herrmann, F. Portier, P. Roche, A. Levy Yeyati, T. Kontos, C. Strunk
Phys. Rev. Lett., **104**, 026801, (2010).

Carbon Nanotube-Based Magnetic Nanohybrids

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Carbon nanotubes (CNTs) with tailored functionalities are multifunctional carriers that can potentially provide new approaches for diagnosis and treatment of diseases. Synthesis of magnetic CNTs with required physical properties (size distribution, magnetic saturation, etc…) for biomedical applications still remains a challenge to accomplish. We developed a simple multi-step chemical route for synthesis of carbon nanotube-based magnetic nanohybrids. On one hand, chemical oxidation of CNTs has been used to control the length distribution of CNTs and provide them carboxylic groups for further functionalisation. On the other hand, superparamagnetic iron oxide (SPIO) nanoparticles have been synthesized as a tool to render the CNTs magnetic. Finally, covalent functionalisation was used to decorate the oxidised CNTs with the SPIO nanoparticles. Tuning magnetic properties of such carbon nanotube-based complex has been achieved using mainly different types of pristine CNTs (SWNTs and MWNTs) prior to oxidation, but also by changing covalent connection conditions. Such carbon nanotube-based nanohybrids can be used for various biomedical applications as imaging (MRI contrast agent) or sensoring (nanoparticles-based diagnostics).

Plasma Post-Synthesis Treatment of Carbon Nanowalls and Their Characteristics

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Carbon nanowalls (CNW) represent an interconnected network of bidimensional lamelar nanostructures, assembled from few layers of graphene sheets placed perpendicular to the substrate. These CNW present specific features: reduced dimensionality, sharp edges and large surface area, which recommend them for high technology applications. Thus, recent research in the field presents nanowalls as efficient materials for field emission, to achieve superhydrophobic surfaces, as materials for gas sensors, templates and supports for catalysts, electrodes for batteries and membranes for fuel cells. We already reported [1-3] the growth of CNW and controlling their density, size and shape using an expanding radiofrequency argon plasma beam injected with acetylene and hydrogen. It is shown that some CNW characteristics can be easily selected and influenced by changing certain parameters (plasma and substrate conditions) during CNW synthesis. Another way of tuning their properties is represented by post-synthesis treatment.

We also investigated the characteristics of the obtained materials in relation to several applications like wettability, cell attachment and synthesis of metal-CNW nanocomposites (for nano-sensors, catalysis, batteries and fuel cells). After plasma post-synthesis treatments of the carbon nanowalls layers we obtained a remarkable wettability control, switching from super-hydrophobic to super-hydrophilic behavior while the surface morphology was preserved.

[1] S. Vizireanu, L. Nistor, M. Haupt, V. Katzenmaier, C. Oehr, G. Dinescu, *Plasma Processes and Polymers*, **5**, Issue 3, 263-268, (2008).
[2] E.C. Stancu, M.D. Ionita, S. Vizireanu, A.M. Stanciuc, L. Moldovan, G. Dinescu, *Materials Science and Engineering B*, **169**, 119-122, (2010).
[3] S. Vizireanu, S.D. Stoica, C. Luculescu, L.C. Nistor, B. Mitu, G. Dinescu, *Plasma Sources Science and Technology*,**19**, 034016, (2010).

Magnetoconductance of Carbon Nanotubes: From Spin-orbit Interaction to Band-gap Engineering

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We have investigated the magneto-conductance (MC) of carbon nanotubes (CNTs) in pulsed, parallel magnetic fields up to 60 T. From the MC of semiconducting CNTs, we report the direct observation of the predicted band-gap closure and there opening of the gap under variation of the applied magnetic field. We also highlight the important influence of mechanical strain on the MC of the CNTs [1]. For chiral metallic CNTs, we find a peculiar split MC peak close to the charge neutrality point. Our analysis of the data reveals that this splitting is intimately connected to the spin-orbit interaction and the tube chirality. Band structure calculations suggest that the current in the peak regions is highly spin-polarized, which calls for application in future CNT-based spintronic devices [2].

[1] S. H. Jhang et al., *Phys. Rev. Lett.* **106**, 096802, (2011).
[2] S. H. Jhang et al., *Phys. Rev. B* **82**, 041404(R), (2010).

Tuning of Metal Work Function and Schottky Energy Barrier Using Different Terminal Group of Thiolated Molecules in Carbon Nanotube Based Schottky Device

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Carbon nanotubes have been considered to be promising materials in nanoscale electronic devices due to its outstanding electrical properties such as reduced carrier scattering rates and high current carryng capability. [1,2] In carbon nanotube based electronic devices, there is a substantial Schottky barrier (SB) formed between metal and semiconducting nanotubes and it has an effect on the device working principle dominantly. Herein we report tuning of the schottky energy barrier using different thiolated molecules, which formed self-assembled monolayer (SAM) on center gold electrode. Four thiolated molecules such as, 8-mercaptooctanoic acid, 1-heptanethiol, 8-amino-1-octanethiol, and 6-mercapto-1-hexanol solutions (0.3 mM) were immobilized on gold surface to examine terminal group dependent work function modulation. During the monolayer formation on gold surface, the conductivity was measured by using semiconducting analyzer in real time and the total dipole moment of thiolated molecules were calculated by using ab-initio Hartree-Fock method. [3] Both the results showed that 8-amino-1-octanethiol molecule has highest total dipole moment values and conductivity changes among the four thiolated molecules. This result suggests that the conductance change follows the change in gold work function and it was influenced by the total dipole moment formed on modified gold surface.

[1]C.T.White, T.N.Todorov, *Nature*, **393**, 240, (1998).
[2]S. Frank, P. Poncharal, Z.L. Wang, W.A. de Heerm, *Science* **280**, 1744, (1998).
[3]I. H. Campbell, S. Rubin, T. A. Zawodzinski, J. D. Kress, R. L. Martin, and D. L. Smith, *Phys. Rev. B*, **54**, R14321–R14324, (1996).

SWCNT Alignment By Different Techniques

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Ordered assemblies of nanoparticles and nanowires have promising technological applications since they provide effective building blocks for physical, chemical, and biological systems. Single Walled Carbon Nanotubes (SWCNTs) represent an anisotropic and perfectly one-dimensional group of nanowires with extraordinary electronic, mechanical, chemical and thermal properties. Mostly, SWCNTs are kept in solution for processing, and for any application benefitting from ordering and alignment it is necessary to bring them on the surface in an organized way. We present different techniques for the alignment of SWCNTs on planar unstructured and structured silicon surfaces. This includes large area alignment by a modified dielectrophoresis technique as well as alignment techniques by spray techniques. Key for the successful deposition is the control of the interface properties between the substrate and the SWCNT containing medium (liquids, vapours). The poster presentation includes a comparison of theoretical and experimental results regarding the achieved degree of orientation.

Liquid-phase Alkali-doping of Individual CNT FETs

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We have studied the influence of liquid-phase alkali-doping on electronic transport in individual carbon nanotube (CNT) field-effect transistors (FETs). The study complements previous alkali-doping experiments on individual CNTs, that to the best of our knowledge all have been performed in gas-phase. Our CNT FETs were exposed to an active solution of Li cations and naphtalene anions in THF, while kept in the inert environment of an argon-filled glovebox. The electronic transport characterization consistently shows complete reversal from p- to n-type behavior, while maintaining a similar ON/OFF ratio and subthreshold slope in both states. In real time measurements during liquid-phase doping, we detect attachment of alkali cations to the CNT FET with a signal response that ranges over more than three orders of magnitude. The doping is fully reversible upon exposure to oxygen, and the doping cycle is repeatable. Liquid phase alkali-doping of CNTs is a simple, inexpensive and scalable method, and shows again the good potential for CNTs to be utilized as nano-sensors.

Using Double Wall Carbon Nanotubes as Electromechanical device

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Carbon Nanotubes (CNTs) are interesting materials from the viewpoint of applications due to some of their astounding properties such as the possibility of being metal or semiconductor - depending on its chirality - as well a large Young’s Modulus (about 1TPa). Because of these properties the CNTs could be used in nanosensors, nanodevices and reinforcements in polymer matrices. Experimental studies have shown that low doses of ion irradiation can create links between the walls of nanotubes and consequently modify their proprieties even further, in particular their mechanical and electrical ones. In this work we theoretically address the possibility of building an electromechanical device using double-wall carbon nanotubes (DWCNTs) connected by different cross-links. For this study we have investigated the Wigner Defect – consisting of the Frankel pair composed by a vacancy-interstice with connections between the walls of the DWCNTs. We investigate two distinct systems: first we study a device composed by two different electrodes, one (10,10) and other (5,5) CNT in a telescope-type arrangement connected by a defect within a double wall segment. The second arrangement considers a weight-type arrangement where an (5,5) nanotube connects two (10,10) CNTs via a double-wall region that contains the defect. Using Density Functional Theory with Non-equilibrium Green's Function we show how the mechanical properties could alter the electronic transport in these systems. For all systems we will show that the transmittance has several resonances, which depend on the particular relative positions of the atoms in the nanotubes. Thus we will demonstrate how small displacements of the inner tube can alter the position of these peaks for the above systems leading to a device that could be used as a mechanical sensor for length scales in the nanometer and subnanometer range.

Preparation of Iron Catalyst Nanoparticle for Single-Walled Carbon Nanotube Forest from Various Iron Compounds

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Catalysts are one of the most important factors that govern the structure of single wall carbon nanotube (SWNT). When SWNTs are synthesized in high yield on substrates, in most cases, pure iron thin films sputtered or e-beam deposited on an Al_2O_3 support layerare annealed in hydrogen to form small catalytic nanoparticles [1-3].In this presentation, wehave studied this pre-annealing process, denoted as the "formation process", of Fe/Al_2O_3 catalyst for SWNT growth. Various Fe compounds, such as iron nitrate, iron chloride, bucky ferrocene, and chemically prepared colloidal iron nanoparticles, deposited on sputtered Al_2O_3 layer by spin-coating or bar-coating, could serve as a catalyst for highly efficient SWNT growth. This generality was explained by subsurface diffusion of Fe atoms into the Al_2O_3 support invoked by hydrogen annealing. As a result, the majority of the deposited Fe left the surface and the remaining Fe reconfigured into small nanoparticles suited to grow SWNTs.Additionally, the average diameter of the SWNTs (and the size of Fe catalysts) grown from all iron compounds studied fell in an unexpectedly narrow range of 2.8-3.1 nm. From experimental observation including XPS, AFM, and SEM-EELS observations, we interpret that interplay between Ostwald ripening that eliminated smaller nanoparticles and subsurface diffusion that reduced the size of larger nanoparticles resulted in a fairly uniform assembly of small catalysts regardless the initial Fe compound.

[1] D. N. Futaba, K. Hata, T. Namai, T. Yamada, K. Mizuno, Y. Hayamizu, M. Yumura, S. Iijima, *J. Phys. Chem. B*, **110**, 8035, (2006).
[2]Y. Q. Xu, E. Flor, M. J. Kim, B. Hamadani, H. Schmidt, R. E. Smalley, R. H. Hauge, *J. Am. Chem. Soc.*, **128**, 6560, (2006).
[3] G. Zhong, T. Iwasaki, J. Robertson, H. Kawarada, *J. Phys. Chem. B*, **111**, 1907, (2007).

Directed Motion Of Carbon Nanotube In Water Driven By Non-uniform Electric Field

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The carbon nanotubes (CNTs) have been used as nanoelectromechanical systems (NEMS) components widely because of their superior mechanical properties, ideal geometry, and chemically inertia. In addition, due to their one-dimensional nature, they are regarded as a promising and powerful tool for molecules transportation. To this end, a variety of novel mass conveyors in molecular scale was proposed experimentally or theoretically.

In this work, a novel type of molecular linear motor in water based on molecular dynamics (MD) simulations is reported. The physical model is composed of two coaxial armchair single-walled CNTs (5,5) and (10,10) immersed inside water cluster and the outer SWCNT(10,10) is shorter than the inner SWCNT(5,5). The axis of CNTs is along the Z direction and a non-uniform electric field is applied in X direction with a linear gradient along the Z axis. The strength is expressed as $E_x = a \cdot z$, where z is coordinate in Z axis and a is the gradient coefficient. The results show that the outer SWCNT starts to move just as the electric field is applied and finally it reaches the end of inner SWCNT where the electric field strength is lower within some nanoseconds. In addition, the velocity of movement dependent remarkably on the gradient coefficient a, but due to the thermal fluctuations the velocity value is no more than 10nm/ns. To study the physical mechanism of this phenomenon, we calculate the VdW interaction energy of the outer SWCNT with water along the Z direction. The results demonstrate that as the strength of electric field decreases the VdW energy also decreases and so the outer SWCNT is forced to the areas where the VdW energy is lower. Also, when the strength of electric field is low, the gradient of the VdW energy is also low and even the trend has a little reverse. We think the inertia could overcome the barrier and the model could be designed exactly to avoid this problem.

Modelling the Effects of High Exciton Density on the Optical Properties of Carbon Nanotubes

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It is now widely accepted that exciton effects play an important role in the optical processes of carbon nanotubes [1]. Recent experimental studies, investigating the photoluminescence process, have demonstrated optical pumping of carbon nanotubes over a wide range of intensities [2]. These experiments are expected to produce excitons at sufficiently high densities that exciton-exciton interactions, and the screening by excitons, should be significant. However, previous theoretical investigations have typically modelled the optical properties of carbon nanotubes only at vanishing exciton density, and by considering screening effects only within a static approximation. It has been demonstrated elsewhere that, for semiconductor quantum wires, these approximations are insufficient at high exciton densities [3]. In this work we use a fully dynamical theory to investigate the effects of varying exciton density on the optical response of carbon nanotubes. We use the Bethe-Salpeter Equation to describe the exciton and many-body effects. The many-body interaction is built upon a tight- binding framework. Dynamical screening is modelled through a multiple Plasmon Pole Approximation and plasmon dispersions are extracted from a fully dynamical calculation of the dielectric function, in the Random Phase Approximation. Our calculations show that as the exciton density increases, the exciton binding energy and the band-gap renormalisation both decrease significantly. However, due to a partial cancelling of these effects, we see only a small shift in the positions of the exciton emission peaks.

[1] M. S. Dresselhaus, et al., *Annu. Rev. Phys. Chem.*,**58**, 719, (2007).
[2] Y. Murakami, J. Kono, *Phys. Rev. Lett.*, **102**, 037401, (2009).
[3] S. Das Sarma and D. W. Wang, *Phys. Rev. Lett.*, **84**, 2010 (2000)

How do Carbon Atoms Assemble at The sp^2-edge?

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It spite of the importance in determining the growth rate and chirality changes, it still remains unclear how carbon atoms are incorporated into the edge of growing carbon nanotube or graphene. We perform atomistic calculations to evaluate the free energy changes accompanying the carbon attachment to different growth sites: armchair (A) or zigzag (Z) edges [1], and the corresponding kinks (KA or KZ) sites, at the interface with various metals, i.e. Ni, Co, Fe, or Cu. It appears that the K sites are most energetically favorable for carbon incorporation, validating the screw-dislocation model [2] for the near-equilibrium growth. With the metal atoms in proximity, the defects (pentagons, heptagons, etc.) are efficiently annealed at the carbon incorporation stage, resulting in defect-free growth of nanotube or graphene. This in-situ annealing model can explain why the nanotubes and graphene have much lower defect density than typically observed in rapid MD simulations [3].

[1] Y. Liu, A. Dobrinsky, and B.I. Yakobson, *Phys. Rev. Lett.*, **105**, 235502, (2010).
[2] F. Ding, A. Harutyunyan, and B. I. Yakobson, *PNAS*, **106**, 2506, (2009).
[3] M.A. Ribas, et al. *J. Chem. Phys.*, **131**, 224501, (2009).

Energetics and Electronic Structures of Graphene Adsorbed on HfO_2 Surfaces

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Graphene has the great potential to advance both the low-dimensional sciences and the nano-scale electronic engineering. Recently, the integration of the graphene with a scalable gate dielectric, such as high permittivity (high-*k*) materials, has been the subject of the research with the goal of the realization of graphene-based electronic devices. For the fabrication of the graphene on insulating substrates, an understanding of its interactions with the substrates is critical, since they could directly affect the intrinsic electronic properties of the graphene. However, its underlying characteristics of the interaction are still far from being explained. Thus, we here study the energetics, geometry, and electronic structure of graphene adsorbed on (111) surfaces of cubic hafnia (HfO_2) using first-principles calculations in the framework of density functional theory (DFT) [1].

To simulate a hybrid structure of graphene and HfO_2, we considered an oxygen-terminated (111) surface of a cubic phase of HfO_2 possessing a triangular lattice of O atoms at the topmost layer. The surfaces were simulated using a repeated-slab model that includes five HfO_2 layers, graphene, and a 7 Å -vacuum region.

Our DFT calculations clarify that the graphene is bound to the HfO_2 surfaces with an interlayer spacing of 3.05 Å with a binding energy of about -110 meV per C atom. The electronic structure of the HfO_2-adsorbed graphene originates primarily from that of the graphene near the Fermi level. However, a detailed analysis of the electronic structure shows that the linear bands on the Dirac cone are slightly split, because of the interaction between the graphene and the HfO_2 substrate. The physical origin of this splitting is the hybridization between the π states of the graphene and the O *2p* state with Hf *d* character.

[1] K. Kamiya, N. Umezawa, and S. Okada, *Phys. Rev. B,* **83**, 153413, (2011).

Selective Edge Functionalization of Graphene by Room Temperature Mild Plasma Treatment

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Room-temperature controllable edge functionalization and doping of graphene by a NH_3 plasma has been developed [1]. Based on a detailed Raman mapping analysis and an electrical measurement, a direct correlation between carrier doping and selective edge functionalization has been revealed for the first time. The Raman mapping analysis shows that the D-peak near the edge of the graphene sheet is selectively increased after NH_3 mild (m)-plasma treatment. The electrical measurement reveals that the Dirac point position of the graphene nano ribbon (GNR) device clearly shifts toward a negative gate-bias voltage after NH_3 m-plasma treatment. This selective edge functionalization and doping by controlled plasma treatment could yield outstanding benefits in realizing graphene-based high-performance nanoelectronic device applications.

[1] T. Kato, L. Jiao, X. Wang, H. Wang, X. Li, L. Zhang, R. Hatakeyama, H. Dai, *Small*, **7**, 574, (2011).

Low-wavenumber-extended confocal Raman microscopy on single-walled carbon nanotubes

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We describe the simple modification of a confocal Raman imaging microscope to incorporate two ultra-narrow holographic notch filters [1]. The modified microscope rejects the laser excitation line(Rayleigh peak) by a discrimination factor of ~10^{11}, reducing the Rayleigh peak to intensities comparable to typical Raman scattering signals and allowing simultaneous measurements of Stokes/anti-Stokes Raman shifts as close as ~10/20 cm^{-1} to the Rayleigh line. This allows us to access a region of Raman features which has remained essentially unexplored in measurements of bulk single-walled carbon nanotubes (SWNTs) samples and which has so far been unreachable for Raman spectroscopy of individual SWNTs. We performed low-frequency Raman measurements both on SWNTs in bulk material and on horizontally aligned, CVD grown carbon nanotubes on silicon. Interestingly, we observed a broad feature around the Rayleigh-line (LFB, low frequency band) which is always found in bulk material, but not on all the sites of the horizontally grown carbon nanotubes. As its appearance goes hand in hand with the observation of multiple RBMs on a site, we believe the LFB to be related to the existence of bundles. We found and dismantled such bundles by atomic force microscopy (AFM).

[1] S. Lebedkin et al., *Rev. Sci. Instrum.*, **82**, 013705, (2011).

Raman Spectra on Bilayer and Trilayer Graphene

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Resonance Raman spectroscopy has come up with remarkable optical properties for the carbon materials [1]. From the analysis of the Raman spectra, we obtain the rich information about the physical properties and the sample characterization of graphene. The Raman intensity and resonance condition depend on the layer stacking, energy of excitation light, and lattice vibration of graphene. Thus we can characterize a graphene sample by resonance Raman spectroscopy. The G, D, and G' (or 2D) bands have been mainly studied for the purpose of the optical and sample characterization of graphene. For example, the Raman intensity and shift of the G' band is weak and broad with increasing the number of graphene layers [2]. Moreover the stacking fault of graphene changes the G band intensity [3]. According to the double resonance Raman scattering theory [4], it is expected that many resonance Raman peaks appear in the Raman spectra as possible overtone or combination phonon modes. The intensity of such Raman peaks is weak compared with that of the G, D, and G' bands. However, the information obtained from the weak Raman peaks is useful for characterizing the stacking order of multi-layer graphene [5,6]. Here we show the Raman intensity and shift of different layer stacking of graphene in order to evaluate the origin and property of the Raman peaks. The Raman intensity is calculated for the possible overtone or combination phonon modes by using the extended tight binding method and the force constant model. Our calculated Raman spectra of the overtone of the oTO phonon and of combinations of the LO, ZO, and ZA phonons in bi-layer graphene reproduce the experimental results well [7]. We discuss the dependence of the Raman intensity and shift on the layer stacking of graphene. The calculated results are compared with the experimental results.

[1] A. Jorio et al., *Raman Spectroscopy in Graphene Related Systems, Wiley-VCH* , (2011).
[2] J. S. Park et al., *Carbon*, **47**, 1303-1310, (2010).
[3] Z. Ni et al., *Phys. Rev. B*, **80**, 125404-1-5, (2009).
[4] R. Saito et al., *Phys. Rev. Lett.*, **80**, 027401-1-4, (2001).
[5] R. Rao et al., *ACS Nano*, **5**, 1594-1599, (2011).
[6] C. Cong et al., *ACS Nano*, **5**, 1600-1605, (2011).
[7] K. Sato et al., submitted.

The Raman Study of Strained Graphene during Micro Transfer Printing Process

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We have investigated the unintended strain of graphene that occurs when it is transferred onto the target substrate using the micro transfer printing technique. In the transfer printing process, there are several sources of the strain. For example, when preparing the polymethylmethacrylate (PMMA) membrane on exfoliated graphene, a baking process is utilized which could add undue stress to the graphene sample. Furthermore, the PMMA-graphene film is then separated from the SiO_2/Si substrate with 4M KOH(aq) etchant near the solution boiling point before being transferred to another substrate. The Raman spectrum of each step of the process was checked to confirm the effect of strain. The 2D mode and G mode Raman spectra showed blue shifts at each step of the process, which are believed to be caused by a compressive strain. To reduce this strain, the PMMA membrane that is separated from bare SiO_2/Si substrate was attached onto exfoliated graphene, so we effectively avoided the spin-coating and baking processes. Finally, the transfer printing of graphene was accomplished with the separation of PMMA-graphene film with 4M KOH at 300K. Without thermal variation, it was found that the measured spectra were similar to that of the original mechanical state of graphene.

Collection-Mode Near-Field Nanoscopy of Individual CNTs

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Applications of luminescent single-wall carbon nanotubes (CNTs) in nanosized optoelectronics and photonics devices envisioned for the next future [1] require suitable optical characterization methods addressing individual CNTs. Within this frame, the abilities exhibited by non-propagating electromagnetic fields in overcoming the diffraction limits affer unique possibilities. For instance, photoluminescence (PL) from emitting CNTs adsorbed on transparent samples has been imaged and analyzed by tip-enhanced microscopy several years ago [2].

We are presently using a collection-mode, polarization-controlled scanning near-field optical microscope (SNOM) to analyze PL and scattering from individual CNTs. Collection is accomplished in near-field by an aperture-probe, whereas excitation is provided in far-field by an optical fiber-focuser. Since the focuser is placed on the same side of the sample where near-field collection takes place, the system can be adopted for both transparent and opaque substrates. Moreover, the polarization status of the excitation radiation can be reliably controlled by polarizing optics put in front of the optical fiber. Since the focuser holder is mounted on a piezoelectric translator driven independently from the sample scanner, the excitation spot can be freely adjusted on the sample surface with respect to the probe. Thus, effects of the optical interaction between the CNT and any neighboring nanostructures such as surface plasmon waveguides and concentrators can be easily analyzed. Preliminary results indicate a spatial resolution in the few tens of nanometer range and sensitivity suitable to collect optical scattering from individual CNTs with a photon-counting detector.

[1] P. Avouris, M. Freitag, V. Perebeinos, *Carbon Nanotubes, Topics Appl. Physics*, **111**, 423-454 (2008); A. Jorio, G. Dressehlhaus, M.S. Dresselhau,(Eds.), Springer-Verlag Berlin Heidelberg 2008.
[2] A. Hartschuh, H. Qian, A.J. Meixner, N. Anderson, and L. Novotny, *NanoLett*. **5**, 2310-2313, (2005).

Optical Heterodyne Detection Visualizes the Spatial Resonance of Multilayer Graphene Cantilevers

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Graphene resonator is anticipated as ultrasensitive mass detectors and biosensors. To investigate the vibration of the graphene cantilever in various environments toward mass sensors of biological molecules, we developed the optical actuation and optical heterodyne detection based on the opto-mechanical heterodyne technique. [1] The graphene flakes were mechanically exfoliated over predefined 9µm-wide trenches on SiO_2 (300nm)/Si wafer to fabricate cantilevered graphene resonators. The length and width of the typical cantilevered graphene used in this study were 7µm and 7.5µm, respectively. For optical actuation of graphene resonators, we irradiated the graphene with a red laser (660nm, 300µW) for thermal expansion by modulating the laser intensity, and with a blue laser (406nm, 1µW) to detect vibration amplitude by the optical detection technique. The modulation frequencies of two lasers were set with a small difference, Δf, resulting in the detection of the resonance at the frequency of Δf. First, to investigate the effects of gaseous dissipation of the graphene vibration, we measured the Q factors of the graphene vibration at the pressure of $1{\sim}10^4$ Pa. The Q factor at the pressure over 500 Pa was inversely proportional to the pressure, indicating that the graphene cantilever acts as in the free molecular flow. In contrast, the Q factor at the pressure below 500 Pa remained constant, implying that the energy loss induced by the collision of gas molecules was much smaller than the intrinsic energy loss of the graphene resonator. One of the advantages of our excitation/detection technique is that the vibration amplitude of the graphene can be spatially visualized over the surface of the graphene by changing the position of the laser that detects the vibration. This vibration mode analysis was examined using a combination of experiments and finite element method. In contrast, by changing the position of the laser that excites the vibration, thermal propagation of the graphene can also be estimated in order to determine where induces the vibration efficiently. This is crucial in the application using graphene-based nanoelectromechanical resonators in liquid.

[1] A. Yoshinaka et al., *Appl. Phys. Lett.*,**98**, 133103, (2011).

Direct Measurement of the Bending Stiffness of Individual Vertically Aligned Carbon Nanofibers (VACNFs)

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Vertically aligned carbon nanofibers (VACNFs) are synthesized in a plasma-enhanced chemical vapor deposition process (PECVD) in which the position, diameter, length, and alignment of individual nanofibers can be controlled accurately. This has provided an unprecedented opportunity to realize a new bottom-up-engineered material with excellent mechanical and electrical properties which could exploit the third dimension at a reasonable cost. VACNFs have been already employed in a number of applications including electron emitters [1], gene delivery arrays [2], and nanoelectromechanical systems [3, 4]. However, no direct measurement of the Young's modulus of VACNFs has been reported yet. Qi *et al.* have used nanoindentation method to measure the collective response of a forest of VACNFs with a distribution in length and diameter of the constituent nanofibers [5]. Kaul *et al.*, have reported *in situ* uniaxial compression tests on individual VACNFs but they have not provided enough information to evaluate the accuracy of their measurements [6]. Indirect estimation of the VACNFs Young's modulus has also been reported by Eriksson *et al.* from measurements of the resonance frequency of a nanofiber deposited on top of an excitation electrode [7]. Here, we report on direct measurements of VACNFs Young's modulus using a piezoresistive atomic force microscope (AFM) cantilever implemented inside a scanning electron microscope (SEM). The VACNFs were grown from Ni catalyst seeds, patterned using electron-beam lithography on top of a stoichiometric TiN underlayer. The VACNFs were grown in a commercially available PECVD chamber (AIXTRON BlackMagic™). The nanofibers were approached from the side and pushed at the tip (resembling a cantilever beam) and force- deflection curves were obtained. By calibrating the AFM sensor the bending stiffness of the nanofiber could be determined. The Young's modulus was then estimated by taking the nanofibers dimensions into account. The sub-nano Newton force precision provided by the AFM force-sensor together with the fact the individual VACNFs could be observed in the SEM simultaneously during the measurements, has enabled us to measure the nanofibers Young's modulus with a high precision. Preliminary measurements indicate that VACNFs possess a Young's modulus between 40 to 100 GPa which is comparable to CVD grown carbon nanotubes of similar diameters [8].

[1] M.A. Guillorn, A.V. Melechko, V.I. Merkulov, E.D. Ellis, C.L. Britton, M.L. Simpson, D.H. Lowndes, L.R. Baylor, *Applied Physics Letters*, **79**, 3506, (2001).
[2] D.G.J. Mann, T.E. McKnight, A.V. Melechko, M.L. Simpson, G.S. Sayler, *Biotechnology and Bioengineering*, **97**, 680-688, (2007).
[3] J.E. Jang, S.N. Cha, Y. Choi, G.A.J. Amaratunga, D.J. Kang, D.G. Hasko, J.E. Jung, J.M. Kim, *Applied Physics Letters*, **87**, 163114-163111, (2005).
[4] J.E. Jang, S.N. Cha, Y.J. Choi, D.J. Kang, T.P. Butler, D.G. Hasko, J.E. Jung, J.M. Kim, G.A.J. Amaratunga, *Nature Nanotechnology*, **3**, 26-30, (2008).

[5] H.J. Qi, K.B.K. Teo, K.K.S. Lau, M.C. Boyce, W.I. Milne, J. Robertson, K.K. Gleason, *Journal of the Mechanics and Physics of Solids*, **51**, 2213-2237
[6] A.B. Kaul, K.G. Megerian, A.T. Jennings, J.R. Greer, *Nanotechnology,* **21**, (2010).
[7] A. Eriksson, S. Lee, A.A. Sourab, A. Isacsson, R. Kaunisto, J.M. Kinaret, E.E.B. Campbell, *Nano Letters*, **8**, 1224-1228, (2008).
[8] K. Lee, B. Lukic, A. Magrez, J. W. Seo, G. A. D. Briggs, A. J. Kulik, and L. Forró, *Nano Letters*, **7**, 1598-1602, (2007).

Wall-Selective Probing Of Double-Walled Carbon Nanotubes Using Covalent Functionalization

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Double-walled carbon nanotubes (DWNTs) present an original coaxial geometry in which the inner wall is isolated by the outer wall, while the latter is in direct interaction with the environment. Covalent functionalization, performed using an aryldiazonium salt, is presented here as an efficient tool to investigate DWNT devices. Optical and electrical properties of DWNTs are measured in pristine, functionalized and defunctionalized states. Absorption and resonant Raman spectroscopy measurements, on individual DWNTs and networks, show that the functionalization is reversible upon thermal annealing and occurs strictly at the surface of the outer wall, leaving the inner wall essentially unaltered by the chemical bonding. Individual DWNT field-effect transistors are operated in functionalized state with current flowing mainly through the inner wall, with a current intensity comparable to a pristine single-walled carbon nanotube device. Electrical transfer characteristics are demonstrated to provide unambiguous identification of the metallic or semiconducting character of both walls. Current saturation at high bias is also measured in the inner wall of functionalized DWNT, leading to novel insight on the current saturation mechanism. Finally, opportunities enabled by the wall-selectivity of the functionalization are discussed: fundamental experiments about wall to wall interactions in DWNTsare made possible, but also the design of novel environment-sensitive electronic devices in which the inner wall is used for electrical transport while the outer wall chemically interacts with external stimuli.

Isolated and shape defined graphene layers in a single litographic step

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Graphene layers produced by micromechanical cleavage are always surrounded by thicker, unwanted graphitic material that could interfere with the fabrication of electronic devices as it results in shorts or compromises lithography. Also, they are randomly shaped, while shape control is required for application.

Here we present a technique that allows, in a single and quick lithographic step, the production of fully isolated graphene samples of defined shape. Graphene flakes are first obtained by micro-mechanical exfoliation on a Si+SiO_2 substrates and characterized by optical microscopy and Raman spectroscopy. PMMA is spin-coated onto them and patterned via e-beam lithography in order to define on the graphene sample the contour of the desired shape. After resist development, oxygen plasma is used to etch the uncovered part of the graphene. This results in an island (graphene covered in PMMA) of desired shape isolated from the rest of the polymer film. The latter is then removed by immersion in de-ionized water, while the lithographically defined island remains on the substrate. All the graphitic material is removed from the substrate together with the polymer film. PMMA is eventually dissolved leaving a completely isolated and shaped graphene sample. The frame width is few microns wide and requires only seconds to be e-beam written. The plasma is very mild, as just part of the monolayer has to be etched, and does not affect the polymer-covered part of the flake. Raman spectroscopy shows the process does not induce any structural defects in the resulting shape-defined flakes.

On the Doping of Carbon Nanotubes by Phosphorus Atoms

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Designing nanotube-based nanoscale materials and devices requires the controllable modification of the physical and chemical properties of CNTs [1], because inclusion of noncarbon atoms into the hexagonal network of CNTs modifies the electronic and chemical properties due to variations in the electronic structure. In this sense, CNTs doped with impurity atoms such as nitrogen, boron and phosphorus have been increasingly attracted the attention of numerous research groups in order to control the parameters crucial for modification of their desired properties [2, 3].Particularly, the role of phosphorus during the growth of carbon nanotubes has been studied as a new element used as a promoter for Fe catalyst to produce carbon filaments by the floating catalyst method [4]. It was shown that only an optimal amount of phosphorus addition can make the feedstock (ferrocene and triphenylphosphine diluted in benzene)grow into carbon filamentous otherwise carbon spheres are formed. Recent studies show that the use of phosphorus as co-catalyst produces a compartmentalized kind of carbon nanotubes consisted of CNTs units weakly linked together with periodically insertion of nanoparticles in between as a result of a possible poisoning of the catalytic particles [5]. Others works suggest the successfully synthesized of P- and N-doped carbon nanotubes by a CVD method, using benzylamine and triphenylphosphine as nitrogen and phosphorus sources, and confirmed by EDX and EELS elemental maps and profiles [3].In this work, the incorporation of phosphorous in MWCNTs synthesized by the Spray Pyrolysis (liquid floating catalyst) method using a solution of ferrocene ($Fe(C_5H_5)_2$) and triphenylphosphine ($P(C_6H_5)_3$) in toluene (C_7H_8) was investigated. The concentration of ferrocene was fixed in 2.0 wt %, while the concentration of triphenylphosphine was varied from 0.15 to 0.65 wt % as a phosphorous source of atoms while the oven temperature was kept constant at 850 °C. These nanotubes exhibit a special bamboo type morphology, like a carbon necklace growth, probably due to the direct formation of iron phosphate catalytic nanoparticles during the growth process, confirmed by high resolution electron microscopy, X-ray photoelectron spectroscopy and X-ray diffraction analysis. STEM elemental line scan of the P-doped tubes using EDX, reveals that the phosphorus atoms are mainly located in the catalytic particles instead inside the tubes.XPS also shows evidence of C-P bonds formation. Raman spectroscopy results confirm the good quality of the as grown tubes.

[1] A. Jorio, et al., *Carbon Nanotubes: Advanced Topics in the synthesis, structure, properties and Applications* (Springer-Verlag: Berlin, 2008).
[2] P. Ayala, *Reviews of Modern Physics*, **82**, 1843, (2010).
[3] E. Cruz-Silva, et al., *ACS Nano*, **2**, 441,(2008).
[4] L. Ci, et al., *Carbon*, **37**, 1652, (1999).
[5] V. Jourdain, et. al, *Adv. Mater.*, **16**, 447, (2004).

Controlling the Dopant Concentration in Nitrogen-doped Multi-walled Carbon Nanotubes

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Carbon nanotubes (CNTs) are expected to have many applications. However, these applications are heavily dependent on CNT properties. Therefore, CNTs with customised properties need to be synthesized at commercially viable cost and doping is a reliable option to gain control over nanotube properties.

Introducing heteroatoms in carbon hexagonal network modifies physical and chemical properties [1, 2] of the tubes and paves the way towards many applications such as field emission [3, 4], easier functionalisation of the nanotubes, and further their use in composites [5].

Herein, we investigate and compare the effect of nitrogen doping at low concentrations (<2 at %) and higher concentrations (2-3 at %) on CNTs synthesized by aerosol assisted chemical vapour deposition. Results show that nitrogen when incorporated in the tubes at concentrations less than 2 at %, induces significant and most importantly different changes in nanotubes than the case with higher concentrations (2-3 at %). There appears to be transitional changes in nanotube properties as the nitrogen content in the tubes increases up to a certain concentration. We studied properties such as diameter, length, defect density, oxidation resistance and yield in relation to nitrogen content and temperature.

[1] A.A. Koos, M. Dowling, K. Jurkschat, A. Crossley, N. Grobert, *Carbon*,**47**, 30-37, (2009).
[2] A.A. Koos, F. Dillon, E. A. Obraztsova, A. Crossley, N. Grobert, *Carbon*, **48**, 3033-3041, (2010).
[3] R.B. Sharma, D.J. Late, D.S. Joag, A. Govindaraj, C.N.R. Rao, *Chemical Physics Letters*, 428, 102-108 (2006).
[4] K. Ghosh, M. Kumar, T. Maruyama, Y. Ando, *Carbon*, **48**, 191-200, (2010).
[5] G. Otieno, A.A. Koos, F. Dillon, A. Wallwork, N. Grobert, R. I. Todd, *Carbon*, **48**, 2212-2217, (2010).

Noncovalent Functionalization of Carbon Nanostructures: A DFT Investigation of Charge Transfer with Electron Donor-Acceptor Molecules and Protonation by Superacid

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Noncovalent doping of carbon nanostructures by charge transfer from/to donor/acceptor molecules (EDA) or protonation by H_2SO_4, be it with holes or electrons, is usually thought as potentially interesting for many applications of carbon based nano-devices. However, from a theoretical point of view, little is known about such “charge transfer” processes. Employing first-principles method based on Density Functional Theory (DFT), we have studied in details the interaction between a prototypical donor molecule the tetrathiafulvalene (TTF), a standard acceptor organic molecule, tetracyanoethylene (TCNE) and carbon nanostructures: grapheme layer and SWNTs with various chiral indices. Additionally, we have studied the adsorption properties of sulfuric acid molecules. Main results concern structural and thermodynamic aspects including dispersion forces effects, and evidently electronic structure modifications of the nanostructures. At very low coverage values, we have estimated a charge transfer of 0.45e from the graphene to TCNE, a value of 0.12e from TTF to graphene and more interestingly no charge transfer is observed in the H_2SO_4@graphene case. We have found a charge transfer decreasing while the curvature of nanotubes is increasing, and a strong influence of the metallic/semi-conductor character of the SWNTs is obtained. The results of this work could help to understand the charge transfer of carbon nanostructures by means of noncovalent functionalization, which is a promising method for their future applications.

Tunable Separation of Single-Walled Carbon Nanotubes Using Density Gradient Ultracentrifugation

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We present the selective enrichment of single-walled carbon nanotubes (SWNTs) with different diameters or electronic types using density gradient ultracentrifugation (DGU), and discuss the effects of surfactant in this separation. We used bile salt sodium deoxycholate (DOC) and anionic salt sodium dodecyl sulfate (SDS) as co-surfactant encapsulating agents, and through analysis of the buoyant densities, layer positions, and optical absorbance spectra of separated SWNTs, we clarify the roles and interactions of these two surfactants in yielding different DGU outcomes. This understanding can help in designing new DGU experiments by qualitatively predicting outcomes of different starting recipes, improving the efficacy of DGU and simplifying post-DGU fractionation. Finally, using the DGU experiments performed on SWNTs formed by different isotopes (^{12}C or ^{13}C) and comparing their corresponding results, more information about the SWNT-surfactant assembly can be obtained.

[1] M. S. Arnold, A. A. Green, J. F. Hulvat, S. I. Stupp, M. C. Hersam, *Nat. Nanotechnol.*, **1**, 60-65, (2006).
[2] P. Zhao, R. Xiang, E. Einarsson, J. Shiomi, Y, Murakami, S. Maruyama, *J. Phys. Chem. C*, **114**, 4831-4834, (2010).
[2] P. Zhao, E. Einarsson, G. Lagoudas, J. Shiomi, S. Chiashi, S. Maruyama, *Nano Res.*, online (DOI: 10.1007/s12274-011-0118-9)

Synthesis and Electronic Properties of Silicon-Nitrogen Hetero-doped Single Walled Carbon Nanotubes

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We have investigated the electronic and structural properties of several hetero-doped carbon nanotubes using first-principles density functional theory calculations. Silicon, silicon-nitrogen, and silicon-oxygen species were incorporated within the lattice of semiconductor (10,0), semimetallic (9,0), and metallic (5,5) carbon nanotubes. The structural stability, electronic density of states, dopingenergy, band structure, and HOMO and LUMO were analyzed in detail. When silicon and nitrogen are bonded and inserted in the nanotube lattice, the electronic properties change significantly, thus producing non-dispersive bands around the Fermi level. These localized (non- dispersive) states make the silicon-nitrogen doped carbon nanotubes highly reactive and an excellent candidate for anchoring different chemical species around the doped site(e.g. CO_2, NH_3, Aminoacids, Co, Br, Cl). The Nitrogen arranged in a pyridine- like fashion together with a silicon atom placed inside the vacancy was also studied.

Interestingly,this structural configuration becomes more stable than the substitutional nitrogen embedded in the (9,0) and (5,5) nanotubes. We havecarried out experiments targeting the synthesis of Si and SiN-doped single-walled carbon nanotubes (CSixNy-SWNTs) by aerosol assisted (ultrasonic) chemical vapor deposition. The CVD involves the decomposition of a solution containing ferrocene, ethanol, benzylamine and methoxy trimethylsilane under an Ar atmosphere at 950 °C. We carried out Raman spectroscopy, high-resolution electron microscopy (HRTEM), thermo gravimetric analysis (TGA), electron energy loss spectroscopy (EELS), energy- dispersive X-Ray spectroscopy (EDS), and X-Ray photoelectron spectroscopy (XPS) characterization,in order to identify the presence of both dopants within the nanotube graphitic lattice. Both theoretical and experimental results are correlated and analyzed.

Thermal Expansion Of Single-Walled Carbon Nanotubes From Experiment

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Thermal Expansion is the 2nd most relevant thermal property of carbon nanotubes after thermal conductivity and might be negative along the nanotube axis (similar to graphene and graphite) which would make SWCNTs extremely attractive for zero thermal expansion composites. However, despite of 18 years of thorough investigation into the nanotube properties, the thermal expansion behavior of SWCNTs at temperatures above 100 K is still completely unknown. This is due to some experimental difficulties involving functionalization issues, gas adsorption, clamping at surfaces, has to do with the nano-size of the nanotubes, their flexibility and limited length.

Theory and simulations which could shed light on the issue are not helpful either as positive or negative values for both the radial and axial thermal expansion coefficients have been obtained even in the most recent contributions. This includes different opinions on possible chirality dependences of the thermal expansion.

To exclude any unwanted effects from gas adsorption, substrate clamping effects or different functionalizations, free-floating nanotube aerosols have been measured in a specifically designed and heated tube furnace directly after the nanotube synthesis.

Temperatures between room temperature and 1050 °C have been used. To measure the thermal expansion behavior, a modified optical absorption spectroscopy setup for in-line measurements has been used. After correcting the obtained signals for tempera-ture related effects, a signal pointing to a strongly positive radial thermal expansion coefficient for the semiconducting and metallic nanotubes (both have been monitored) could be observed. The results are pointing towards a chirality dependence of the nanotube thermal expansion.

B-C-N Nanotubes and Layers: Effects of Disorder and Stoichiometry

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Boron-carbon-nitrogen (B-C-N) graphene-type layers and nanotubes have attracted recent interest in the literature due to their novel structural, optical and electronic properties. Regarding structural properties, recent experimental results on graphene-type B-C-N layers show segregation into either graphene islands in a planar BN matrix or BN islands in a graphene matrix, depending on the B-C-N stoichiometry. Regarding optical and electronic properties, it is clear from the available experimental data that the band gaps of B-C-N nanotubes are determined not only by stoichiometry, but also by other structural properties. In the present work we investigate theoretically the role of the (B,C,N) stoichiometry and positional disorder in the electronic structure of B-C-N nanotubes and graphene-type layers employing a combination of ab initio and model calculations. First, we apply a bond-energy model, parametrized from first principles, to a simulated annealing process. Then, the electronic structure of selected configurations is investigated from first principles. Near B/N perfect stoichiometry, we find [1] that the carbon atoms segregate into isolated islands. This is consistent with recent experimental results. As the islands are formed, we also find that the electronic density of states evolves from a featureless, gapless D(E) to one that has a band gap near the Fermi level. We also consider N-rich alloys. Different from the stoichiometric limit, where both calculations and experiments indicate BN/C segregation, the N-rich alloys show carbon dilution within the boron sublattice. Also in contrast with the B/N = 1 limit, where an insulating behavior is predicted, the N-rich alloys depict a (~2 eV) wide, half filled carbon impurity band thatshould result in either hopping conduction of metallic behavior, consistent with recent experiments.

[1] J. R. Martins and H. Chacham, *ACS Nano* **5**, 385 (2011)

Density Controlled Growth of Horizontally Aligned Single-Walled Carbon Nanotubes on R-cut Crystal Quartz Substrates

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Alignment control of single-walled carbon nanotubes (SWNTs) is very important for device application. It is known that horizontally aligned SWNTs are grown on crystal quartz substrates along the surface atomic structure [1]. Density of horizontally aligned SWNTs has been improved toward high-performance devices [2, 3]. For further improvement and control of SWNT density, understanding of alignment-growth mechanism is necessary. In this study, we performed chemical vapor deposition (CVD) growth of horizontally aligned SWNTs using R-cut crystal quartz substrate which is cut parallel to the natural R-face (1 0 1). R-cut crystal quartz substrates were pretreated by chemical etching in ammonium hydrogen fluoride and annealing in air at 900 °C. Patterned catalysts were prepared by photolithography and vacuum evaporation and SWNTs were grown by alcohol catalytic CVD method [4] using ethanol as the carbon source gas. Grown SWNTs were characterized by scanning electron microscopy, atomic force microscopy and Raman spectroscopy. It was found that the carbon feeding rate which was determined by both pressure and decomposition rate of ethanol gas affected the density of horizontally aligned SWNTs. Low carbon feeding rate was found to be suitable for high-density growth.

[1] C. Kocabas et al., *Small*, **1**, 1110-1116, (2005).
[2] C. Kocabas et al., *J. Phys. Chem. C*, **111**,17879-17886, (2007).
[3] L. Ding et al., *J. Am. Chem. Soc.*, **130**, 5428-5429,(2008).
[4] S. Maruyama et al., *Chem. Phys. Lett.*, **360**, 229-234, (2002).

Growth Kinetics of Narrow-Chirality and -Length Distributed Single-Walled Carbon Nanotubes by Time-Programmed Plasma CVD

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We have realized the direct growth of narrow-chirality and -length distributed single-walled carbon nanotubes (SWNTs) by time-programmed plasma CVD (TP-PCVD) [1]. The length distribution of SWNTs grown for a short time (2-5 sec) is fairly narrow and almost all the SWNTs are very short (< 100 nm). In addition, the precise time-restricted growth reveals that there is a clear dependence of the tube diameter on the incubation time of the initial SWNTs growth. Furthermore, the direct photoluminescence (PL) study reveals that the chirality distribution is narrowed by strictly controlling their growth time at the initial stage, and (7, 6) and (8, 4) dominant narrow-chirality distributed short-length SWNTs are directly synthesized by TP-PCVD. Our produced freestanding as-grown short SWNTs with narrow-chirality distribution are expected to contribute to the fabrication of high performance bio molecule sensors.

[1] T. Kato and R. Hatakeyama, *ACS Nano* ,**4**, 7395, (2010).

Narrow-Chirality Distributed Growth of Single-Walled Carbon Nanotubes from Nonmagnetic Catalyst by Diffusion Plasma CVD

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The narrow-chirality distributed SWNTs growth from a nonmagnetic catalyst is realized by diffusion plasma CVD [1]. Through the systematic investigation using the different combinations of catalyst types (magnetic or nonmagnetic) and CVD methods (thermal CVD or plasma CVD), plasma CVD with the nonmagnetic catalyst under an appropriate H2 concentration is found to be critical for the narrow-chirality distribution. This narrow-chirality distributed SWNTs selectively grown from the nonmagnetic catalyst could be attractive to both fundamental studies of intrinsic magnetic properties of SWNTs and industrial applications to nanoelectronics.

[1] Z. Ghorannevis, T. Kato, T. Kaneko, and R. Hatakeyama, *Journal of the American Chemical Society* **132**, 9570, (2010).

The Effect of Root Morphology of Carbon Nanotube Forest on Spinnability

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Carbon nanotube (CNT) forests have been used to directly spin into long CNT yarns. The "spinnablility" of a CNT forest is extremely sensitive to the reaction conditions. Complete understanding of the spinnable CNT forests has not yet been achieved, but one consensus is that CNTs should be highly vertically aligned in order to be spun. Here, we controlled the morphology of the root region of CNT forests, and confirmed that the root part of the CNT forest as well as the upper part should maintain high alignment for its spinnability.

Synthesis of SWCNTs by Using Size-Controlled Nanoparticles from Polymerized Hemoglobin

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Polymerized hemoglobin (polyHb) was used as a catalyst for the growth of single-walled carbon nanotubes (SWCNTs). PolyHb was obtained by polymerization of Hb using crosslinking agent, glutaraldehyde and had a broad molecular weight distribution. Size-exclusion chromatography was used to separate them by size. The fractionated polyHb was deposited onto hydrophilic treated substrate by spin coating method and oxidized at 800 ℃ to form iron oxide nanopaticles. The diameter of SWCNTs synthesized from the nanoparticles was determined by the size of polyHb. Because Hb has defined iron atoms per molecule, the fractionated polyHb can allows to control the diameter of catalytic nanoparticles by controlling the number of iron atoms in the nanoparticles.

Diameter Control Growth of Single-walled Carbon Nanotubes by Nano-diamond Catalysts

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Chirality control is one of the most challenging topics in single-walled carbon nanotube (SWNT) growth research. Tube diameter control techniques using solid phase catalysts are one of the approaches being used to realize this goal. In this study, we used nano-diamond as catalyst from which we synthesized SWNTs [1]. Acolloidal nano-diamond solution was dispersed on a silicon substrate and then pre-heated (500-800 °C) in air in a thermogravimetric analyzer (TGA). In the TGA device, the sample temperature and atmosphere are precisely controlled. The pre-heating in air decreased the diameter of the diamond particles. The heating rate was 1°C/min and the sample was kept at the target temperature for 150 min. During SWNT synthesis the CVD temperature was 800 °C and the pressure of ethanol gas was 1.2 kPa.

SEM observation revealed that SWNTs uniformly grew on the silicon substrate from nano-diamond particles while their density was not so high. It indicated that the catalyst activity of nano-diamond particles for SWNT growth was lower than ordinary metal particle catalyst (Fe, Co, and so on). However, Raman scattering measurement showed that the tube diameter distribution of SWNTs from nano-diamond was relatively narrow and it was ~0.3 nm, which was roughly equal to the diameter distribution of nano-diamond particles before the pre-heating treatment. Moreover, the average tube diameter simply decreased with increasing the pre-heating temperature.

Diamond is quite stable even at the CVD temperature. Therefore, the tube diameter could be easily controlled by the pre-treatment of nano-diamond particles. It indicated that the stability of the catalyst particles was necessary for the structure control of SWNTs.

[1] D. Takagi, et al., *J. Am. Chem. Soc.*, **131**, 6922, (2009).

Vertically-aligned Carbon Nanotube Growth In High Aspect Ratio Through-silicon Vias

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Carbon nanotubes (CNTs) are promising materials for interconnect in next generation microchips due to their high current-carrying capacity of about 10^9 A/cm^2, high thermal conductivity of up to 6600 W/m K and high aspect ratio (AR) that can easily reach $>10^3$ (length/diameter). Tremendous work focused on growing CNTs from vias has been carried out recently [1-2]. However, the use of CNTs in practical interconnects, especially in the high AR through-silicon vias (TSV) [3], has not been realised yet because it is difficult to deposit catalytic nanoparticles onto the bottom of the deep TSV for aligned CNT growth.

In this study, we successfully synthesized high density MWNTs from a 25 μm deep TSV structure with an AR of 5, which is much deeper and narrower than the most advanced CNT vias (typical depth of 500 nm and AR of 1.5). In our work, a dip-coating step in Fe-containing salt solution plays an important role in catalyst deposition at the bottom of the TSV. The growth carried out in a cold wall chemical vapour deposition (CVD) system shows that aligned CNTs (multi-walled) grow vertically from the bottom of the vias while the growth from the side walls of the vias is negligible. The as-grown CNTs fill the whole TSV with a density of 4×10^{10}/cm^2.

These results show that high density CNTs can be successfully synthesized in deep and high AR TSV structures. This technique can be used in the realization of CNT-based next generation three-dimensional electronic devices and multichip modules.

[1] D. Yokoyama, T. Iwasaki, T. Yoshida, H. Kawarada, S. Sato, T. Hyakushima, M. Nihei, Y. Awano. *Appl. Phys. Lett.* **91**, 263101, (2007)

[2] J. Dijon, H. Okuno, E. Quesnel, M. Fayolle, T. Vo, J. Pontcharra, D. Acquaviva, D. Bouvet, A.M. Ionescu, C.S. Esconjauregui, J. Robertson. *IEDM*, 10-760,(2010).

[3] M. Motoyoshi. *Proceedings of the Ieee*, **97**, 1, (2009)

Large Scale SWCNT Synthesis: Kilograms Per Day

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Single-Walled Carbon Nanotubes (SWCNTs) are considered to be the class of nanotubes with the most-interesting overall properties of all nanotubes, due to the many exciting findings made on them revealing several property world records [1]. In addition to their exceptional properties, SWCNTs are also extremely small and extremely lightweight in comparison to, for example, multi-walled carbon nanotubes. For bulk composites, SWCNT additives let expect both a much reduced weight impact and also a much reduced impact on the basic properties of the matrix material while still getting the wanted 'nanotube functionality'. However, one of the main drawbacks is the low SWCNT availability and horrendous SWCNT prices. Many attempts to develop an up-scaled SWCNT synthesis which can operate at the kg / day scale have been seen in the last decade – mostly based on cheap CVD-processes – but up to now this goal hasn't been achieved in a single reactor.
At our Fraunhofer pilot plant, we made it different. Given the limited success of CVD methods, we started optimizing the old-fashioned arc-discharge SWCNT synthesis by adding a lot of improvements to the process [2]. By optimizing physical parameters, the catalyst chemistry, the arcing conditions – all this guided by a self-developed in-line characterization method [3] it was possible to speed up the whole synthesis development feedback cycle until finally the pilot plant was able to deliver 500g / day of SWCNTs.
While 700g of SWCNT containing material (500g SWCNTs plus by-products) has been produced by a single pair of arc electrodes, an additional up-scaling has been proven to be possible without any degradation of the SWCNT yield by simply adding additional pairs of arc electrodes to the reactor.
Besides ~50-70% of SWCNTsthe material contains 20% of multi-metal catalysts as well as other by-products (mostly graphene-like nanocarbons). No multi-walled nano- tubes are present. The SWCNT show a length of 10+ µm, a mean diameter of 1.2 nm with a narrow unimodal size distribution. Raman spectra typically show a G/D ratio >10 (with the mentioned impurities still being present).

[1] M.S. Dresselhaus, G. Dresselhaus, *P. Avouris, Carbon Nanotubes*: "Synthesis, Structure, Properties and Applications", vol. 80 of Springer Series in Topics in Appl. Phys., Springer-Verlag, Berlin, (2001).
[2] A. Roch, M. Märcz, U. Richter, A. Leson, E. Beyer, O. Jost, *Phys. Status Solidi B* **246**, 2511–2513, (2009).
[3] M. Leistner, *Master Thesis, Dresden University of Technology*, (2009)

Preferential Synthesis Of Metallic And Semiconducting SWCNTs

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While there have been a few reports about the preferential synthesis [1] of either metallic or semiconducting Single-Walled Carbon Nanotubes (SWCNTs), such a preferred synthesis is up to now a completely trial-and-error guided process. While it is assumed (with some evidence by experiment) that the different facets of the catalyst particles are responsible for the preferred synthesis of either metallic (m-SWCNTs) or semiconducting (sc-SWCNTs) nanotubes [2], a lot of open questions exist, and, as we show from experiment, different facets alone do not explain the observed dependencies.

At first, a characterization method based on optical absorption spectroscopy has been developed for the semi-quantitative determination of the ratio of metallic and semi-conducting SWCNTs. This was followed by an experimental investigation into the role of different physical and chemical synthesis parameters during the synthesis of SWCNTs. The synthesis has been performed in a modified arc-discharge system which allowed to adjust physical parameters like temperature in the synthesis zone.

Multi-element catalysts as well as single-element catalysts showed some minor degree of preference for the formation of metallic nanotubes. Temperatures between room temperature and 1100 °C played no role at all, an existing strong predominance of either type hasn't been altered by temperature adjustments. The gas pressure inside the reaction chamber on the other hand played an important role in determining the m/sc ratio with a certain optimum gas pressure (75 mbars) leading to an exceptionally high content of metallic SWCNTs. Using different electrical parameters during the arc synthesis changed the m/sc ratio as well. With different gases (inert gases only) it turned out to be possible to strongly modify the m/sc ratio, from preferably metallic to preferably semiconducting. It was possible to increase the content of m-SWCNTs to ~70% while on the other hand up to ~80% sc-SWCNTs could be obtained as well. It should be noted that all the observed chirality dependencies did not correlate in any way to diameter changes of the SWCNTs. This all points to a significant role of different gases for the synthesis of m-SWCNTs and sc-SWCNTs.

[1] A.R. Harutyunyan, G. Chen, T.M. Paronyan, E.M. Pigos, O.A. Kuznetsov, K. Hewaparakrama, S.M. Kim, D. Zakharov, E.A. Stach, G.U. Sumanasekera, *Science* **326**, 116-120, (2009).
[2] H. Zhu, K. Suenaga, J. Wei, K. Wang, D. Wu, *J. Crystal Growth* **310**, 5473-5476, (2008)

A New Mechanism for Understanding Chiral Angle Control in SWCNTs Synthesized by CVD

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A widespread consensus has emerged from both modelling and experimental studies that the graphitization ability of close-packed facets in transition metal nanoparticles is central to their role in catalysing the synthesis of single and multiwall carbon nanotubes (CNTs) in chemical vapour deposition processes. It is also known that the addition of small quantities of non-metallic elements, such as sulphur and nitrogen, can greatly enhance the growth rate and enable selectivity of chiral angle of CNTs under certain conditions. However, the high structural lability of metallic nanoparticles observed by in situ TEM makes it hard to understand how the surface structure of catalyst can systematically control the geometry of the growing nanotube. In order to better comprehend this, we present a combination of evidence from experimental observations of SWCNTs in contact with iron particles and semi-empirical quantum mechanical simulations that support a model for nucleation of CNTs in a circumferential “belt” around an elongated catalyst particle. The enhanced stability of close-packed metal facets in particular orientations relative to the axis of catalyst particle leads to the establishment of a favoured orientation for graphene sheet, which is then capped and extruded as a CNT from the catalyst particle. In this way, it is possible to prepare SWCNTs with highly monodisperse distributions of chiral angle.

HiPco Synthesis and the Effect of Growth Conditions on Individual Nanotube Chirality

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This work shows that controlled perturbations in HiPco growth conditions yield marked changes in individual nanotube length, chirality, and structural quality. SWNTs were synthesized under variable HiPco conditions and enriched, aqueous suspensions of individual nanotubes were prepared by ultrasonication and ultracentrifugation. Three optical characterization methods (absorption, photoluminescence and Raman spectroscopy) provided a complete assessment of individual SWNT electronic character.

This combination of optical characterization revealed that HiPco SWNTs with the smallest average diameter possessed a narrow chiral distribution with an increasing D/G ratio, whereas larger diameter nanotubes had a much broader distribution of semiconductors. These findings will aid in the understanding of HiPco growth mechanisms and parameters that will enable chirality controlled growth of individual SWNTs.

Raman Probing of Adhesion Loss in Carbon Nanotube – Reinforced Composite.

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Raman spectroscopy of a carbon nanotube - reinforced phenolic resin is used to study the interaction of nanotubes with a host matrix. The observed sublinear dependence of the Raman G-band shift on the matrix strain, accompanied by inhomogeneous broadening of the spectral line, is interpreted as a gradual loss of adhesion between nanotubes and the polymer. An approach to simulate the ensemble-averaged Raman response of the nanotubes in composite is proposed, that takes into account nanotube orientation, angular dependence of the polarized Raman response of nanotubes, and adhesion loss between the nanotubes and the polymer. The comparison of the observed Raman line shapes and Raman shifts with simulation results provides interesting insights into the micromechanics of nanotube interaction with polymer.

Formation of Bulk Hollow Cylinders Consisting of Bamboo Shaped C-N Nanotubes and their Use in the Hydrocarbon Filtration

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The present investigations describe the formation of bamboo-shaped C-N nanotubes filter and its use in the filtration of heavier hydrocarbons from gasoline. We have synthesized macro hollow cylinder consisting of bamboo like carbon-nitrogen (C-N) nanotubes via spray pyrolysis of $C_{10}H_{10}Fe$ and CH_3CN solution at 900 °C temperature using argon as a carrier gas. The hollow cylinders consisting of C-N nanotubes converted into filter like configuration by capping one end of hollow cylinder and keeping the other end open for entering the unfiltered solution. Our new cylindrical membrane filtration unit (dia.~7 mm, length ~ 7 cm) involving C-N nanotubes having bamboo-like structures. Thus, the inner hollow tunnel of the tubes gets compartmentalized through the formation of bamboo like structure along directions nearly perpendicular to the length of the C-N nanotubes. The result of filtration of heavy hydrocarbons from gasoline using the C-N nanotube filter revealed that even when the central tunnel of the CNTs was blocked, the filtration did take place. This clearly exhibits that the filtration process embodies restriction of flow of heavy hydrocarbons mainly through interstitial spaces between the nanotubes. The present studies revealed that the bamboo like C-N nanotube configuration leads to the formation of new and better filter than CNT filter developed earlier by our group. This work provides a basis for future development of a C-N nanotubes filter. Such a filter would be exceptionally robust and could be used in various filtration and separation purposes.

Strain Rate Sensitivity of CNT Reinforced PMMA

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Carbon nano tubes (CNT) have unique and outstanding mechanical properties due to their nano structure and high surface to volume ratio. Incorporating CNT's into a thermoplastic matrix will therefore affect the mechanical properties of the material. These changes depend on the concentration, dispersion, compatibility of the CNT's to the matrix, as well as the dimensions of the CNT.

While the aim of incorporating CNT into a thermoplastic matrix is usually to enhance its mechanical properties, little is known on the composite material's behavior at high strain rates. As for other materials, high strain rates at the order of 10^2-10^4 sec^{-1} are expected to cause a different mechanical response and failure modes when compared to quasi-static strain rates. The assessment of high-rate mechanical properties is critical for ballistic armor design purposes.

In this study, the high strain-rate behavior of cylindrical samples of CNT dispersed in PMMA at low concentrations will be examined using a Hopkinson Split Pressure Bar (SHPB) apparatus. Different types of CNT's at different concentrations will be examined, in conjunction with different surface treatments applied to the CNT's to increase their adaptation to the thermoplastic matrix. Quasi-static mechanical characterization will also be performed to provide a reference baseline. The static and dynamic mechanical behavior of the composites will be reported and discussed.

Formation Of Thick Dielectrophoretic Carbon Nanotube Fibers

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The aim of this work was to elucidate the formation process of dielectrophoretic (DEP) carbon nanotube fibers (CNT-fibers) and characterize the fiber properties relevant to their technological applications. The fiber diameter was shown to increase when applied voltage was increased (up to 350 Vpp) and when retraction speed was decreased (up to 400 $\mu m\ s^{-1}$) in accordance with theoretical expectations. This work represents the first demonstration of the formation of thick DEP CNT-fibers (up to ~Ø0.5 mm). This is an intriguing result, as it expands the diversity of possible applications of the fibers and facilitates their characterization by analytical methods that require large quantities of the material. The performance of these thick fibers was as follows: a density of 0.35 $g\ cm^{-3}$, a tensile strength of 15 MPa, a Young's modulus of 1 GPa, and an electrical resistivity of 25 $m\Omega\ cm$.

Dispersion and Alignment of Carbon Nanotubes in Fiber Spinning Process

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The mechanical and conducting properties of carbon nanotubes(CNTs)/polymer composites are affected by several factors such as polymer-nanotube interaction and nanotube alignment in the polymer matrix as well as characteristics of CNTs themselves [1]. In this study, we have investigated dispersion and alignment of CNTs in fiber spinning process such as melt spinning and electrospinning. CNT dispersion in melt spinning has been controlled by using hyperbranched polymer [2]. CNT alignment in electrospinning was also achieved by using co-electrospinning which resulted in obtaining core-shell fibers. It was found that the CNT orientation in core-shell nanofibers during co-electrospinning could be enhanced by using CNT composites as a sheath part. The mechanical and conducting properties of melt-spun and electrospun fibers are measured and compared in viewpoint of dispersion and alignment of CNTs. The alignment of multi-walled carbon nanotubes in poly(ethylene terephthalate) and polyurethane fibers is analyzed by the polarized Raman spectroscopy measurements as well as TEM observation.

[1] N.G. Sahoo, S. Rana, J.W. Cho, et al, *Progress in Polymer Science*, **35**, 837-867, (2010).
[2] B.W. Steinerta, D.R. Dean, *Polymer*, **50**, 898-904, (2009).

Effects of Carbon Nanotube Strength on Mechanical Properties of Carbon Nanotube/Alumina Composites Prepared by Pressureless Sintering

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Engineering ceramics such as Al2O3, Si3N4, SiC and ZrO2 produced by conventional manufacturing technology have high stiffness, excellent thermostability and relatively low density, but extreme brittle nature restricted them from many structural applications. In order to overcome the toughness problem, carbon nanotubes (CNTs) are researched as reinforcing fillers toproduce tougher ceramic materials [1].

Unfortunately, making ceramic composites with CNTs has been a significant challenge, only little or no improvement in fracture toughness have been reported, presumably owing to the difficulties in homogeneous dispersion of CNTs in the matrix and in formation of adequate interfacial connectivity between two phases [2]. In particular, load bearing abilityof CNTs in the sintered ceramics is the key issue that affects the ability to transfer load from the matrix to the CNTs.

In this work, four different types of multi-walled carbon nanotubes (MWCNTs) i.e., chemical vapor deposition-grown MWCNTs followed by a series of high temperature annealing at 1200 ˚C, 1800 ˚C, 2200 ˚C and 2600 ˚C were compared as a fibrous reinforcing agent in alumina ceramics. These different annealing temperature leads to significant different structures and tensile strength of the MWCNTs. The objective of this work is to evaluate the effects of tensile strength of the MWCNTs on the fracture behavior and mechanical properties of the macroscopic MWCNT/alumina composites.

The experimental results of the present study showed that the resultant composites had relative density as high as 99% after pressureless sintering at 1400˚C for 1 hour under an Ar + 5% H2 flow. It was found that MWCNT annealed at 1800˚C seemed to be effective in improvement of bending strength and fracture toughness as a reinforcing agent. The addition of this type of MWCNT results in 14% and 12% simultaneous increases in bending strength (675.8 ± 45.9 MPa) and fracture toughness (4.51 ± 0.16 $\mathrm{MPa\cdot m^{1/2}}$), respectively, compared with MWCNT-free alumina.

Transmission electron microscope observations revealed that the MWCNT annealed at 2600˚C, rather than pulling out from the alumina matrix, broke in the outer shells and then the inner core was pulled away, leaving the outer shells of the fragment in the matrix (i.e., they underwent failure in a "sword-in-sheath" fracture mode, as observed for the same type of MWCNT under tensile loading [3,4]). The other types of MWCNTs failed leaving either a very short sword-in-sheath failure or a clean break [5]. These results may provide new insight into the fracture mechanisms and suggest a new design methodology for MWCNT-based ceramic composites, leading to improved fracture toughness.

[1] J. Cho et al., J. Mater. *Sci.* **44**, 1934, (2009).
[2] G. Yamamoto et al., *Nanotechnology,* **19**, 15708, (2008).
[3] M.F Yu et al., *Science* **287**, 637, (2000).
[4] G. Yamamoto et al., *Diam. Relat. Mat.,* **19**, 748 ,(2010).
[5] A.H. Barber et al., *Appl. Phys. Lett.* **87**, 203106, (2005).

A Comparative Study on the Behavior of SWCNT and DWCNT in Phoinduced Electron Transfer Processes.

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Double-walled carbon nanotubes (DWCNTs) are intriguing materials that exhibit properties intermediate between those of single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). These carbon nanomaterials formed from two concentric cylinders of graphene can be routinely synthesized with outer-wall diameters below 2 nm, and they exhibit band gaps that are sufficiently large for use in field-effect transistors. At the same time, DWNTs can offer several of the beneficial properties typically observed for MWNTs, such as improved lifetimes and current densities for field emission and high stability under aggressive chemical, mechanical, and thermal treatments.[1] There are scarcely examples of functionalization of these kinds of tubes but, in all cases, it can permit the selective attached to the sidewall of the outer shell of DWCNTs without disrupting the properties of inner tubes. The target of this communication is to compare and contrast the behaviour of SWCNT and DWCNT when a photoinduced electron transfer process is taken place. For this propose, we have synthesized a functionalized DWCNT (f-DWCNT 2) with dimethylamino groups (DMA) and it analogous functionalized SWCNT (f-SWCNT 1). Both materials have been fully characterized using a variety of complementary techniques, including Raman, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), transmission electron microscopy (TEM) and UV-Vis-NIR absorption spectroscopy. Finally, fluorescence and laser flash photolysis spectroscopy (LFP) has been used to study the photophysical events in both materials.

[1] A. A. Green and M. C. Hersam, *ACS Nano*, **5**, 1459-1467, (2011).

Correlating Chi and Concentration: A General Method For Predicting Nanotube Solubility

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Nanotubes are extremely tough, conductive, quasi-1-D molecules proposed for use in a host of applications ranging from artificial muscles to body armour. However, due to their high aspect ratio, nanotube-solvent mixtures exhibit a low entropy of mixing, inhibiting their dissolution and therefore their processing. Instead, nanotube solubility in liquid media is driven by small or negative values of the enthalpy of mixing, which is directly proportional to the Flory-Huggins parameter χ(chi)[1].Owing to the difficulty in measuring this parameter, the enthalpy of mixing is usually approximated using the Hildebrand-Scratchard equation,or expressed as a function of the difference in nanotube and solvent surface energies respectively. Unfortunately, such expressions are limited due to the fact that they predict only positive values of χ.

In this work we present, for the first time, measured χ values for SWNTs dispersed in various amide solvents and develop a general equation for predicting nanotube dispersion efficiency in such solvents. It is, moreover, shown that the obtained nanotube concentration behaves as a natural logarithm of the χ values measured, which is consistent with regarding the nanotube-solvent dispersions as saturated solutions. These results introduce possibilities for understanding the dispersion of similar low-dimensional materials in common solvents.

[1] Bergin, S. D.; Nicolosi, V.; Streich, P. V.; Giordani, S.; Sun, Z.; Windle, A. H.; Ryan, P.; Niraj, N. P. P.; Wang, Z-T. T.; Carpenter, L.; Blau, W. J.; Boland, J. J.; Hamilton, J. P.; Coleman, J. N. *Adv. Mater.*, **20**, 1876–1881 (2008).

Influence of the Nanomanipulation on the Structural Properties of Individual Carbon Nanotubes Serpentines

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In last few decades the investigation of physical properties of carbon nanotubes (CNT) has received a great amount of attention due to their potential to be applied in nanodevices. Consequently, the search for new geometrical configurations as well as for the control of carbon nanotubes growth is a rich research field. Recently, a new type of tube configuration, named serpentine, was obtained [1]. It was shown that, for serpentines, the tube-substrate interaction is strongly affected by the substrate orientation. The modifications in the tube substrate interaction can be used to modulate the electronic properties of the serpentine which can exhibit metallic or semiconductor behavior in the same (n,m) tube [2]. Based on the exposed facts the investigation of the physical properties of this new type of CNTs is important, in order to explore its great potential to perform active nanoengineering. In this work we employed an experimental configuration that combines atomic force microscopy with confocal spectroscopy, similar to that presented in Reference [3], to investigate the changes on the serpentine vibrational modes when manipulated with a gold tip. The manipulation was performed both by pressing the serpentine deposited on crystalline quartz substrate, perpendicular to substrate plane, as well as dragging the serpentine on the substrate plane. The structural modifications were probed via Raman scattering, exciting the tubes at 632.8 nm. In the uniaxial pressure experiments we observed changes in the G-band region, the band caused by the in-plane C-C bond stretching [4]. A band split and the observation of a new vibrational mode was monitored for different pressure levels and different tubes. Both reversible and irreversible changes were observed, the later indicating a permanent modification of the serpentine structure. In the drag experiments we observed a clear downshift of the G-band frequency that propagates along the tube. In order to quantify the behavior of the observed G-band frequency shift, we used the continuum model of elasticity theory in the small deformation limit, describing the serpentine locally as a thin cylindrical pipe under unilateral extension. The authors are very grateful to FAPEMIG, CNPq and CAPES for the financial support of this research.

[1] N. Geblinger et al, *Nature Nanotech*, **3**, 195-200, (2008).
[2] J. S. Soares et al, *Nano Lett.*, **10**, 5043-5048, (2010).
[3] A. Hartschuh et al, *Phys. Rev. Lett.* **90**, 095503, (2003).
[4] M. S. Dresselhaus et al, *Nano Lett.* **10**, 751-758, (2010).

Chirality Controlled and (6,5) Selected CVD Growth of Single-Walled Carbon Nanotubes on Flat Substrate

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Modifying electrical and optical properties of single-walled carbon nanotubes (SWNTs) has been obtained by structure controlling [1,2] or chemical doping [3,4]. Because of their intrinsic electrical property, those nanotubes have been given an emphasis on many applications. The direct synthesized SWNTs, however, are still lacked of structure controlling.

In this study, we investigated the optical property and structure of SWNTs synthesized from acetronitrile. The Co/Mo binary catalyst was deposited on amorphous quartz substrate by a liquid dip-coating process [5] with a precursor of 0.01 %wt of each metal. SWNTs can be simply produced by chemical vapor deposition (CVD) process through no-flow condition using acetronitrile as a carbon source. The dip-coated catalysts were purged by Ar containing 3 % of H_2 (Ar/H_2) while heating up to growth temperature. After the temperature reached 800 °C, the CVD chamber was evacuated and sealed before introducing acetronitrile, followed by cooling process. Dispersed SWNTs were prepared in D2O with sodium deoxycholate used as the surfactant. The SWNTs were thoroughly characterized by resonance Raman spectroscopy with three excitation wavelengths (488, 514, 633 nm), optical absorption spectroscopy, as well as photoluminescence. The resulted SWNTs were compared with that grown from alcohol, as well as HiPco sample.

As for the Raman and optical absorbance results, the SWNT diameter seems to be dramatically small, and the diameter distribution was also narrowed, compared to that from alcohol. Additionally, there may have some possibility of nitrogen (N) doping into nanotube structure, because of high G to D ratio and blue shift of G-band6, indicating the presence of disorder morphology inside structure. Surprisingly, the selectivity of (6,5) SWNT can be also achieved from this method. The diameter distribution, comparable to HiPco sample, is extremely narrow.

[1] R. Xiang, E. Einarsson, J. Okawa, T. Thurakitseree, Y. Murakami, J. Shiomi, Y. Ohno, S. Maruyama, *J. Nanosci. Nanotech.*, **10**, 3901, (2010).
[2] T. Thurakitseree, E. Einarsson, R. Xiang, S. Aikawa, S. Chiashi, J. Shiomi, S. Maruyama, *J. Nanosci. Nanotech.*, (2011), accepted.
[3] C. Zhou, J. Kong, E. Yenilmez, H. Dai, *Science*, **290**, 1552, (2000).
[4] C. Ehli, C. Oelsner, D. M. Guldi, A. M. Alonso, M. Prato, C. Schmidt, C. Backes, F. Hauke, A. Hirsch, *Nat. Chem.*, **1,** 243, (2009).
[5] Y. Murakami, Y. Miyauchi, S. Chiashi, S. Maruyama, *Chem. Phys. Lett.*, **377**, 49, (2003).
[6] T. Susi, Z. Zhu1, G. R. Soria, R. Arenal, P. Ayala, A. G. Nasibulin, H. Lin, H. Jiang, O. Stephan, T. Pichler, A. Loiseau, E. I. Kauppinen, *Phys. Stat. Sol. (b)*, **247,** 2726, (2010).

Vertical Array Of Fullerene Nanotube (FNT) Spin Valves For Ultra-High Density Spintronic Memory

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Magnetic random access memory (MRAM) has recently attracted significant attention since it has the potential to emerge as a universal memory [1]. The basic MRAM cell has a "spin valve" configuration in which a tunnel barrier is sandwiched between two ferromagnetic contacts. The resistance state (R) of this memory cell is "bistable"; it takes a small value (say Ron, encoding logic bit "0") when the magnetizations of the contacts are parallel and switches to a high value (say Roff , encoding logic bit "1") when they are antiparallel. This phenomenon can be explained by invoking spin-polarized carrier tunneling between the ferromagnetic contacts [2].

Scaling of tunnel junction based MRAM cells faces two main challenges:(1) The barrier needs to be ultrathin (< 1nm) and uniform to achieve reliable read-operation and (2) Ferromagnets, scaled to small dimensions, exhibit superparamagnetism behavior, which leads to increased soft-error rate.

Due to these reasons current MRAM chips (as marketed by EVERSPIN Technologies [3]) exhibit poor storage capacities ranging from 256 kb to 16 Mb. Therefore it is necessary to investigate alternative designs for MRAM cells.

Carbon nanotube [4] and organic semiconductor spin valves [5] have been reported, which exhibit promising switching characteristics. However, these devices work only at a low temperature and high density integration of such devices is largely underdeveloped.

To address these issues we propose to use vertically standing fullerene nanotubes (FNTs) as the active layer of the memory cell. These tubes can be self-assembled at a very high density approaching $10^{12}/\text{cm}^2$. Fullerenes offer weak spin-orbit coupling and negligible hyperfine interaction, which can potentially result in large spin relaxation lengths and high $R_{\text{off}}/R_{\text{on}}$. This will allow reliable read-operation without the need for ultrathin barriers. The ferromagnetic contacts will be patterned in a nanopillar geometry which avoids the superparamagnetism problem due to large shape anisotropy.

The fabrication process starts with an anodic aluminum oxide (AAO) film containing a high density of hexagonally ordered nanopores. A ferromagnetic nanowire contact is electrodeposited at the bottom of each pore. Fullerene nanotubes are grown on top of this ferromagnet using a novel process that combines a traditional dip-and-dry method [6] with simultaneous centrifugation. A second ferromagnetic contact is sputtered on top of the template to complete the spin valve device. The switching characteristics of the spin valve arrays have been measured as a function of applied bias and temperature, which sheds light on spin relaxation mechanisms in FNTs.

[1] J. Åkerman, *Science*, **308** 508 - 510, (2005).
[2] E. Tsymbal et al., *J. Phys. Cond. Matter.*, **15**, R 109, (2003).
[3] http://www.everspin.com/
[4] L. Hueso et al., *Nature*, **445,** 410-413, (2007).
[5] K. M. Alam and S. Pramanik, http://arxiv.org/abs/1005.1118, to appear in Nano-

Semiconductors: Devices and Technology, CRC press, Ed: Kris Iniewski.
[6] H. Liu et al., J. *Am. Chem. Soc.*, **124**, 13370-13371, (2002).

Aerosol-Synthesized SWCNT Networks With Tunable Conductivity And Transparency By A Dry Transfer Technique

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Single-walled carbon nanotube (SWCNT) networks are promising for future electronics because of their unique optical and electrical properties. Optically transparent conductive electrodes are one of the potential application areas, as components of widely utilized electrical devices, such as thin displays and touch sensors. Currently used transparent metal oxides such as indium-tin oxide (ITO) have several drawbacks, including a high refractive index and haze, spectrally no-uniform optical transmission, limited flexibility, restricted chemical robustness, and a limited raw material supply.

We demonstrate an aerosol CVD process to dry deposit large-area SWCNT networks with tunable conductivity and optical transmittance on a wide range of substrates including flexible polymers. SWCNTs were synthesized by the catalytic decomposition of carbon monoxide (CO) on iron nanoparticles formed by thermal decomposition of ferrocene vapour and then membrane filtrated to form randomly oriented SWCNT networks at the outlet of the synthesis reactor. These SWCNT networks can be chemically doped after the room temperature press transfer process to reach a sheet resistance of as low as 110 Ω/sq at 90% optical transmittance [1]. A wide application potential of these networks is demonstrated by fabricating SWCNT network-based devices such as a transparent capacitive touch sensors, thin-film transistors (TFTs), and bright organic light-emitting diodes (OLEDs).

[1] Kaskela, A., A. G. Nasibulin, M. Y. Zavodchikova, B. Aitchison, A. Papadimitratos, Y. Tian, Z. Zhu, H. Jiang, D. P. Brown, A. Zakhidov and E. I. Kauppinen
Nano Letters. **10**(11) 4349-4355.

Fabrication of Carbon Nanotube Based Interconnect Devices

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Carbon nanotubes (CNTs) can carry a current density up to $\sim 10^9$ A/cm^2 [1] that exceeds the maximum current density of 6×10^6 A/cm^2 of copper before it fails due to electromigration. They have been widely investigated as promising candidates to replace copper as interconnects in integrated circuits beyond the 22 nm node [2-3].

Although groups have reported progress in CNT integration for interconnect applications, the most advanced CNT via is limited to 300-500 nm in diameter and aspect ratios of below 2 [2-3]. One of the major obstacles is the difficulties in patterning the CNT catalyst at the bottom of small and deep via holes using the conventional PVD (physical vapor deposition) technique. There is also a great challenge to pattern catalyst on a vertical surface with high repeatability and low level of contamination.

In our study, cobalt silicide was found to be a thermally and chemically stable material under CVD conditions, including high temperature treatment at 650 °C and exposure to gas mixtures containing H_2 and C_2H_2. Vertically aligned and high density Multi-walled CNTs (MWNTs) can be grown on $CoSi_2$ using Fe as the catalyst, with a carbon shell density approaching 10^{12}/cm^2.

We also found that, after plasma etch and reduction step in H_2 at the CVD temperature, both cobalt and nickel silicides were able to catalyze CNT growth in a purely thermal CVD process. We also present X-ray Photoelectron Spectroscopy (XPS) data to understand the mechanism of catalyst formation in this process flow [4]. This finding is very important in integrating CNTs in via/interconnects structures as catalyst patterning in small via holes and/or on vertical surfaces is extremely challenging.

Using the techniques presented here, a horizontal CNT interconnect structure is fabricated by growing arrays of horizontal CNTs from a $CoSi_2$ layer patterned on a vertical surface of the electrodes. The process is demonstrated to solve the problems of catalyst patterning at the bottom of small and deep (depth-to-diameter ratio over 3) via. Electrical measurements show an Ohmic contact between $CoSi_2$ and the as-grown CNTs, with resistance per tube/contact in the order of tens of kΩ. This value is comparable to the state-of-the-art values for contact between CNTs and metals (e.g. Pd, Cr) fabricated through lithography steps after CNT growth, which is not a CMOS compatible.

[1] Wei, B.Q.; Vajtai, R.; Ajayan, P. M.; *Appl. Phys. Lett*. **79**, 1172-1174, (2001).
[2] Yokoyama, D.; Iwasaki, T.; Yoshida, T.; Kawarada, H.; Sato, S.; Hyakushima, T.; Nihei, M.; Awano, Y. *Appl. Phys. Lett*. **91**, 263101-263103, (2007).
[3] Dijion, J.; Fayolle, M.; Vo, T.; Pontcharra, J.; Acquaviva, D.; Bouvet, D.; Ionescu, A.; Esconjauregui, C. S.; Capraro, B.; Quesnel, E.; Robertson, J.; *Tech. Digest IEDM 2010*, **33**.4.1, (2010).
[4] Bayer, C. B..; Hofmann, S.; Castellarin-Cudia, C.; Blume, R., Baehtz, C.;

Esconjauregui, S.; Wirth, C. T.; Oliver, R. A.; Ducatti, C.; Knop-Gericke, A.; Schlögl, R.; Goldoni, A.; Cepek, C.; Robertson, J.; *J. Phys, Chem. C*.
dx.doi.org/10.1021/jp102986f, (2011)

Reductive Dissolution And Separation Of Single-Walled Carbon Nanotubes

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Current single-walled carbon nanotube (SWCNTs) syntheses produce a heterogeneous mixture of nanotubes of varying lengths, diameters and chiralities. Although SWCNTs have outstanding optical and electronic properties, the presence of both metallic and semi-conducting types in as-grown materials has hindered their widespread use in practical applications. Post-synthetic sorting is essential in unlocking these remarkable properties, although most separation techniques rely on high-quality dispersions of individual SWCNTs to function. The use of aggressive ultrasonication and repetitive ultracentrifugation are required to make these dispersions – often destructive and suited only to small-scale studies. We have developed a simple, scalable technique involving the dissolution of SWCNTs in dry, air-free, non-aqueous solvents without the need for sonication and centrifugation. Upon the reduction of the as-received SWCNTs, we observe significant swelling due to intercalation of solvent between nanotube bundles causing the exfoliation and debundling of the SWCNT networks, generating a nanotubide (SWCNT n-) dispersion. Nanotubes appear to be dispersed individually from AFM and TEM analysis, and we observe the significant enrichment of metallic SWCNTs as shown by comparative Raman spectroscopy of the raw, dissolved and undissolved nanotubes.

In terms of the dissolved species, amorphous carbon and defective SWNTs are charged and dissolved preferentially, but prolonged reduction leads to the dissolution of purer material as observed by a decrease in the I_D:I_G ratio over time in Raman spectroscopic analysis.

Carbon Nanotube Films Preparations for Electronic, Sensors and Bioengineering Application

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Carbon nanotubes films (CNTF) are suggested to be more technological material in production process of devices and systems. It's now considered as radiation resistive transistors and sensors [1], transparent and conductive layers for optoelectronics devices, scaffold material for biological application in tissue engineering. Nevertheless different technological methods of carbon nanotubes films formation biased on chemical vapor deposition, electrophoresis and ink printing are suggested.

In this work we describe the development of different methods carbon nanotubes deposition for electronic, sensors and bioengineering with making use of chemical vapor deposition (CVD), dielectrophoresis (DEF) or deposition from surfactant solvents. It was shown the different methods produce different film that can be used or specific applications. CNTF films produced by low temperature CVD demonstrate rather good conductive and transparent properties for nanotubes with diameters 10 – 100 nm. The carbon nanotubes film deposited with making use of dielectrophoresis techniques allow us to control concentration and geometry of nanotubes film. We used DEF for sensor's active layer development based on quasi-one-dimensional structures composite of carbon nanotubes and oxide zinc nanorods. The different surfactants was investigated for CNTF production. To produce biocompatible material we suggested to use bovine albumin (BSA) as surfactant for single-wall carbon nanotubes dissolution. Earlier we used nanotubes-albumin composite as scaffold material for cartilage regeneration [2]. This method was used for transparent conductive film formation by rolling up method on cover slips. We investigated the optical and electrical properties of such film and used them for cell growth electro-stimulation.

Thus different methods can be used for CNTF formation. We have shown that method based on carbon nanotubes solution with biological surfactant provide transparent conductive biocompatible films.

[1] D.V. Gromov, V.V. Elesin, G.V. Petrov, I.I. Borinetskii, V.K. Nevolin. Radiation Effects in Nanoelectronic Elements, *Semiconductors*, **44** (13), 1699–1702, (2010).
[2] S.A. Ageeva, I.I. Bobrinetskii, V.K. Nevolin, V.M. Podgaetskii, S.V. Selishchev, M.M. Simunin, V.I. Konov, V.V. Savranskii. Nanotube-based three-dimensional albumin composite obtained using continuous laser radiation, *Semiconductors*, **43**(13), 1714- 1718, (2009).

The Methods of Cell Growth on Carbon Nanotubes Substrates with Making Use Of Electrostimulation

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Over the past thirty years the influence of electric stimulation on the accelerated tissue healing and cell growth was investigated. Traditional methods of bringing the external electric field failed to localize a field in the healing area, so whole organism had to be exposed to electric stimulation. Increasing the work area and the distance between electrodes and the healing area implies increasing of electrical field intensity, required for stimulating individual cells. In that case we show efficiency of using implant nanocomposite electrodes, which intend to help localizing electric field in a specific area. Accelerated tissue regeneration can be achieved by using tiny implant electrodes with a lower intensity amplitudes, and low-frequency signal.

Nevertheless, similar invasive methods demand use of the biodegradable materials which help to minimize the influence onthe tissue micro environment. The way of electric stimulation of cell growth, using system of the planar electrodes is well-known. Such electrodes are creating fields which can be localized mainly in the area of an organism where the electric field and current are required. The last results in nanotube ferment-based degradation are discussed as a new scaffold material for tissue regeneration [1]. System of in vitro cell growth, involving a substrate, nanocomposite monolayer and gold needle electrodes was developed. 2 mg of single-walled carbon nanotubes were ultrasonicated with 10 mg of bovine serum albumen and 10 ml of distilled water to create nanocomposite solution. Substrate was treated with sputter deposition of gold to form contact area and then covered with 70 nm nanocomposite film to provide current supply to cells. Embryonic fibroblasts were cultured on 24x24 mm coverslips. Cells were incubated in 6 well plates for 76 h, at 37 °C and 5% CO_2, fixed with 4% glutaraldehyde, washed twice with PBS, and then dehydrate using 50%, 70% and 96% ethanol for microscopy analysis.

Electro-stimulation with 10, 50, 100 and 200mVpulse signal, at 1 kHz frequency, with 1 sec period was applied for 48 h after one day of standard cultivation. We used MTT method to determinate proliferation index, and investigated cells morphology with optical, atomic-force and scanning electron microscopy. The proliferation index increases on 20% after 50 mV pulses.

Dense cell monolayer was found on samples exposed to current on a third day of incubation. As a result, we have shown another way of providing electrical stimulation of cells by using biocompatible conductive albumen-nanotube composite.

[1] L.B. Allen, G.P. Kotchey, Y. Chen et al, *Am. Chem. Soc.*, **131**(47), 17194–17205, (2009).

Adsorption Of Procion Blue MX-R (Reactive Blue 4) Dye From Water Solutions By Single-Walled Carbon Nanotubes And Multi-Walled Carbon Nanotubes

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Carbon nanotubes (CNTs), with nano-sized diameter and tubular microstructure, have been the worldwide hotspot of study since their discovery because of their unique morphologies and various potential applications. Because of their relatively large specific surface areas and easily modified surfaces, much attention has been paid to the adsorption by CNTs of contaminants such as heavy metals [1-7] and biological contaminants [8,9], in aqueous effluents. However, the use of CNTs for dye decontamination of aqueous effluents has not yet been extensively employed [10-15].
In the present work, single-walled carbon nanotubes (SWCNT) prepared by catalytic chemical vapour deposition (CCVD), with mean diameter of 1,37 nm, were compared with commercial multi-walled carbon nanotubes (MWCNT) and these materials were used as adsorbents for the successful removal of Procion Blue MX-R (Reactive Blue 4) textile dye from aqueous solutions The adsorbents were characterised by Raman spectroscopy, N2 adsorption/desorption isotherms and scanning and transmission electron microscopy. The effect of temperature on the equilibrium adsorption of Procion Blue MX-R (Reactive Blue 4) dye from aqueous solution using both CNTs was investigated. The equilibrium adsorption data were analyzed using three widely applied isotherms: Langmuir, Freundlich and Liu. Kinetic analyses were conducted using pseudo-first, second-order, Avrami fractional-order and the intra-particle diffusion models.

[1] C.S Lu, H.S. Chiu, *Chem Eng Sci*, **61**, 1138-1145, (2006).
[2] C. Lu, C. Liu, J *Chem Technol Biotechnol*, **81**, 1932-1940, (2006).
[3] Y.H.Li, S. Wang, Z. Luan, J. Ding, C. Xu, D. Wu, *Carbon*, **41**,1057-1062, (2003).
[4] Y.H.Li, Z. Di, J. Ding, D. Wu, Z. Luan, Y. Zhu,*Water Res*, **39**, 605-609, (2005).
[5] J. Hu, C. Chen, X. Zhu, X. Wanga, *J Hazard Mater*,**162**, 1542-1550, (2009).
[6] K. Pillaya, E.M. Cukrowska, N.J. Coville, *J Hazard Mater*, **166**, 1067-1075, (2009).
[7] C.Y. Kuo, *Desalination* **249**, 781-785, (2009).
[8] V.K.K.Upadhyayula, S. Deng, M.C. Mitchell, G.B. Smith, *Sci Total Environ*, **408**, 1-13, (2009).
[9] V.K.K. Upadhyayula, S. Deng, G.B. Smith, M.C. Mitchell, *Water Res*, **43**, 1-9, (2009).
[10] C. Wu, *J. Hazard. Mater.*, **144**, 93-100, (2007).
[11] C.Y. Kuo, C.H. Wu, J.Y. Wu, *J. Colloid Interface Sci.*, **327**, 308-315, (2008).
[12] J.L. Gong, B. Wang, G.M. Zeng, C.P. Yang, C.G. Niu, Q.Y. Niu, et al., *J. Hazard. Mater.* **164**, 1517-1522 (2009).
[13] A.K. Mishra, T. Arockiadoss, S. Ramaprabhu, *Chem. Eng. J.*, **162**, 1026-1034, (2010).
[14] G.P. Hao, W.C. Li, S. Wang, S. Zhang, A.H. Lu, *Carbon*, **48**, 3330-3339, (2010).

[15] Y. Yao, F. Xu, M. Chen, Z. Xu, Z. Zhu, *Bioresou. Technol*., **101**, 3040-3046, (2010).

Modification Of The Electronic Structure In Single-walled Carbon Nanotubes With Aromatic Amines

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We investigated the interactions of two aromatic amines, N,N,N'N'-tetramethyl-p-phenylenediamine (TMPD) and tetramethylpyrazine (TMP) with single-walled carbon nanotube (SWNT) networks.
Adsorption and intercalation of amine molecules in bundled SWNTs is expected to modify electronic structure of nanotubes in a similar way as has already been observed for alkali metals. Our ab initio density functional calculations demonstrate that TMPD donates electron to the nanotube and produces donor-like states below the conduction band whereas the effect of the TMP treatment is very weak. The electron transfer to the nanotubes has been supported experimentally by the XPS valence band spectra which show strongly modified spectral features. Especially an increase of the electronic density at the Fermi level upon adsorption of TMPD and TMP is clearly demonstrated. Rather intensive feature between π^* and σ^* transitions in the NEXAFS spectrum of the pristine SWNTs attributed to the oxidized carbon functional groups are chemically modified upon adsorption of amines on the networks. This fact suggests that the aromatic amines evidently react with the defects, remove or replace oxygen species responsible for the p-type doping of SWNTs, and thus acting also as a de-doping agent for the naturally p-type doped semiconducting SWNTs.

A Chemists Method For Making Pure Clean Graphene

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Graphene is a two dimensional highly crystalline material and can be described as a single layer of all-sp2 carbon atoms packed into a benzenoid ring structure [1]. It is widely used to describe the structural and electronic properties of many carbon-based materials, including graphite, fullerenes and nanotubes. For example, carbon nanotubes are usually thought of as graphene sheets rolled up into nanometre-sized cylinders. In 1859, Brodie discovered that pure graphite, when treated with potassium chlorate and nitric acid, formed crystalline graphitic acid (also known as graphitic oxide or graphene oxide). It is likely that he also made small amounts of graphene and in any case he speculated a new form of carbon was present and proposed the name Graphon (Gr)[2]. However, graphene was not shown to be stable until 2004 when Geim and Novoselov [3] described the “Scotch tape” method to peel graphene from samples of crystalline graphite. This mechanical exfoliation method is slow and labour-intensive as an optical microscope is required to hunt for single and few-layer graphene (FLG) amongst the material peeled-off.
Currently, the interest of physicists in graphene is enormous, but the interest of chemists has so far not been as great, probably resulting from the absence of well-established large scale methods to produce graphene. Therefore, the most important role chemists can play is the establishment of an inexpensive and simple wet-chemical method for making graphene. For example, intercalation compounds of graphite have been of interest for many years [4]. More than 100 reagents can be intercalated into graphite [5]. In this talk, we describe an intercalation method to make clean graphene that has good electrical properties [6]. The graphene material was characterized by HRTEM, Raman, AFM and FET measurements.

[1] J. Wu, W. Pisula and K. Müllen, *Chem Rev*, **107**(3)., 718-747, (2007).
[2] B. C. Brodie, *Philos Trans R Soc Lond A*, **149**., 249-259, (1859).
[3] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos and I. V. Grigorieva, *Science*, **306**., 666-669, (2004).
[4] L. B. Ebert, Annu *Rev Mater Sci*, **6**.,181-211, (1976).
[5] M. S. Dresselhaus and G. Dresselhaus, *Adv Phys*, **51**., 1 (2002).
[6] S. Malik, A. Vijayaraghavan, R. Erni, K. Ariga, I. Khalakhan and J. P. Hill, *Nanoscale*, **2**., 2139-2143, (2010).

Mechanism of CVD Graphene Growth

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The graphene chemical vapor deposition (CVD) growth on transition metal (TM) surface is the most promising method for high quality and large area graphene synthesis.
While its mechanism remains a mystery in spite of the great experimental success. Here we are going to present our recent theoretical study on the mechanism of graphene CVD growth:
(1) C cluster' structural transition from one dimensional (1D) C chain to two dimensional (2D) graphene island and its impact on graphene growth.
(2) The great advantage of graphene nucleation near a metal step edge than that on a terrace.
(3) The magic sized C cluster formation on metal surface.
Based on our theoretical studies, we propose the use of seeded graphene to synthesize high-quality graphene in large area.

Interaction Between Two Graphene Sheets With A Turbostratic Orientational Relationship

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The interaction energy of two rigid defect-free graphene sheets with various turbostratic orientational relationships is examined systematically using a Lennard-Jones potential. When one layer is rotated from the AB stacking order, maxima and minima in the intersheet potential energy surface occur periodically at angles corresponding to the AA and AB stacking orders, respectively. The energy gap between the AA and AB stacking orders is estimated to be much smaller than the average thermal energy at room temperature. Furthermore, the turbostratic structure with a just few degrees of rotational displacement from the AB stacking order diminishes the energy gap during translational displacement effectively to zero. We conclude that the presence of defects or cross-links is required to explain even the low shear strengths inferred from experimental studies of fibres made from pure carbon nanotubes in which there is no commensurate orientation of graphene sheets. In addition, the interaction between flexible graphene sheets with defects will be discussed.

An inner look into biscrolled CNT yarns: Studies on their different typical internal morphologies by microscopic analyses of their cross sections

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The biscrolling process is a suitable way to produce multifunctional weavable yarns of otherwise unspinnable nanofibers or particulate materials using twisted aligned CNT sheets as host. In brief, the biscrolling technique involves the deposition of guest material over one or several CNT sheets and their subsequent scrolling into a biscrolled yarn. Applications of this technique are broad and some of them have been shown by making yarns of superconductors, lithium-ion batteries, catalytic nanofibers for fuel cells and of particulate titanium oxide for photocatalysis.[1]

During the scrolling process, nanometric-thick CNT host sheets produce complex irregular galleries along the yarn that act as confinement sacks for the guest material. Aiming to understand the general relation between the complex inner yarn morphology generated by the biscrolling process itself, microscopic studies were made on biscrolled yarn cross-sections prepared by focused ion-milling (FIB).

Mechanisms such as pleating and additional folding during twist derive into the complex inner yarn morphologies found. However, general trends in the resulting morphology of biscrolled yarns were identified to depend upon factors such as (1) the deposition method used for the guest material and (2) the liquid-densification of the host CNT sheets or its absence either before or during the twisting process.

The lateral migration of CNT sheets during the scrolling process was studied with patterned guest material deposition used as contrast marker on the CNT host sheets. This resulted in ways to engineer the location of guest material along the radius of a biscrolled yarn achieving production of core-shaft morphologies.

Understanding the main causes of internal morphology variations in biscrolled yarns (apparent void space, guest location, etc.) could lead to a development of new feasible applications and encourage more studies of the mechanisms involved in yarn formation by twisting and spinning.

[1] M.D.Lima, S. Fang, X. Lepró, C. Lewis, R. Ovalle Robles, J. Carretero González, E. Castillo Martínez, M. Kozlov, J. Oh, N. Rawat, C.S.Haines, M.H.Haque, V. Aare, S. Stoughton, A.A. Zakhidov, and R.H. Baughman, *Science*, **331**, 51-55 (2011).

Dispersion and Separation of Single Walled Carbon Nanotubes by Polysaccharides

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Chitosan, various neutral pH water-soluble chitosan derivatives and heparin sodium salt were investigated as dispersants of single-walled carbon nanotubes (SWNTs). Chitosan (CS) can disperse SWNTs well, but only in acidic pH condition. Our two novel derivatives, O-carboxymethylchitosan (OC) and OC modified by poly(ethylene glycol) at the -COOH position (OPEG), were able to produce highly effective debundling and dispersion of SWNTs in neutral pH aqueous solution.

Debundling of the nanotubes into individuals was confirmed with transmission electron microscopy (TEM), atomic force microscopy (AFM), photoluminescence (PLE) and UV-vis-NIR spetroscopy.

The solubilities of individually dispersed SWNTs in neutral water are 0.021 and 0.032 g/L for OC and OPEG, respectively, which are comparable to 0.038 g/L for SWNTs using CS in acetic acid.

When heparin sodium salt was used as dispersant for CoMoCAT nanotubes, (8, 4) tubes were preferentially extracted and enriched in the supernatant. Pristine CoMoCAT nanotubes are dominated by the (6, 5) species, which has smaller diameter than the (8, 4) species. After threefold extraction, the composition percentage of (8, 4) tubes, determined by PLE spectroscopy, increased from 7% to 60%. Computer modeling verified that, of the four seminconducting species abundant in CoMoCAT samples, the (8,4) species has the lowest binding energy with heparin. Nanotube solutions enriched in the (8, 4) species were successfully used for fabrication of network field-effect transistors, confirming the easy removability of heparin. Polysaccharide dispersed SWNTs solution also can be used as reinforcement materials in alginate hydrogels. The results show that SWNTs can improve the mechanical and electrical properties of alginate hydrogels.In summary, we found that several polysaccharides can effectively debundle SWNTsin neutral aqueous solutions using a mild and easy-to-implement process. Also centain polysaccharide-heparin sodium salt can extract (8,4) chirality from CoMoCAT dispersion. Some polysaccharide-SWNTs solutions can be used to reinforce alginate hydrogels.

Optical response of single-walled carbon nanotubes in far-infrared region

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A carbon nanotube (CNT) is one-dimensional and hollow cylindrical structure formed by wrapping a graphene sheet, and becomes either metallic or semiconducting depending on its geometry. Usually, single-walled carbon nanotubes (SWCNTs) have the order of a few nanometers in diameter and the order of several micrometers in length. Optical spectroscopy such as Raman scattering and photoluminescence is well-known to be effective technique to characterize their properties for electronic and optoelectronic applications. In addition, using infrared (IR) spectroscopy and terahertz time domain spectroscopy (THz-TDS), there has been reported the small band-gap and antenna effects of metallic SWCNTs [1-4]. The former has so far been reported theoretically and experimentally [1-3,5]. The small gaps in a few tens of meV at Fermi level were induced by the curvature effect and intertube interactions [5].

The latter, antenna effects by plasmon resonance have been predicted theoretically that frequency in far-IR spectroscopy and THz-TDS is proportional to the inverse tube length that has been one of the on-going themes in CNTs [4]. We here report optical response of SWCNTs by using FT-IR spectroscopy in mid- and far-IR range. Several types of SWCNTs were used and prepared on silicon wafer and polyethylene sheet. In case of arc discharge SWCNTs, the IR spectra exhibit a broad band around 100 cm^{-1} in low-frequency range and a sharp peak near 5580 cm^{-1} in high-frequency range. The latter is thought to be S1 interband transition of semiconducting SWCNTs. The former is considered to be a small gap or antenna effects-induced signal of metallic SWCNTs. To clarify the origin of this signal, we have investigated the doping dependence with F4TCNQ dopant and treatment time dependence by using tip ultrasonication which cut long SWCNTs into short pipes. Upon doping, the absorption intensity was enhanced or not decreased depending on a substrate in low-frequency region along with the strong reduction of the peak of S1 interband transitions. In addition, depending on treatment time of tip ultrasonication, the signals in low-frequency region were shifted upward, whereas no peaks of S1 interband transitions were shifted. The possible mechanisms for the experimental observations will be discussed in detail.

[1] M. E. Itkis, S. Niyogi, M. E. Meng, M. A. Hamon, H. Hu, and R. C. Haddon, *Nano Lett.*, **2**, 155, (2002).
[2] H. Nishimura, N. Minami, and R. Shimano, *Appl. Phys. Lett.*, **91**, 011108, (2007).
[3] N. Akima, Y. Iwasa, S. Brown, A. M. Barbour, J. Cao, J. L. Musfeldt, H. Matsui, N. Toyota, M. Shiraishi, H. Shimoda and O. Zhou, *Adv. Mater*. **18**, 1166, (2006).
[4] T. Nakanishi, T. Ando, *J. Phys. Soc. Jpn*., **78**, 114708 (2009). 18, 1166.
[5] M. Ouyang, J.-L. Huang, C. L. Cheung and C. M. Lieber, *Science*, **292**, 702 (2001).

Multifunctional Free-Standing Single-Walled Carbon Nanotube Films

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The unique properties of single-walled carbon nanotube (SWNT) films, such as high porosity and specific surface area, low density, high ratio of optical transmittance to sheet resistance, high thermal conductivity and chemical sensitivity, and tunable metallic and semiconducting properties, open up a new avenue for a wide range of applications. Free-standing films offer a unique form factor for novel applications. We report here a simple and rapid method to prepare multifunctional free-standing SWNT films with thicknesses from a sub-monolayer to a few micrometres having outstanding properties for a broad range of exceptionally performing devices.

We have fabricated state-of-the-art key components for nanoparticle filtration with a figure of merit of 147 Pa^{-1}, transparent and conductive electrodes with a sheet resistance of 84 Ω/□ and a transmittance of 90%, electrochemical sensors with extremely low detection limits below 100 nM, and polymer-free saturable absorbers for ultrafast femtosecond lasers. Furthermore, the films performed as the main components in gas flow meters, gas heaters and thermoacoustic loudspeakers.

[1] Nasibulin et al. *ACS Nano*. Publication date (Web):March 1, 2011.DOI: 10.1021/nn20033

Synthesis And Characterization Of Single-Walled Carbon Nanotubes-Al_2O_3 Nanocomposites

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Carbon nanotubes (CNTs) have been investigated extensively over the past decade for adsorption and sensors applications. This paper reports the synthesis and characterization of single-walled carbon nanotubes (SWCNT)-alumina nanocomposites. SWCNTs (mean diameter of 1,63 nm) were produced by catalytic chemical vapor deposition for the preparation of such nanocomposites. To obtain a good dispersion of SWCNTs in the alumina matrix, they were functionalized by:one covalent (with nitric, sulfuric and chloridric acids) and two non-covalent (with polyvinyl alcohol, PVA, and sodium dodecyl sulfate, SDS) functionalizations. Nanocomposites were prepared by chemical precipitation using $Al(NO_3)_3.9H_2O$ and $NH_3.H_2O$ as starting material for Al_2O_3. Then, these composites were submitted to a thermal treatment at 500 °C for 2h in argon atmosphere. Structural defects on SWCNTs and the resulting interaction between matrix and the SWCNTs were verified by Raman spectroscopy. To study the microstructure of these nanocomposites specific surface area (BET), scanning (SEM) and transmission (TEM) electron microscopy were carried out, while energy dispersive X-ray (EDX) and X-ray diffraction (XRD) were used to verify the crystallization of alumina. The surface area of the resulting nanocomposites reached 265.90 m^2/g for covalently functionalized ones, 280.80 m^2/g and 211.52 m^2/g for the non-covalently functionalized with PVA and SDS, respectively. EDX spectrum revealed that the covered products are indeed alumina, while XRD confirmed crystallization of gamma- alumina. Then, the preeminent properties of the SWCNTs-Al_2O_3 nanocomposites could be interesting to use as adsorbents devices, due to high surface area and interface reactive properties.

[1] Y. Li, S. Wang, A. Cao, D. Zhao, X. Zhang, et al., *Chem. Phys. Lett.*, **350**,. 412-416, (2001).
[2] B. Gómez, J. M. Martínez-Magadán, *J. Phys. Chem. B*, **109**, 14868-14875(2005).
[3] J. Goering, U. Burghaus,*Chem. Phys. Lett.*, **447**, 121–126, (2007).
[4] M.D. Lima, M.J de Andrade, A. Locatteli, et al.,*Physica Status Solidi B-Basic Solid State Physics*, **244**, 3901-3906, (2007).
[5] M.J de Andrade, A. Weibel, C. Laurent, et al., *Scripta Materialia*, **61**, 988-991, (2009).
[6] Q. Yang, Y. Deng, W. Hu, *Ceram. Int.*, **35**, 1305-1310, (2009).

Comparative Electrical Studies Of Ni/MWNT Bulk Composites

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Nickel matrix composites reinforced with multiwalled carbon nanotubes (Ni/MWNT) were manufactured by spark plasma consolidation, which consists in applying a high pressure to a Ni/MWNT blend and a high current pulse for a short period of time. Different loads were tested in order to observe the influence on the densification of the composites. The samples were characterized with x-ray diffraction and FIB/SEM dual beam cross sections. Densities were determined by Archimedes' method. We have observed that the final density was about 92% of the theoretical density estimated by the mixture law. X-ray diffractograms of the composites show no carbide formation, even though a very high current is used in the processing (approximately 195 kA). This indicates that there was no CNT degradation due to high temperature sparking. The electrical performance of the composites was investigated in a four-terminal sensing device at room temperature and compared to Ni/MWNT samples, manufactured with different powder metallurgical methods, as well as to a high purity Ni rod (99.9%). For spark plasma consolidated samples, results have shown an improvement in the electrical conductivity up to 6.5 times compared to measurements in pure Ni under the same conditions. This enhancement can be justified by the presence of a network of multiple quasi-ballistic conduction paths that reduce the composite's effective resistance [1]. Also, as the density increases, the interface between the matrix and reinforcement is improved facilitating the electron transport through the material [2-4]. The low electrical resistance showed by these rapid manufactured composites could find their application field as electrical contact materials in low voltageswitching devices.

[1] M. Stadermann et al., *Phys. Rev. B*, **69**, 201402 (2004)
[2] R. Sanjinés et al. *Surf. Coat. Technol.* (2011) doi:10.1016/j.surfcoat.2011.01.025 (In Press)
[3] K. Yan et al., *Nanotechnology*, **18**, 255705 (2007)
[4] S. R. Bakshi et al., *Int. Mat. Reviews,* **55**, N°1, 41-64 (2010)

Top-down Process Based on Electrospinning for Producing CNT Yarns

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Multi walled carbon nanotube (MWNT)/poly (vinyl butyral) (PVB) yarns were prepared by electrospinning, twisting, and heat treatment. The TEM analysis showed that the MWNTs are highly oriented along the fiber axis in the prepared composite fibers. This is due to the electrified liquid jet formed by the electrohydrodynamic spinning process. While the addition of the MWNTs improved the mechanical properties of the composite fiber yarns, the electrical conductivity of the yarns was determined by the matrix polymer. The heat treatment determined the characteristics of the CNT out of the composite nanofiber yarns and enhanced their mechanical, thermal, and electrical properties. In particular, the electrical conductivity of the heated yarn was significantly enhanced. The maximum value of the electrical conductivity was 154 S cm^{-1}, which was an order of magnitude higher than that of the other electrospun CNT composite materials. During heat treatment, most of the matrix polymer was thermally decomposed and carbonaceous residues were formed above 400 °C. The carbon residues functioned as a conductive binder between the nanotubes. These results demonstrated that the combination of electrospinning, twisting, and heat treatment provide a promising option for simple and large-scale producing CNT assemblies. The 1D CNT assembly is potentially applicable to the high-performance materials such as electrodes for fuel cells, secondary batteries, and capacitors, lightweight heat sinks, and reinforcements for lightweight composites.

Formation of Bulk Hollow Cylinders Consisting of Bamboo Shaped C-N Nanotubes and their Use in the Hydrocarbon Filtration

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The present investigations describe the formation of bamboo-shaped C-N nanotubes filter and its use in the filtration of heavier hydrocarbons from gasoline. We have synthesized macro hollow cylinder consisting of bamboo like carbon-nitrogen (C-N) nanotubes via spray pyrolysis of $C_{10}H_{10}Fe$ and CH_3CN solution at 900 °C temperature using argon as a carrier gas. The hollow cylinders consisting of C-N nanotubes converted into filter like configuration by capping one end of hollow cylinder and keeping the other end open for entering the unfiltered solution. Our new cylindrical membrane filtration unit (dia.~7mm, length ~ 7cm) involving C-N nanotubes having bamboo-like structures. Thus, the inner hollow tunnel of the tubes gets compartmentalized through the formation of bamboo like structure along directions nearly perpendicular to the length of the C-N nanotubes. The result of filtration of heavy hydrocarbons from gasoline using the C-N nanotube filter revealed that even when the central tunnel of the CNTs was blocked, the filtration did take place. This clearly exhibits that the filtration process embodies restriction of flow of heavy hydrocarbons mainly through interstitial spaces between the nanotubes. The present studies revealed that the bamboo like C-N nanotube configuration leads to the formation of new and better filter than CNT filter developed earlier by our group. This work provides a basis for future development of a C-N nanotubes filter. Such a filter would be exceptionally robust and could be used in various filtration and separation purposes.

Biscrolling nanotube sheets and functional guests into yarns

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Powders of particles or nanofibers are well known additives for introducing new and improved functionality into yarns, and the importance of this area motivates new advances [1-3]. Exploited methods use additive dispersion in a fiber matrix or incorporation on fiber surfaces, but problems remain: (1) powder loading levels are typically low, (2) nanoparticle and nanofiber functionality can degrade whenprocessing decreases accessible surface area, and (3) powders on yarn surfaces can lack durability. Powders are rarely spinnable into yarns without changing basic structure. Strong, weavable multifunctional yarns could be seamlessly integrated into intelligent clothing, structural textiles, and woven electrodes that are flexible, durable, and hierarchically engineered in porosity by yarn weaving, thereby providing advantages over conventional multifunctional film and bulk composites. Our goal was to spin porous multifunctional yarns in which a low concentration of strong host enables weavability, flexibility, and durability, while a high guest concentration adds functions like energy storage, harvesting, and conversion. Generically applicable methods were demonstrated for producing continuous yarns comprising up to 95 wt. % of otherwise unspinnable particulate or nanofibers powders that remain highly functional [4]. These methods utilize the strength and electronic connectivity of sometimes minute amounts of carbon nanotube sheets that are helically scrolled in the yarns. Scrolled 50 nm thick nanotube sheets or sheet stacks can confine nanopowders, micropowders, or nanofibers in the corridors of often irregular spiral sacks, whose observed complex topologies are related to twist-dependent extension of Archimedean or Fermat- related spirals or spiral pairs into helices. This technology is used to make yarns of superconductors, Li-ion battery materials, graphene ribbons, catalytic nanofibers for fuel cells, and TiO_2 for photocatalysis. The mechanical properties of these yarns enables applications for wearable electronic textiles and for strong woven electrodes of batteries and fuel cells. Using patterned deposition for bilayer stacks, TiO_2 guest can be located in the sheath of a biscrolled yarn, thereby optimizing light absorption for such applications as self-cleaning textiles and Graetzel solar cells. Also, it was demonstrated the use of CNT sheets as removable templates for making spinnable sheets of inorganic nanotubes what extends biscrolling to new hosts and provides a route to other types of nanotube yarns.

[1] D. Li ,Y. Xia, *Adv. Mater.* **16**, 1151 (2004).
[2] H. Ye, H. Lam, N. Titchenal, Y. Gogotsi, F. Ko., *Appl. Phys. Lett.* **85**, 1775 (2004).
[3]M. J. Uddin et al., *J. Photochem. Photobiol. A:Chem.***199**, 64(2008).
[4] M.D. Lima et al., *Science*, **331**, 6013 51-55(2011).

Highly Organized Two and Three Dimensional Singlewalled Carbon Nanotubes-Polymer Hybrid Architectures

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Over the past decade, artificially engineered carbon nanotube architectures, designed for a range of micro- and macroscopic functional devices, have made remarkable progress [1-3]. However, despite these progresses the fabrication of scalable and tightly controlled multi-dimensional micro-scale functional flexible systems that harness horizontal as well as vertical architectures of organized single walled carbon nanotubes (SWCNTs) has remained largely elusive. Such methodologies would allow a seamless integration of SWCNTs based functional elements (e.g. active sensing arrays[4] and field-emission pixels [5]) with the possible flexible SWCNTs-based circuitry constructed in a flexible matrix, enabling highly functional all-SWCNTs flexible devices. Developing and fine-tuning methods that not only maintains multi-dimensional structural integrity, but also high-quality electrical properties (especially at junctions and interfaces) of the said hybrid structure has so far remained a considerable practical challenge. Further, maintaining scalability of such process up to macroscopic dimensions that would enable realistic devices is an additional roadblock. Here, we present unique two- and three-dimensional SWCNTs network-polymer hybrid architectures by combining unprecedented control over growth, assembly, and transfer processes of SWCNTs. Several SWCNTs architectures have been built on polymer materials ranging from two-dimensional suspended SWCNTs micro-lines on PDMS micro-channels to three- dimensional “PDMS-vertically aligned SWCNTs-PDMS” sandwich structures. Also a combined lateral SWCNTs micro-lines and vertically aligned SWCNTs flexible device was demonstrated with good electrical conductivity and low junction resistance. The results reported here open the path way for the development of SWCNTs based functional systems in various flexible device applications.

[1] Z. Wu, Z. Chen,X. Du, J. Logan,J. Sippel, M. Nikolou, K. Kamaras, J. Reynolds, D. Tanner, and A. Hebard, *Science*, **305**, 1273-1276, (2004).
[2] J. Ahn, H. Kim, K. Lee, S. Jeon, S. Kang, Y. Sun, R. Nuzzo, andJ. A. Rogers, *Science*, **314**, 1754-1757, (2006).
[3] S. Kang, C. Kocabas, T. Ozel, M. Shim, N. Pimparkar, M. Alam, S. Rotkin, and J. A. Rogers. *Nature Nanotech.*, **2**, 230-236, (2007).
[4] E. Snow, F. Perkins, E. Houser, S. Badescu, and T. Reinecke, *Science*, **307**, 1942-1945, (2005).
[5] Y. J.Jung, S. Kar, S. Talapatra, C. Soldano, G. Viswanathan, X. S. Li, Z. L.Yao, F. S. Ou, A. Avadhanula, R. Vajtai, S. Curran, O. Nalamasu, and P.M. Ajayan, *Nano Lett.*,**6**, 413-418, (2006).

Semiconducting Single-Walled Carbon Nanotubes Based Infrared Solar Cells

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Semiconducing single-walled carbon nanotubes (S-SWNTs) have many interesting optoelectronic properties, which make them promising candidates for fabrication of solar cells. The multiple bands in the S-SWNTs are expected to participate in the optoelectronic conversion process in solar cells. More importantly, the near-infrared band gap transition of S-SWNTs makes them suitable to harvest the infrared solar spectrum. In this work, we have systematically investigated the possibility of making infrared solar cells, based on n-type silicon and p-type S-SWNTs including pristine S-SWNTs and C_{60} encapsulated semiconducting SWNTs (C_{60}@S-SWNTs) which serve as energy conversion material. Our results have demonstrated that S-SWNTs can be used to convert the infrared light (800-1550 nm) into the electrical energy under the configuration of solar cells. Interestingly, the performance of solar cells based on S-SWNTs is much better than that observed in solar cells fabricated by SWNTs containing both metallic and semiconducting SWNTs, and the solar cells based on C_{60}@S-SWNTs are found to show a better power conversion efficiency than pristine S-SWNTs due to the charge transfer effect between SWNTs and C_{60} fullerene [1]. The densities of C_{60}@S-SWNTs are found to have an important influence on the characteristics of the solar cell, and the short circuit current is increased due to the density increase of C_{60}@S-SWNTs. In addition, it is found that when the light energy is higher than two times the first van Hove transition energy of S-SWNTs (E_{11}), the efficiency suddenly increases, suggesting the possibility for the occurrence of multiple exciton generation in the C_{60}@S-SWNTs based solar cell.

[1] R. Hatakeyama, Y.F. Li, T. Y. Kato, and T. Kaneko, *Appl. Phys. Lett.*, **97**, 013104-1-3, (2010).

Lightning Strike Performance Of Carbon Nanotube Loaded Aerospace Composites

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The increased use of carbon fibre composites in aerospace components brings to the surface issues related to their poor lightning strike performance. Metallic meshes or foils, co-cured within the outer layer of laminates, are currently used for protection. This solution comes at a cost in terms of weight and manufacturing complexity, presents difficulties in repair and most importantly does not provide full protection. The influence of multi-wall carbon nanotubes (MWNTs) on the lightning strike performance of carbon fibre composites is investigated in this work. A high temperature aerospace grade epoxy resin (Hexcel RTM6) was used as matrix. The resin was modified with MWNTs (NanocylTM NC7000) at a content of 0.3 wt.% to produce a masterbatch. An excellent state of dispersion was achieved following a sequence of bath ultrasonication (MWNT suspension in acetone) and high shear mixing (MWCNT in RTM6). The masterbatch was diluted to 0.1 wt.% MWNT and subsequently used in the infusion of a bindered carbon fibre preform using the vacuum assisted resin transfer moulding process. Panels of carbon fibre/RTM6 (Control), carbon fibre/RTM6 with a protective copper mesh layer (Control-Mesh), carbon fibre with MWNT modified RTM6 (CNT), and carbon fibre with copper protection and MWNT modified RTM6 (CNT-Mesh) were produced. The existence of polymeric binder in the fibre preform enhanced nanoparticle filtration and resulted in a nanotube rich zone in the outer layers of the cured laminates (30-60 μm in thickness). The specimens were subjected to simulated zone 2A lightning strike, comprising three current components: (i) D (100 kA, ≤ 500 μs); (ii) B (2 kA, ≤ 5 ms); and (iii) C(200 – 800 A, 0.25 – 1 s). Visual observations and ultrasonic C-scans revealed significant influence of the presence of the MWNT rich layer on lightning strike performance. Damage in the Control laminate is manifested as fibre tufting, several layers deep, at the vicinity of the lightning attachment region as well as degradation of the upper resin rich layer. The mode of damage in the CNT laminate is qualitatively the same; however, the extent of damage is 40% lower. Damage in the Control-Mesh laminate is limited to its surface and involves copper mesh sublimation and resin degradation, which as in the case of Control are concentrated in the area around the lightning attachment point. The CNT-Mesh laminate also undergoes mesh sublimation and surface resin degradation, which occur over an area 60% smaller than in the Control- Mesh case. Laminates containing MWNTs do not show any damage in the contact area between the composite and the metal frame of the experimental setup. This is in contrast with unmodified epoxy laminates which display resin degradation in these regions. The outcome of this work demonstrates that under optimal manufacturing conditions MWNT modification improves the lightning strike performance of carbon fibre composites. This can lead to direct application of hybrid composites within primary aerospace structures.

Preparation and Charaterization of Carbon Nanotubes Functionalized with Silica and Their Application in Shear Thickening Fluids

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Shear thickening fluids (STFs), flowable at low shear rates, become macroscopically rigid at high shear rates. A typical STF of silica suspension in polyethylene glycol (PEG) can be used for protective materials, such as bulletproof vests, at high shear rates. However, the brittleness and low resistance to mechanical stress of silica reduced the performance of silica/PEG STFs. To enhance the protective performance of the silica/PEG STFs, carbon nanotubes (CNTs) canbe used as additional nanofillers. However, the effects of CNT addition are not expected to be good because of the low dispersibility of CNTs in silica/PEG STFs. In this study, to increase the dispersibility of CNT, silica-coated multiwalled carbon nanotubes (S-MWNTs) were prepared through covalent bonding and characterized. The effect of S-MWNT addition to silica/PEG suspension on the rheological property was also investigated.Amino group-introduced MWNTs (MWNT-NH2) with a nitrogen atom content of up to 20 wt % was prepared by reacting acid-treated MWNTs and ethylene diamine using 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride and N- hydroxysuccinimide as catalysts. Then, various amounts of silica were formed through covalent bonding on the surface of the MWNTs initiating from the amino groups by using a sol-gel method. The silica formation on the MWNT surface was confirmed by field emission electron microscopy, transmission electron microscopy, elemental analysis, and Fourier transform infrared spectroscopy. The S-MWNTs exhibited good dispersion stability in water and PEG because of the increased hydrophilicity. When 5 wt % of pristine MWNTs was added to the silica/PEG suspension, they were not dispersed well in the suspension and the shear thickening property was not exhibited. On the other hand, the suspension containing 5 wt % of S-MWNTs showed similar shear thickening behavior to that of simple silica/PEG. The critical shear-thickening point of silica/S-MWNT suspension in PEG moved to a lower shear rate with increasing S-MWNT content.

Composites Of Aligned Carbon Nanotubes And Polymers

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Aligned multiwalled carbon nanotubes (MWCNT) were synthesized on 4 inch silicon wafers by chemical vapour deposition (CVD) using ethylene (C_2H_4) as carbon source. For increasing CNT growth rate 100 ppm water vapour was added resulting in CNT length up to 95µm after 150 minutes deposition time. CNT quality was characterized by SEM, TEM and Raman spectroscopy. The average inner and outer diameters of the MWCNT are 5nm and 10nm, respectively. For the composite production the space between MWCNT on wafer was filled with different polymer matrixes. Two approaches were used. Vacuum infiltration was utilized for epoxy filling, whereas doctor blade method was applied for polyamide 6 (PA), polystyrene (PS) and polyphenylene oxide (PPO) infiltration. In the case of PA, PS and PPO the solvent, thermal processing, traverse speed and traverse height were varied. Focussed ion beam (FIB) preparation in combination with SEM analysis was applied to investigate the infiltration result. Closed porosity was observed in case of CNT-PA composite. This is probably caused by insufficient wetting behaviour of the polar solvent formic acid and shrinking by crystallization of PA. In contrast, the space between individual carbon nanotubes was completely filled with polymer without any cavities if amorphous PS, PPO and epoxy are applied. Obviously the solvent toluene used for the infiltration with PS and PPO allows for the formation of a nonporous composite. Additionally, pore-free infiltration was verified by TEM analysis in case of PS, PPO and epoxy. TEM images show the CNT maintaining their vertical alignment after infiltration process. The composites can easily be separated from silicon wafer substrate achieving very comfortable flexible CNT-polymer composites. Possible applications are seen as flexible polymers with high electrical conductivity as well as flexible sensors.

Polymer and Aluminum Oxide Reinforced Single Walled Carbon Nanotube Networks

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Composite materials of single walled carbon nanotubes (SWCNTs) are drawing a great deal of attention, since they can exhibit some of the unique mechanical, electrical or optical properties of SWCNTs combined with the properties of bulk materials. We report a simple and fast way to produce highly transparent nano composites consisting of 80 ± 20 nm thick free standing SWCNT film, afterwards coated with 0.3-5 nm thick amorphous aluminum oxide (Al_2O_3) layer utilizing atomic layer deposition (ALD) technique. Moreover, to produce transparent, flexible and mechanically tough electrodes, we also utilized solvent drop casting technique to create 1-40 µm thick Kraton and polystyrene layer enclosing the freestanding SWCNT network. To prove the concept, mechanical strength of both pristine and reinforced SWCNT films was evaluated using a modified Erichsen cup test. Our measurements revealed the aluminum oxide coating increased the ultimate tensile strength of the free standing SWNT films from 70 MPa to over 300 MPa, while the polymer coating was found to increase the impact toughness of the films 50 - 400%, depending on the coating thickness and the polymer of choice. These proposed composite materials are potential components for example for micro machined resonators, super-capacitors, load transducers and transparent touch screens.

Nitrogen-Doped SWCNT Thin Films Exhibiting Anomalous Sheet Resistances

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Nitrogen doping of single-walled carbon nanotubes (SWCNTs) was proposed already in 1993 [1], just two years after the discovery of nanotubes, with the first experimental reports on multiwalled nanotubes (MWCNTs) following a few years later [2]. Only much later have there been a handful of successes in synthesizing doped SWCNTs [3], which has proven inherently more difficult, particularly using chemical vapor deposition (CVD). We synthesized nitrogen-doped SWCNT using a floating catalyst CVD method [4], with carbon monoxide as the carbon source, ammonia as the nitrogen source [5], and iron particles derived from evaporated iron as the catalyst. The material was deposited as grown on various substrates directly from the gas phase as films and subsequently characterized by Raman and optical absorption spectroscopies, sheet resistance measurements, electron microscopy, energy-loss spectroscopy, and X-ray photoelectron spectroscopy. The sheet resistance measurements revealed that the doped films had unexpectedly high resistances. This stands in contrast to the case of N-MWCNT films, where decreased resistance has been reported with N-doping [6]. To understand this effect, we developed a resistor network model [1], which allowed us to disentangle the contribution of bundle−bundle contacts when combined with data on undoped films [7]. Assuming doping does not significantly change the contacts, the increased resistances of the doped films are likely due to enhanced carrier scattering by defect sites in the nanotubes [8]. This work represents the first experimental report on macroscopic N-SWCNT thin films.

[1] J.Y. Yi and J. Bernholc, *Phys. Rev. B*, **47**, 1708-1711, (1993).
[2] M. Terrones et al., *Appl. Phys. Lett.*, **75**, 3932-3934, (1999).
[3] P. Ayala et al., *Rev. Mod. Phys.*, **82**, 43-86, (2010).
[4] T. Susi et al., *Chemistry of Materials*, article ASAP (2011), doi: 10.1021/cm200111b.
[5] T. Susi et al., *Phys. Status Solidi B*,**247**, 2726-2729, (2010).
[6] J.D. Wiggins-Camacho and K.J. Stevenson, *J. Phys. Chem. C*, **113**, 19082, (2009).
[7] A. Kaskela et al., *Nano Lett.*,**10**, 4349-4355, (2010).
[8] S. Latil et al., *Phys. Rev. Lett.* **92**, 256805, (2004).

Investigation of Sensor Properties of a Carbon Nanotube and ZnO Nanorod Composite.

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One of unsolved technological problems in artificial sensorium is an electronic nose development. It will be based on different chemical sensors or may be a whole sensor matrix like in digital cameras. For electronic nose development there must be achieved such goals as selectivity of a system, high sensitivity of each sensor and characteristics stability. It can be noted that a composite of different nanoscale materials should be used to accomplish above mentioned requirements. A composite of single walled carbon nanotubes and ZnO nanorods were chosen as a material for chemical sensor development. ZnO nanorods are a promising material for sensors because of its high sensitivity for different chemicals, biocompatibility and modification ability by various methods. Large sensing area that results in better sensitivity is one of the biggest advantages of this composite. Sorption properties of the mixture were studied. It was shown that addition of 20% of carbon nanotubes increase specific surface on the order. Sensor structures based on carbon nanotubes and ZnO nanorods composite were made. There were two types of solutions for composite creation: isopropanol and CTAB water solution. Composite was deposited between electrodes by dielectrophoresis with applied voltage from 10 to 20 volts and frequency from 1 to 100 kHz. Nanotubes in this system acts both as sensitive layer and as molecular electric contacts to ZnO nanorods. Then sensing properties of structures were investigated. Sensors were exposed by ethanol, isopropanol and ammonia vapors. Chemical agent concentration varied from 100 to 1000 ppm. It was shown that conductivity of the structure can increase or decrease depending on exposed vapor. Also it was shown, that response time of composite based structures is near to that of serial sensors Figaro TGS 2620 based on thick oxide films. Nevertheless the desorption rate of composite based sensor structures is less than serial sensors because of lack of heater. But without heater power consumption of new sensors is less than of serial devices so composite based sensors can be used in portable gas analyzers. Thereby a result of this work is an important step in development of a new generation of high sensitivity nanocomposite sensors towards to creation of an electronic nose.

Improvement of Single Walled Carbon Nanotube Transparent Conductive Films by Transition Metal Doping

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We applied a spray coating process with transition metal (Au, Ni, Ir etc.) doping to SWCNT networks to make transparent conductive films(TCFs) based on single-walled carbon nanotubes (SWCNTs). Schottky contact between metallic and semiconducting SWCNTs changed to Ohmic contact due to the reduction of transition metals on the SWCNT surfaces via direct conversion from solution. We have demonstrated the cost-effective, simple, and facile spray-coating fabrication of SWCNT-TCFs and measured the doping effects, including introduction of Ohmic contact, on the SWCNT networks due to the presence of reduced metals. In case of doping with 1 mM Ni, the percent reduction in sheet resistances after was estimated to be 60%. This technique resulted in high-transparency conductive SWCNT- TCFs that may be suitable for use in commercial processes and applications such as flexible and/or touch panels.

Synthesis of Carbon Based Hybrid Type Thermal Conductive Filler

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Carbon based thermal conductive filler of nanocarbon such as carbon nanotubes (CNTs) and graphene with hybridization of carbon fiber (CF) and graphite can improve the thermal conductivity for the various heat sink or transfer applications. Hybrid type of synthesized CNTs on CF has enabled improvements in thermal conductivity performance due to their remarkable synergetic effect between the CNTs and CF. In this study, we demonstrate the synthesis of hybrid type of CNT on CF surface by thermal chemical vapor deposition. For the formation of transition metal catalysts on the external surface of CF, it was deposited on the CF using various techniques including the impregnation technique. CNTs have been successfully synthesized directly on CF surface using decomposition of C_2H_2 at 800 ℃.

Exploration of Optimized SWCNT Diameter for Transparent Conductive Films

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As the transparent conductive film (TCF) widely used for electrodes in touch screen, liquid crystal display and so on, indium tin oxide (ITO) films have been monopolized the market in the last several decades. However, ITO films generally have a disadvantage of brittleness that is critical for the forthcoming flexible electronics application. It is reported that the strains of ~1% for ITO films would be result in loss of their conductivity seriously. In addition, the price of indium that has soared in the past decade increases the cost of ITO films unfavorably. Single-wall carbon nanotubes (SWCNTs) or several-walled carbon nanotubes are an ideal candidate for replacing ITO as a flexible and light material. Many studies on SWCNT electrodes for new TCFs and their capability for replacing traditional ITO have been reported. But still the detailed properties of SWCNT-TCFs such as the correlation between the tube diameter and the surface resistivity have not been fully clarified yet. Here we would like to report the influence of tube diameter on the performance of TCFs. SWCNTs were synthesized by enhanced direct injection pyrolytic synthesis (eDIPS) method. Among the various growth techniques for SWCNTs, eDIPS method is excellent for controlling tube diameter and getting highly graphitized SWCNTs1. SWCNT-TCFs consisted of resin and SWCNTs were prepared by using reported common procedures. Briefly, SWCNTs were dispersed in the aqueous solution of sodium carboxymethylcellulose (CMC) by using an ultrasonic homogenizer under ice cooling bath. Dispersions were applied to a polyethylene terephthalate (PET) film using a bar coater and air-dried to fix SWCNTs on the PET film. Properties of SWCNTs-TCFs such as the total luminous transmittance (%TT) and the sheet resistance (Rs) were characterized by using a haze meter (Nippon Denshoku Industries co., Ltd., NDH4000) and a 4-probe resistometer (Dia Instruments co., Ltd., Loresta EP MCP-T-610) in accordance with JIS K7105 and JIS K7149. Note that the following data of the transmittance are for SWCNT-TCFs including PET film of %TT = 92 %. In the case of using SWCNTs with the mean tube diameter of 1.8 nm, performances of SWCNT-TCFs was Rs= ca. 700 ohm/sq and %TT= 85%. The other case of different diameters and their effect on TCF performances will be discussed in the presentation.

[1] T. Saito, S. Ohmori, B. Shukla, M. Yumura, and S. Iijima *Appl. Phys. Express* **2** 095006 (2009).

Spinning of Thermosetting Composite Fibers Reinforced with Covalently and Noncovalently Functionalized Single-Walled Carbon Nanotubes

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Homogeneous dispersion of carbon nanotubes, strong nanotube/matrix interfacial bonding and good alignment of nanotubes are key requirements for exploiting the superior mechanical properties of carbon nanotubes in structural composites. Here we report a novel spinning approach for fabrication of thermosetting composite fibers reinforced with both covalently and noncovalently functionalized single-walled carbon nanotubes (SWNTs). The composite fibers were prepared by first dispersing SWNTs in thermosetting matrix solution, followed by solvent evaporation, pre-polymerization to achieve a suitable viscosity, spinning, and then curing. In the first part of our work, SWNTs grafted with amino groups were used as fillers to reinforce cyanate ester (CE) fibers. Only 1 wt% of amino-functionalized SWNTs increases the tensile strength, elongation and toughness by 85%, 140% and 420% compared to neat CE. In the second part of our work, SWNTs were covalently grafted with generation0 to 2 dendritic poly(amidoamine) (PAMAM) and added to epoxy (EP) to spin composite fibers. Epoxy fibers reinforced with generation 2 PAMAM show high values of Young's modulus and tensile strength per unit weight fraction ($dE/dW_{NT} = 118$ GPa and $d\sigma/dW_{NT} = 7022$ MPa). In the third part of our work, SWNTs were noncovalently functionalized by a novel comb-like polymer, polyimide-*graft*-bisphenol A diglyceryl acrylate (PI-BDA), which is found to be highly effective at individually dispersing SWNTs. PI-BDA functionalized SWNTs were added to a thermosetting resin blend of 70 wt% of cyanate ester with 30 wt% of epoxy (CE-EP), and the composites were successfully spun into fibers. Mechanical testing shows that 1 wt% of SWNTs/PI-BDA increases the Young's modulus, tensile strength and toughness by 80%, 70% and 58% as compared with neat CE-EP. Nanotube dispersion, alignment, and nanotube/matrix interfacial adhesion of all three types of composites were studied by optical microscope, field-emission scanning electron microscope (FE-SEM), Fourier transform infrared (FT-IR) and Raman spectra. This is the first report of spinning of carbon nanotube reinforced thermosetting resin and would be useful for making high strength and light weight composites.

Nanocomposites Formed Between Carbon Nanotubes, Silver Nanoparticles And Polyaniline: Synthesis, Characterization And Acid Concentration Influence On The Final Material

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Carbon nanotubes (CNTs) have attracted extensive attention owing to their exciting potential applications in nanocomposites or advanced materials with new electronic and optical properties. Metal nanoparticles (NPs) are also very attractive because of their size- and shape-dependent properties. The combination of these two classes of materials yields novel and functional nanocomposites with synergistic properties and potential applications in several fields. Novel routes to synthesize CNTs [1], NPs [2] and their nanocomposites with conducting polymers [3] were developed in recent years. Here we present a simple one-step procedure to synthesize carbon nanotubes (CNTs) decorated simultaneously with silver nanoparticles and polyaniline in a aqueous acid CNT dispersion medium. Both metal nanoparticles and conducting polymer are concomitantly produced, and this procedure results in well-structured CNT/silver NPs/polyaniline nanocomposites. The study of acid concentration influence shows that the amount of conducting polymer is related with the medium acid concentration. We believe that the CNT act as a substrate in which the silver nanoparticles and the polymer grow up. Samples without CNTs didn’t produce nanocomposites, showing that the CNT presence is basic for the reaction occurrence.

[1] M.C. Schnitzler, M.M. Oliveira, A.J.G. Zarbin, *Chem. Phys. Lett*. **381**, 541 (2003).
[2] M.M. Oliveira, D. Zanchet, D. Ugarte, A.J.G. Zarbin, *J. Colloid Interf. Sci*. **292**, 429 (2005).
[3] M.M. Oliveira, C.D. Canestraro, E.G. Castro, L.S. Roman, D. Zanchet, D. Ugarte, A.J.G. Zarbin, *J. Phys. Chem. B*, **110**, 17063 (2006).

CCVD Of Aligned Carbon Nanotubes On Aluminium Foils And Their Tests As Components Of Supercapacitors

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Supercapacitors (SCs) have attracted much attention because they satisfy desirable requirements for energy accumulation and they also possess a high specific power, a simple construction, and a long life time [1, 2]. SCs store the charge electrostatically using reversible adsorption of ions of the electrolyte onto active material. A typical SC is composed of a flexible current collector, electrically connected to an inert electrode with a high surface area. An aluminium current collector coated with nanostructured carbon seems to be the most appropriate combination for the preparation of SCs with desired properties [1, 2]. Discovery of carbon nanotubes (CNTs), owing to their electrochemical stability and high surface area, has opened up new ways for preparation energy accumulating assemblies. Carbon nanotubes (CNTs) grown directly on Al foil are apparently attractive candidates for the construction of SCs. The output of SC, namely the stored specific power and specific energy density, is strictly dependent on the surface area of the electrode material, the electrolyte properties and an efficient interaction of the electrode surface and the electrolyte for a fast ionic transportation. Zhang et al. have reported that vertically aligned CNTs are more suitable and promising electrode materials for SC in terms of their capacitance, compared to entangled CNTs with an irregular pore structure [2]. Mainly a transfer methodology by removing as-grown aligned CNTs from the substrate and then by pasting the same on a current collector was reported so far. However, such approach limits industrial production of SCs based on aligned CNTs. Recently a few publications appeared about direct catalytic chemical vapour deposition (CCVD) of aligned CNTs on the surface of current collector and their tests as elements of SCs. Analysis of the available publications shows that aligned CNTs, directly grown on Al current collector, are not investigated as a component of SCs in detail till date. Apparently the main reason is that the low melting point of Al (660 °C) prevents it from successfully withstanding the high temperatures employed in thermal CCVD. We report a scalable method for the atmospheric pressure CCVD of CNTs on different Al foils to make electrodes for SCs. We demonstrate the influence of surface topography of the Al foil for the growth of CNTs, their alignment and adhesion to the current collector. A comparative study of electrochemical properties of CNTs grown on such different foils is presented. We discuss about the parameters that influence the properties of the resulting SCs.

[1] P. Simon, et al., *Nature Materials*, **7** (11), 845–854, (2008).
[2] L. L. Zhang, et al., *Chem. Soc. Rev.*, **38** (9), 2520–2531, (2009).

Development Of A Continuous Chemical Vapour Deposition Process For CNT-Grafted Carbon Fibre For Hierarchical Composites

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Hierarchical composites are composites that contain at least two different length scale reinforcements in a matrix; here we present the combination of CFs (microscale element) and carbon nanotubes (CNTs) (nanoscale element). In this research, we have investigated the growth of CNTs directly on the surface of the CF in order to improve the mechanical interlocking within the matrix and the perpendicular force transfer through the CNTs to the main CF reinforcement. Our CNT grafting route negates the issues regarding individualisation of the CNTs as they are bound to the surface of the CF, thereby significantly minimizing CNT bundling and entanglement. Grafting CNTs directly onto the CF surface has shown impressive improvement (+60%) of interfacial shear strength in a model epoxy composite on the single fibre level[1]. The challenge now is to optimise chemical vapour deposition (CVD) CNT growth on a CF substrate resulting in a uniform and reproducible product at a scale suitable for the fabrication of composite coupons. A continuous CVD method and investigation into the suitable growth parameters (catalyst reduction time, catalyst loading method, CF surface modification and CF type) for the manufacture of CNT- grafted CF are presented. Critical factors in producing CNT-grafted CF were found to be: (a) the reduction time of the pre-deposited catalyst on CF substrate, (b) striking the correct balance between limiting catalyst pitting and catalyst carbon capping during growth procedure, with parameters strongly dependent on catalyst and CF type.

[1] H. Qian et al.,*Chemistry of Materials*, **20**, 1862-1869, (2008).

Biocompatible Single-Walled Carbon Nanotube Films by Surface Modification with Neutral pH Water Soluble Chitosan Derivatives

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Key words: Single-walled carbon nanotubes; biocompatibility Dispersion of carbon nanotubes in biocompatible media are of particular interest for many biomedical and nanomedicine applications. Various biomolecules and biopolymers such as DNA, proteins, poly L–lysine, starch, gelatin, steroid biosurfactants, and chitosan have shown capability for the effective dispersion of carbon nanotubes in water. Chitosan has demonstrated capacity for effective dispersion of single-walled carbon nanotubes (SWNTs) in acidic medium and it also showed tendency to preferentially disperse smaller diameter nanotubes. Herein, we present two chitosan derivatives soluble in neutral pH water [1,2]chitosan–hydroxyphenyl acetamide obtained by functionalizing the amino groups of chitosan with 4-hydroxyphenyl acetic acid, and N-acetylated chitosan prepared by controlled N-acetylation of chitosan using acetic anhydride, for debundling and solubilization of SWNTs in neutral aqueous solutions. The chitosan derivatives demonstrated very good dispersibility and exfoliation of nanotubes, and the characterizations of CNT dispersion by SEM, TEM and AFM imaging revealed that the diameter of nanotubes were in the range of 1.2 to 2.8 nm size. Thin films of chitosan modified SWNTs were used as scaffold for cell culture for over a period of 1 week. The results showed that the SWNT films are highly biocompatible and can serve as good platform for cell adhesion.

[1] A. Ishibashi and N. Nakashima, *Bull. Chem. Soc. Jpn.* **79**, 357 (2006)
[2] T. Takahashi, C. R. Luculescu, K. Uchida, T. Ishiiand H. Yajima, *Chemistry Letters*, **34**, 1516 (2005).

Scalable And Sustainable Covalent Functionalization Of Carbon Nanotubes

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The cycloaddition of azomethine ylides to carbon-carbon double bonds have been exploited to improve the solubility of fullerenes, the most noteworthy cases being the improvement of processability of C_{60} derivatives for photovoltaic applications and the purification of carbon nanotubes (CNTs) from metal nanoparticles and amorphous carbon impurities. Despite many successful attempts at functionalize carbon nanotubes, few effort have been dedicated in both implementing the synthetic procedure with many of the good dispersing agents reported and in developing simple procedures to better characterized the inhomogeneous carbonaceous material obtained. In this work, the implementation of a novel chemical apparatus, together with the use of high boiling solvents, is proposed as a controlled, efficient and sustainable methodology for the scalable production of functionalized carbon nanotubes (CNTs). In particular, we have investigated the 1,3-dipolar cycloaddition of different azomethineylide precursors towards CNTs and we have characterized the functionalized products with a set of subsidiary techniques (UV-vis and Raman spectroscopy, TGA, DLS) which makes possible the comparison between reactions carried out in different conditions and it extends the concept of reaction yield to carbon nanotube chemistry. A thorough characterization evidences that the approach we are presenting affords, in a much shorter time, products with the same features as traditional synthesis.

A role of HNO_3 on transparent conducting film with single-walled carbon nanotubes

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There is some controversy regarding the effects of HNO_3 on films of single-walled carbon nanotubes (SWCNTs). In this study we examined the change in sheet resistance of an HNO_3-modified SWCNT film after different drying times at 85 °C using various analytical techniques. The shift and suppression in the Raman spectra, bleaching of the transition peaks related to van Hove singularities and a shift in the original peak in the C 1s XPS spectra provided evidence for p-type doping. A decrease in sheet resistance was also observed in the SWCNTs films due to the removal of residual N-methylpyrrolidone solvent on the surface and bundle of SWCNTs. These results suggest that p-type doping has a larger effect on the sheet resistance than the removal of residual N-methylpyrrolidone by an HNO_3 treatment.

[1] Dong-Wook Shin, Jong Hak Lee, Yu-Hee Kim, Seong Man Yu, Seong-Yong Park, Ji-Beom Yoo, *Nanotechnology*, **20**, 475703 (2009).

Doping and De-doping in SWCNTs film by the spontaneous redox process

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Single wall carbon nanotubes (SWCNTs) film was deposited with the MnO_2 using spontaneous redox reaction between $MnO4^-$ ions and SWCNTs. Doping and de-doping affects the sheet resistance of the SWCNTs film. The injection of holes in the SWCNTs film bleaches the van Hove singularity transitions (E_{11}^{S}) observed in optical absorption spectroscopy. The observed doping is not permanent and the spontaneous reduction in ambient condition restores the defects and de-doped the SWCNTs film. The de-doping up shifts the Fermi level and restores the van Hove singularity transitions (E_{11}^{S}). Doping and de- doping mechanism of these films have been investigated. Transmission electron microscopy, x-ray photoelectron spectroscopy and optical transmission spectroscopy was used to characterize the films.

Selective Chemical Functionalization of Carbon Nanobuds

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Carbon nanobuds (CNBs) are a novel nanoscale hybrid material consisting of fullerenes, covalently bonded to the outer surface of CNT [1]. The goal of this work is to demonstrate higher chemical activity and selectivity of CNBs in the reactions of the cyclopropanation compared to CNTs. The successful covalent modification of CNBs by double carboxylic group in Biggel reaction was demonstrated. Chemical structures of modified CNBs and CNTs were confirmed by FTIR spectroscopy, TEM and EDX-spectroscopy. It was found that CNBs has the larger chemical reactivity than CNTs. By using of light active molecules of 5,10,15,20-tetra(4-pyridyl)porphyrin was shown that the resistance of modified CNB network reversibly reduced (on 0.1 %) after illumination by low power ultraviolet lamp (0.2 mW/cm^2), the rate of detectable change in resistance is less than 0.3 sec. Utilizing of the properties of functionalized CNBs in optical and chemical sensors was suggested.

[1] A.G. Nasibulin, et al., *NatureNanotechnology,* **2**(3), 156-161 (2007).

Chemistry Way Towards Design and Tailoring of Novel 1D Carbon Materials for Energy Storage

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An energy-efficient and sustainable economy requires the development of novel materials for energy storage and conversion. Carbon materials are widely used in energy storage and conversion systems because of their stable physcochemical properties good electrical conductivity, low cost, and facile availability [1-2]. The technical application of carbon materials requires precise control over their mesoscale and microscale architectures, which call for the development of easy and efficient synthetic protocols towards unprecedented carbon and metal/carbon composite materials.

Here we introduce a novel carbon-rich precursor approach towards the fabrication of well-defined one-dimensional (1D) carbon materials with tailorability at the molecular level. This strategy can further establish the link through the controlled pyrolysis of precursors in confining template state. Therefore, this method stands in contrast to other chemical means of carbon synthesis in terms of its 1) size, shape and component fine control; 2) structural perfection and 3) feasible process ability. Prominent applications have been achieved with using these carbon materials and their carbon-metal composite across the range of catalysis, sensing, supercapacitos and batteries.

1D Nanoporous Carbons. Energy storage on nanoporousmatrices is a complicated procedure, since the intrinsic pore characteristics, such as tortuosity, connectivity, size distribution as well as nature of electrolytes, all have to be considered. Briefly, the key point to promote electrochemical behavior of nanoporous carbons is to design a well-defined electrode material with highly porous framework which allows the electrolyte to diffuse and access the entire inner pore surface for energy storage. In this study, 1D nanoporous carbons (NPCs) with highly ordered 3D interconnected pore structure are prepared by the controlled thermolysis of alkyl-substituted hyperbranched polyphenylene in nanoscale channels. Such unique 1D carbonaceous frameworks are composed of appropriate nanopores (about 10 nm)with a surface area as high as 1140 m^2/g. Remarkably enough, using these NPCs as electrode materials, a superior capacitive performance of up to 304 $F\ g^{-1}$ in electrochemical capacitors are obtained [3].

1D Nanoporous Carbon-Metal Nanocrystals Composites. The integration of metallic nanocrystals and 1Delectronically conducting carbons to form metal-carbon hybrids can lead to enhanced physical andchemical properties or even the creation of new properties with respect to single component materials. However, direct access to thermally stable and structurally ordered 1D metal-carbon hybridsremains a primary challenge. We report an in-situ fabrication of Co_3O_4 nanocrystals incorporated into 1D NPCs via an organometallic precursor-controlled thermolysis approach. These unique 1D metal-carbon hybrids exhibit a promising potential in electrochemical energy storage. NPCs/Co_3O_4 is evaluated as an electrode material in a supercapacitor, for which Co_3O_4 nanocrystals contribute an exceptionally high gravimetric capacitance value of 1066 $F\ g^{-1}$ [4]. We have demonstrated a novel strategy for the fabrication of tunablecarbon and carbon-metal composites through pyrolysis of well-designed carbon-rich precursors. Electrochemical results disclose that these materials have promising potential in applications for energy storage. Our findings provide a deeper understanding of precursor-controlled thermolysis as a straightforward processing protocol for the build up of thermally stable and structurally orderedcarbon materials.

[1] J. S.Wu, W.Pisula, K. Müllen, *Chem. Rev.*,107, 718-747, (2007).
[2] L.Zhi, Y.Hu, B. E.Hamaoui, X.Wang, I.Lieberwirth, U.Kolb, J.Maier, K. Müllen, *Adv. Mater.*,**20**, 1727-1731, (2008).
[3] Y. Liang, X.Feng, L.Zhi, U.Kolb, K.Müllen, *Chem. Comm.*, 809-811 (2009).
[4] Y.Liang, M. G.Schwab, L.Zhi, E.Mugnaioli, U. Kolb, X.Feng, K.Müllen, *J. Am. Chem. Soc.*,**132**, 15030-15037,(2010).

Production Of N-Doped Carbon Nanoribbons By Cutting CNx-MWNT: A Thermal Treatment Route

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N-doped carbon nanoribbons have been produced by unzipping N-doped multiwalled carbon nanotubes (CN_xMWNT) using a thermal treatment route. CN_xMWNTs were fabricated through a chemical vapour deposition (CVD) process involving aerosols of benzylamine and ferrocene. The as grown CN_xMWNT were ultrasonically dispersed in methanol and were allowed to dry. Then, the samples were placed in Al_2O_3 crucibles and treated thermally under an inert atmosphere, at different temperatures and during different periods of time (6h, 12h, 16h, 36h, 48h). The heat treated samples were analyzed by SEM, TEM, and Raman Spectroscopy techniques. A possible mechanism for the unzipping of the CN_xMWNT by this thermal treatment will be discussed. It is important to mention that both the synthesis of the nanotubes and the thermal treatments were carried out at atmospheric pressure.

Boron Nitride Nanotubes Grown Axially on Silicon Carbide Fibers

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The promise and potential of nanotechnology has begun to translate into exciting property improvements for many material systems. However many high temperature applications require thermo-oxidatively stable materials, rendering carbon nanotubes inadequate for these purposes. Boron nitride nanotubes (BNNT) are a promising material for power and propulsion applications of interest for many of NASA's future missions. These nanotubes possess many mechanical properties similar to carbon nanotubes but have demonstrated superior high temperature performance. At NASA GRC, high strength thermally stable materials for use within the hot section of gas turbine engines are of great interest. To that end, SiC/SiC composites have been thoroughly investigated. Exploring incorporation of thermally resistant nanotubes such as BNNT into these SiC/SiC composites as well as other ceramic and glass systems is also of interest. Preparation of ceramic and glass compositions with nanotubes is not as straightforward as additions to systems such as polymers due to more rigorous required processing conditions. Previous work done at NASA GRC has demonstrated successful BNNT reinforcement within a glass composite. However systems with a reinforcing fiber phase have not been examined. In this work, the concept of "fuzzy" fibers, previously demonstrated by growing carbon nanotubes on the surface of carbon fibers, is examined for BNNT grown on SiC fibers. It has been suggested that this concept may allow improved interlaminar properties within ceramic composites. BNNT is grown in an axial direction on the surface of Hi-Nicalon S fibers. The impact of axially growing BNNT on SiC fiber tows on the mechanical properties of those coated SiC fibers relative to pristine fiber surfaces is investigated.

Size Control Of Aligned SWCNTs On Quartz Substrate By Using Gold Catalyst

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Precise control of position and orientation of chirality-defined single-walled carbon nanotubes (SWCNTs) is an important issue to realize SWCNT-based nanoelectronics. Precise separation of chiralities has been accomplished by using DNA- [1] and agarose gel- [2] chromatographies. However, these separated nanotubes are bundled, and difficult to control their position and orientation when they are dispersed on a substrate. Therefore, position, alignment, and chirality-controlled synthesis of SWCNTs on the substrate is essential. In this study, we have investigated the diameter control of aligned SWCNTs on ST cut quartz by using gold as the catalyst of SWCNT growth. SWCNTs are known to be aligned along a specific crystalline orientation [3]. Since gold has a high vapor pressure compared to conventional catalysts such as iron, cobalt, and nickel, it is easier to reduce the particle size to less than 1 nm by annealing. We have optimized the annealing atmosphere and temperature, and succeeded in obtaining the gold catalyst particles smaller than 2 nm. Half of them were even smaller than 1 nm. Then, chemical vapor deposition was performed with a mixture of ethanol vapor and Ar/H_2 gas, and aligned SWCNTs were synthesized. Narrow distribution of the catalyst particle size opens up the possibility to synthesize SWCNTs whose diameters are smaller than 1 nm because the catalyst particle size determines the upper limit of SWCNT diameter [4]. Furthermore, the narrow diameter distribution is expected to restrict the variety of chiralities.

[1] X. Tiu et al.,*Nature*,**460**, 250-253, (2009).
[2] H. Liu et al., *J. Phys. Chem. C*, **114**, 9270-9276, (2010).
[3] C. Kocabus et al., *J. Phys. Chem. C*,**111**, 17879-17886, (2007).
[4] D. Takagi et al., *Chem. Phys. Lett.*, **445**, 213-216, (2007).

Electrical Properties Of Platinum-Single Wall Carbon Nanotube Films

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Since their discovery carbon nanotubes have attracted a great deal of attention due to their potential for a wide range of applications such as memory devices,[1] sensors[2] and fuel cells.[3,4] In particular, carbon nanotubes are ideal candidates as catalyst support since their large surface area allows the reduction of the amount of platinum (Pt) catalyst used in fuel cells.[5] Consequently, research has been carried out for the Pt functionalization of carbon nanotubes[6] and the characterization of Pt/CNT electrodes.[7] However, nothing is known about their conduction mechanism. Although cyclic voltammograms suggested efficient electronic conduction mechanisms for nitrogen-containing carbon nanotube-platinum nanoparticle composites,[8] little is known of the conduction mechanism in Pt enriched carbon nanotube films. In this study, the fabrication of Pt-enriched single-wall carbon nanotube (SWCNT) films is reported, and their electronic conduction mechanism proposed. The pyridine functionalization of SWCNTs via diazonium radical additions of pyridine groups has been demonstrated.[9] Here, pyridine-SWCNTs were characterized by Raman and UV-visible-near IR spectroscopy, CHN analysis and thermogravimetry coupled with mass spectroscopy. Complexes were created between the pyridine moieties on the CNT and the Pt complex Pt(DMSO)2Cl2 using the nitrogen's lone pairs. The Pt coordination was confirmed by XPS analysis. The deconvolution of N1s band showed a contribution at 398.4 eV attributed to the Pt-N bonds created. SWCNT films were fabricated by filtration of 10 mL of Pt-SWCNTs supernatant dispersed in dimethylformamide at 1:10 mg/mL on nylon membranes, and were dried overnight in a vacuum oven at 120 °C. Ti/Au top electrodes were deposited by e-beam evaporation using a shadow mask with 50 microns electrode separation. Pt-SWCNT films displayed an electrical conductivity of 7.3×10^{-4} $S.cm^{-1}$ at room temperature. The current-voltage and current-temperature characteristics of these Pt-SWCNT films were investigated and found to be best described by a modified quantum tunnelling conduction model.

[1] M. F. Mabrook et al.,*Mat. Sci. Eng. B-Solid*, **159–160**, 14-17 (2009).
[2] M. F. Mabrook et al.,*Carbon* **47**, 3, 752-757 (2009).
[3] K. Matsumoto et al.,*J. Mater. Chem.*, **21**, 1187-1190 (2011).
[4] A. L. Dicks, *J. Power Sources*, **156**, 128-141 (2006).
[5] D. C. Higgins et al., *J. Phys. Chem. C*,**114**, 21982–21988 (2010).
[6] H. Kim et al.,*Carbon*,**49**, 1491-1501 (2011).
[7] C.-T. Hsieh et al.,*Int. J. Hydrogen Energy*, **35**, 16, 8425-8432 (2010).
[8] C.-L. Sun et al.,*Chem. Mater.*, **17**, 3749-3753 (2005).
[9] M. K. Bayazit et al.,*J. Am. Chem. Soc.*,**132**, 15814-15819 (2010).

Carbon Nanotube Nanogap Electrodes

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Nanogaps in Carbon Nanotubes have been successfully used in the past e.g. to contact single organic molecules [1]. Often these nanogaps are created by current-induced breakdown. Recently the cutting of carbon nanotubes [2] and sputtered carbon [3] using electron beam stimulated oxidation has been shown. In a scanning electron microscope, oxygen is injected into the chamber, directly above the nanotube contacts. A linescan over any area of the nanotube then becomes a precise scalpel. This enables the fabrication of nanogaps in a lithographic fashion. We have studied electron beam stimulated oxidation of carbon nanotubes in an active device configuration, measuring the conductance during the cutting process. Here we present the results of the nanogap fabrication on different substrates as well as a model that can explain the resolution limit of around 10nm.

[1] Marquardt et al., *Nat. Nano.*,**5**, (2010); Guo et al., *Science*, **311**, (2006)
[2] Liu et al., *Appl. Phys. Lett.*,**89**, 113104, (2006)
[3] Spinney et al., *Nanotechnology*,**20**, (2009)

Investigation of comparative growth kinetic of the carbon nanotubes and graphene multilayers of the thermal-oxidative ethanol pyrolysis method

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Practical realization of nanostructures based on graphene in electronics and optoelectronics has raised the question of obtaining high-quality graphene samples of large area. One of the promising method of monolayers graphite formation (graphene) and other electrically conductive layered materials is the chemical vapour deposition (CVD) that allows to produce large area graphene multilayers. We suggest the methodic of graphene growth based on the ethanol pyrolysis from the gas phase.

The investigation of growth methods was carried out on carbon nanotubes growth system CVDomna, which allows growing carbon nanotubes by ethanol pyrolysis method. Unlike the devicesof a similar type, CVDomna can synthesize a variety of carbon nanomaterials on different substrates with dimensions up to3 inches. The reaction was controlled precisely, because the material oxidation takes place simultaneously with the growth process when ethanol vapour mixture is used. The dissolution process of chemically active carbon monoxide in a metal catalyst (in this work Ni film of 200 nm thickness) occurs before the complete dissolution of the liberated carbon in the bulk of the catalyst.

Thus, the saturation of carbon-film catalyst and the formation of solid solution of metal-carbon bonds occur. When the critical carbon quantity is reached the reaction chamber cooling leads to faster release of carbon and termination of graphene multilayers growth. Consequently, the higher the temperature of the reaction, the more carbon will react with the catalyst, and the faster the reaction chamber is cooled, the less carbon is formed on the catalyst surface. The thickness of graphene multilayers synthesised using this technology, was investigated by scanning probe microscopy. It was shown that the thickness of catalytic layer determines the type of carbon material. The thin layer catalyst leads to CNT growth, whereas thick layer catalyst leads to graphite monolayers formation. Cooling rate, which determines the surface morphology, also affects quality of the carbon material. In case of fast cooling rate a homogeneous graphene layer is obtained, otherwise separated graphene islands are formed. These results show that further study of the reaction mechanism at the substrate-catalyst border is required. The results of graphene synthesis properties investigation in CVD process can be used to develop industrial graphene synthesis process.

Carbon Nanotube Double Helices From Layered Double Hydroxides

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Three-dimensional (3D) micro-coiled or nano-coiled carbon materials have attracted extensive attentions because of their unique conformations and outstanding mechanical and electromagnetic properties. The combination of two congruent helical coils with the same axis or differing by a translation along the axis leads to the formation of a double-helix structure, which is the basic structure of deoxyribonucleic acid (DNA). In this contribution, we reported our recent progresses on the directed fabrication of carbon nanotube double helices based on layered double hydroxides (LDHs) by simple chemical vapor deposition.

Reduction of FeMgAl-CO_3^{2-} LDH flakes can lead to the formation of FeMgAl layered double oxides (LDOs) flakes with high density Fe nanoparticles embedded on both sides. Aligned double-walled CNTs (DWCNTs) can synchronously grow and extend perpendicularly from both sides of the LDO flakes. With the continuous growth of the CNT arrays, the array tips met space resistance attributed from the neighboring flakes or CNT arrays. In order to minimize the stresses associated with the growth of CNTs, the arrays started to twist and coil on themselves around the ultra-light LDO flakes (~0.2 ng), leading to the further assembly of CNT double helices with a length of tens of micrometers and a diameter of several micrometers. LDHs with a composition of FeCoMgAl-CO_3^{2-} were demonstrated to be effective for the growth of multi-walled CNT double helices [1]. MoO_4^{2-} can be intercalated into FeMgAl LDH layers through anion exchange method by guest-host chemistry [2] or during the direct coprecipitation process [3]. The intercalation of MoO_4^{2-} can lower the catalyst particle size and improve its density. As a result, single-walled CNT double helices can be successfully fabricated on the as-obtained FeMoMgAl LDO flakes. This is an easy route to build 3D double helical nanoarchitectures by bottom-up self-assembly strategy between one-dimensional CNTs and two-dimensional flakes. The CNT double helices are demonstrated to be of with good extension characteristics and the CNT yarns in the double helices are able to carry high current. This double helical structure provides a platform towards the design of hierarchical nanocomposites that can be used in areas such as high-performance CNT yarns, nanoelectronics, magnetic devices, and energy conversion.

[1] Zhang Q, Zhao MQ, et al.*Angew. Chem. Int. Ed*, **49**, 3642 –3645, (2010).
[2] Zhao MQ, Zhang Q, et al. *J. Am. Chem. Soc.*, **132**, 14739–14741, (2010).
[3] Zhao MQ, Zhang Q, et al. *Carbon*, **49**, 2148-2152, (2011).

Localization And Tunneling Mechanism in Carbon Nanotubes Aggregates

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Transport mechanism in single wall carbon nanotubes (SWCNT) aggregates has been widely studied and understood on the basis of the transport theories currently used for disordered conductors. Variable range hopping (VRH) [1] and temperature fluctuation induced tunnelling (FIT) [2] seem to be the most successful models for explaining the resistivity behaviour in a wide temperature range. Both models assume that localized states are formed inside the bundles and that charge transport happens by hopping or tunneling through the bundles-bundles interface junctions. Commonly, the junction at the interface is naturally formed by the action of van der Waals forces and it can be described as a potential barrier for charge carriers whose characteristics (width and height) depend on the nature of the interface and on the electrical properties of the SWCNT. Because SWCNT aggregates comprise both semiconducting and metallic individuals, the junctions play the role of insulating barriers along a conducting path. Therefore, interesting effects as thermal activation, tunneling and hopping can be evidenced in an experiment where charge transport is monitored. Which of these effects rules the physics of these systems can be understood by transport measurements performed in a wide temperature range. In this talk we study the transport properties of two kinds of SWCNT aggregates: oriented arrays of SWCNT bundles [3] and aligned SWCNT fibres [4]. Resistance vs. temperature (R-T), magnetoresistance vs external magnetic field (MR) and current vs voltage (I-V) measurements have been performed in a wide temperature range. The R-T data showed 3-dimensional localization of the charge carriers above a temperature T^* which is different for the two systems. This mechanism is confirmed by negative MR at low field due to the interference between the wavefuctions of the hopping electrons between localized states. Moreover, the finite value of the resistance in the limit of zero temperature ($T<T^*$) signals the presence of potential barriers ascribed to the SWCNT-SWCNT interface junctions. These measurements, together with I-V characteristics at different temperature, yield the width and the height of the potential barriers, which are higher in oriented arrays than fibres. Because of the difference in the fabrication of the two analysed systems, which affects the nature of the SWCNT-SWCNT junctions, the experimental results could help in determining the role of the junction interfaces on the transport mechanism of CNT aggregates.

[1] N.F. Mott, E.A. Davis Electronic Processes in Non-Crystalline Materials Claredon Press-Oxford (1979)
[2] P. Sheng, *Phys. Rev. B* **21**, 2180 (1980).
[3] M.L. Terranova et al. , *J.Phys.D: Condensed Matter* **19**, 2255004 (2007).
[4] L.M. Ericson et al. *Science* **305**, 1447 (2004)

Carbon Nanotubes Array As Template For Metallic Interconnection

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Modern integrated circuits are mainly speed-limited by their interconnects and presently many new materials and systems are being developed to address the needs for higher temperature operation and longer working life. Conventional materials, like Cu, are limited in carrying high current densities by metal atoms electromigration that leads to structural failures and reduction of device reliability. Moreover thermal expansion/contraction processes can cause shear strain at the joints (end bonding). In the last decade significant advances in material performances have been made by using carbon nanotubes, that, owing to their extraordinary electrical, mechanical an thermal properties, may provide solutions for interconnects and chip cooling in future IC technologies [1]. On the other hand, nanostructured Cu and Ni have been proposed as reliable primary interconnection materials in view of the enhanced properties of mechanical resistance exhibited by these metals at the nanoscale [2]. In order to comply with these indications, practical solutions must be found for the fabrication of well defined architectures assembled by nanosized Cu or Ni deposits. Because the electrical properties of the Ni decorated SWCNT are expected to depend on the concentration of Ni nanoparticles, we started to deposit low concentration of about 50 nm Ni nanoparticles on the surface of SWCNT fibres with diameter of 100 µm [3]. Resistance vs. temperature and current voltage measurements show that the metallic properties of the fibres are enhanced by this interaction. Moreover, magnetoresistance measurements indicate this effect can be attributed to the delocalization of the electron wavefunction. All these results gave a strong effort in the use of SWCNT as good templates for interconnection in integrate circuits. Depositing Ni nanoparticles on arrays consisting of aligned SWCNT bundles [4,5], experimental data show a complete transition to metallic behaviour starting from the semiconducting character of the bare SWCNT bundle array observed before the Ni deposition. Comparing the results obtained for the fibres and the bundle arrays covered by Ni nanoparticles with that obtained for the same samples before the Ni deposition, interesting indications on the influence of Ni on the transport mechanism inside the SWCNT are acquired.

[1] A. Nieuwoudt and Y. Massoud *IEEE Transactions on Electron Devices* **55** (2008) 2097-2110
[2] A.O.Aggarwall et al. *IEEE Transactions on Electronics Packaging Manufacturing* **31** (2008)
341-354
[3] L.M. Ericson *et al. Science* **305**, 1447(2004)
[4] E. Tamburri, F. Toschi, V. Guglielmotti, E. Scatena, S. Orlanducci, M.L. Terranova, (2008) *Journal of Nanoparticle Research*, **11**, 1311, (2009)
[5] S. Orlanducci, E. Tamburri, V. Guglielmotti, F. Toschi, M.L. Terranova, M. Lucci, I. Ottaviani, M. Salvato, M. Cirillo, (2010), *IEEE Transactions on Nanotechnology*: (in press).

Multi-walled Carbon Nanotube Dispersion for Conductive Films

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Many research works on conductive films using carbon nanotubes (CNTs) with excellent electrical properties have been reported. A lot of companies give positive consideration to industrial use of economically feasible multi-walled carbon nanotubes (MWNTs) in the field of next generation conductive films. To make conductive films based on CNTs, several methods including vacuum filtration, spray coating, bar coating are used and they all require CNTs dispersed in liquid. For this case, physical and chemical properties of the CNT solution significantly affect characteristics of the conductive films. In this study, we investigated the effect of MWNT dispersion conditions on physical properties of the final conductive films. We adjusted sonication conditions to control the degree of dispersion of MWNTs. We made conductive films by using the CNT solutions with different degree of dispersion and measured optical transmittance and electrical resistance of each conductive film. Based on the results, we found dispersion guidelines for highly conductive MWNT films.

Dispersions Of Nanotubes And Graphene Particles In Petroleum Products

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Presently, applications of carbon nanoparticles in the petroleum industry are considerably limited. However, a few solutions that have been published, seem to be promising. Among them, improving the thermal conductivity of cooling liquids, reduction of coefficient of friction for lubricating oils, improving the combustion efficiency of diesel and gasoline fuels, improving the energetical efficiency of jet fuels as well as reduction of undesirable exhaust gas emissions in two-stroke engines, are the most interesting. The paper discusses problems refering to the preparation of stable dispersions of carbon nanoparticles in petroleum products by using two types of multi-walls nanotubes, basic and chemically modified graphene. Applied nanotubes were commercially available products, while graphene was synthesized using the chemical method from graphite. Chemical transformation of graphene oxide leads to modified graphene. Synthesized products were characterized by FT-IR spectra. The Turbiscan method was induced to measure the dispersion state (particle aggregation, sedimentation) of carbon nanoparticles in the continuous phase of petroleum products. Results of AFM imaging of liquid samples containing carbon nanotubes, have been also presented.

Functionalization of Vertically Aligned Carbon Nanotubes with Nitric Acid Vapor

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Millimeter high aligned carbon nanotubes (ACNT) were functionalized with nitric acid vapor in ambient conditions. Depending on the temperature and reaction time used the reaction can lead to uniform sidewall functionalization preserving the desirable alignment, random destruction or reorientation of the nanotubes leading to significant modification of the morphology of the ACNT “forest” or in some cases cutting off the ACNTs from the substrate. Uniform sidewall functionalization of ACNT is important for several technologies, however, there is a certain limit for the functionalization after which the other processes start to dominate.

Sonic Study On Dispersibilty Of Carbon Nanotubes

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The high surface to volume relation and extraordinary properties of carbon nanotubes (CNTs) can be used for improving the electrical and mechanical properties of polymer composites [1,2]. However, success of synthesizing such composites depends on precise control of the CNT volume fraction in the composite, which is a consequence of the ability of CNTs to disperse homogenously within the polymer/precursor mixture. Though the dispersing ability of CNTs is dependent on the medium used (type of solvent); it is also majorly influenced by the sonication techniques used. Effect of sonication parameters on the structure of CNTs and its dispersibilty in various solvents hence becomes very critical [3,4]. In this poster we present the dependency of dispersing ability and structure of CNTs with varying sonication parameters.

[1] E Dervishi, Z Li, V Saini, A R Biris, D Lupu, S Trigwell and A S Biris, *Mater. Res. Soc. Symp. Proc.*, **1018** (2007).
[2] X Zhao, A A Koos, B T T Chu, C Johnston, N Grobert and P S Grant, *Carbon*, **47**, 561-569 (2009).
[3] S D Bergin, V Nicolosi, P V Streich, S Giordani, Z Sun, A H Windle, P Ryan, N Peter, P Niraj, Z T Wang, L Carpenter, W J Blau, J J Boland, J P Hamilton and J N Coleman, *Adv Mater*., **20**, 1876 – 1881 (2008).
[4] J Hilding, E A Grulk, Z G Zhang and F Lockwood, *J. Disp. Sci. Tech.*, **24**, 1-41 (2003).

The Role of Bundles in Separating Metallic from Semiconducting Single Walled Carbon Nanotubes and Selective Bundling of zig-zag SWNTs

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Separation techniques for single walled carbon nanotubes (SWNTs) have become an important research field over the last several years, because present synthesis methods do not allow the growth of nanotubes of one length, diameter, chirality, electronic type (metallic or semiconducting) and free of byproducts. SWNTs are typically grown in a mixture of m- and s-SWNTs, thus hindering widespread electronic applications. Separating SWNTs by electronic type has become a flourishing research field and enrichment of m-SWNTs has been achieved by various techniques including dielectrophoresis [1], density gradient centrifugation (DGC) [2] and agarose gel electrophoresis [3].Recently, it has been shown that a procedure based on gel filtration/size exclusion chromatography (SEC) methods allows high throughput separation of m- from s-SWNTs when using aqueous sodium dodecyl sulphate (SDS) starting suspensions. [4,5] In the current work we demonstrate that by controlled aggregation of s-SWNTs in suspension it is possible to separate m- from s-SWNTsby SEC due to differences in bundle sizes. Due to the sonication conditions used in this work m-SWNTs are preferentially suspended to individuals and s-SWNTs remain in bundles. Evidence is provided by optical absorbance spectroscopy and atomic force microscopy (AFM). A simple, high throughput fractionation procedure for aqueous/SDS suspensions of SWNTs is presented, which yields thin bundles of s-SWNTs with small chiral angles [6]. To demonstrate this we show the photoluminescence signatures of nanotube suspensions that contain almost exclusively zig-zag or near-zig-zag tubes. Starting suspensions and resulting fractions were characterized using optical absorption and photoluminescence spectroscopy. Taken together with literature observations, our findings suggest that near zig-zag edge tubes of similar diameters in a bundle are harder to separate from each other than for other chiral index combinations.

[1] R. Krupke, F. Hennrich, H. von Loehneysen, M. M. Kappes, *Science* **301**, 344 (2003).
[2] M. S. Arnold, A. A. Green, J. F. Hulvat, S. I. Stupp, M. C. Hersam, *Nature Nano.* **1**, 60 (2006).
[3] T. Tanaka, H. Jin, Y. Miyata, H. Kataura, *Appl. Phys. Express* **1**, 114001 (2008).
[4] K. Moshammer, F. Hennrich, M. M. Kappes, *Nano Res.* **2**, 599 (2008).
[5] H. Liu, Y. Feng, T. Tanaka, Y. Urabe, H. Kataura, H.; *J. Phys. Chem. C* **114**, 9270 (2010).
[6] C. Blum, N. Stürzl, F. Hennrich, S. Lebedkin, S. Heeg, H. Dumlich, S. Reich, M. M. Kappes, *ACS Nano*, in press.

Magnetic Characterization Of CNx-MWNT-Encapsulated Ferromagnetic Nanoparticles

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Here we present a systematic study of ferromagnetic nanoparticles encapsulated in N-doped multi-walled carbon nanotubes (CN_x-MWNTs) that were synthesized by chemical vapor deposition (CVD). Benzylamine was used as a carbon-nitrogen source, and ferrocene as the catalytic agent that also become the source of the ferromagnetic nanomaterial. The CVD setup consists of two furnace system and an aerosol is produced from the ferrocene- benzylamine solution. A quartz tube was used to grow the tubes, and the carrier gas was Ar; an acetone trap was placed at the outlet. Three similar experiments were carried by varying the volume of acetone in the trap. Several silicon substrates were placed within the quartz tube (80 cm in total) and eighteen samples were obtained for each experiment (54 in total). Sample characterization was performed by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, thermo-gravimetric analysis (TGA) and magnetic properties using a physical properties measurements system (PPMS). Our results demonstrate that both the acetone volume in the trap, and the position of the Si substrate in the hot zone, affect the properties of CN_x- MWNTS. In particular, when the level of the acetone trap is the lowest (a volume of 100 ml), it was observed than the ferromagnetic nanoparticles encapsulated inside the CN_x-MWNTs consisted of different iron carbide phases showing mainly a preferential crystal orientation. In this work, the effect of all synthetic conditions on the properties of the produced carbon nanotubes is discussed. We demonstrated that it is possible to tune the magnetic properties of the tubes by controlling the experimental synthetic conditions.

Indolizine Modified Fluorescent Single-Walled Carbon Nanotubes For Detection Of Nitroaromatics

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Since nitroaromatics are present in explosive warfare agents including TNT and ammonium picrate, and pollute the environment, detection of trace amount of nitroaromatic compounds is important both in terms of homeland security and environmental monitoring. Herein an indolizine modified SWNT based photochemical sensor has been presented, for the first time, to detect trace amount of nitroaromatic compounds, o-nitrophenol, m-nitrophenol, p-nitrophenol, p-nitrotoluene and 2,4-dinitrotoluene, in solution and solid phase. Indolizines, the simplest hetero-aromatic molecules containing both a π-excessive pyrrole and a π-deficient pyridine ring, have attracted special attention due to their luminescent properties with potential sensing applications.[1,2] Pyridine functionalized single-walled carbon nanotubes (SWNTs),[3] formed following the addition of pyridine diazonium to nanotubes, have been used to prepare pyridinium ylides, generated from simple Kröhnke salts, covalently bound to a nanotube surface which undergo a 1,3-dipolar cycloaddition with dimethyl acetylenedicarboxylate in a 'click' chemistry type fashion to yield indolizine modified SWNTs. The indolizine functionalized SWNTs generated emit blue light when excited at 330 nm.[4] The location and distribution of the functional groups was determined by AFM using electrostatic interactions with gold nanoparticles. The indolizine functionalized SWNTs were further characterized using FTIR, UV-vis-NIR, TGA-MS and XPS. Fluorescent quenching experiments demonstrated that the SWNTs having the fluorescent indolizine groups could be used as a potential photochemical sensor for detection of aromatic nitro compounds with a detection limit of 6.66×10^{-8} M.

[1] F.Delattre, F. Cazier, A. Tine, *Current Analytical Chemistry*, **5**, 48-52(2009).
[2] G. G. Surpateanu, M. Becuwe, N. C. Lungu, P. I. Dron, S.Fourmentin, D. Landy, G. Surpateanu, *Journal of Photochemistry and Photobiology a-Chemistry*, **185**, 312-320(2007).
[3] M.K. Bayazit, L.S. Clarke, K.S. Coleman, N. Clarke, *Journal of the American Chemical Society*, **132**, 15814-15819, (2010).
[4] M.K. Bayazit, K.S. Coleman, *Journal of the American Chemical Society*, **131**, 10670-10676, (2009).

Biocompatibility And Toxicological Research Of Surfaces Modificated With Different Carbon Nanotubes

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Carbon nanotubes (CNTs) are one of the most promising products of nanotechnology, which can be used in tissue engineering of biological objects as a scaffold material. This property of CNTs is due to the fact that they are geometrically similar structure with collagen, which is the main protein of connective tissue of animals. Unique electronic properties, high mechanical strength, high flexibility and low density of CNTs can create biocompatible composite materials with new properties.

At the moment there are a number of researches describing the creation of composite materials based on nanotubes for bio-engineering, in particular the regeneration of bones and cartilages [1]. But there is the issue of biocompatibility and cytotoxicity of CNTs. In the research to determine the toxicological parameters of CNTs, the engineering characterization of nanotubes was developed. The formation process of the scaffold material based on carbon nanotubes and cell growth on these structures was studied. Characterization of the nanotubes was carried out by scanning (SEM) and transmission electron microscopy (TEM), atomic force microscopy (AFM) for identification the geometric dimensions and structure, secondary ion mass spectroscopy (SIMS) for determination the concentration and composition of impurities.

As the nanotubes material were chosen single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) of the three largest Russian suppliers. SWNTs obtained by arc evaporation of graphite, were provided by the Institute of Problems of Chemical Physics with average diameter, 2,9 ± 1,5 nm, length 570 ± 158 nm. MWNTs sample number 1, obtained by catalytic pyrolysis of hydrocarbons, provided LLC STC "Granat" with the average diameter of 4.9 ± 0.5 nm, length 475 ± 120 nm. MWNTs sample number 2, obtained by catalytic pyrolysis of hydrocarbons, provided LLC "NanoTechCenter" with average diameter of 36.0 ± 6.0 nm, length 1203 ± 400 nm.

Culturing Vero cell line on the surfaces of cover glasses the size of 24x24 mm^2 and a thickness of 0.13-0.17 mm, modified with carbon nanotubes, SWNTs, MWNTs number 1 and MWNTs number 2 was carried out. Coverslips with CNTs was placed in culture dish and sterilized in an autoclave at 120 °C, 1 atmosphere, 20 min., followed by the introduction of Vero cells at a concentration of 100,000 cells / ml. Cultivation was carried out in an incubator for 72 hours, and then coverslips were removed from culture dish, fixed and stained for morphological researches. Investigation of cell morphology demonstrated that during cultivation on modified surfaces morphology of normal cells, also formed a dense cell monolayer. The result of the work is the following: carbon nanotubes are not cytotoxic and can be used as a basis for the cells cultivation, as well as a frame material for cell engineering. When cultured glioblastoma cells(GL6) and human embryo fibroblast cells (HEF) on coverslips modified SWNTs and MWNTs number 1 showed a slight decrease in proliferative activity of cell lines and cell viability. While MWNTs number 1 have the greatest toxic effect on tumor cells human glioblastoma.

[1] Zanello L.P., Zhao B., Hu H. *Nano Letters,* **6**[III], 2006; 562-67.

Synthesis Bombesin-Naphthalenediimide Conjugate Functinalized Single Walled Carbon Nanotubes as a Novel Receptor Imaging Probe

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We hereby report a new cancer probe including carbon nanotube, of advanced purity and with well understood physico-chemical properties and which are wrapped with a cancer cells receptor-binding bombesin-naphthalene diimide conjugate (NDI- bombesin)[1]. Our probes are totally biocompatible and soluble in cell medium which makes them particularly attractive for cancer cells receptor imaging. The specific peptide tag helps carbon nanotubes to target Gastrin-Releasing Peptide Receptor (GRPR) which is highly expressed on prostate cancer cells (PC3) membrane and also helps to ferry carbon nanotube into prostate cancer cells. Therefore, our new bombesin- NDI conjugate functionalized carbon nanotubes(BN-NDI-SWNTs) targeting the GRPR can be viewed as promising tools for the non-invasive diagnosis, monitoring and potential treatment of prostate cancer in future.

[1] Pantos, G. D.; Pengo, P.; Sanders, J. K.,Angew. *Chem., Int. Ed.,* **46**（1-2）, 194-197, (2007).

Magnetization in Carbon Nanotubes under Ion Irradiation

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Carbon materials including nanotubes and graphene are known to exhibit magnetic properties. It is conjectured that the localized states at the zig–zag edge of the single walled nanotubes (SWNTs) and graphite sheets can induce magnetic polarization. Defects are also known to induce localized spin moments in carbon materials. Here we report ferromagnetic–like ordering in multi–walled carbon nanotubes (MWCNTs) under ion irradiation that arise from topological defects and mechanical strain. We have performed X-ray photoelectron spectroscopy measurements and *ab initio* simulations to support our magnetic measurement data. MWCNTs grown by chemical vapor deposition technique were irradiated by 70 MeV Ni^{6+} ions at the Inter–University Center for the Accelerators, New Delhi. DC magnetization data were recorded using a vibrating sample magnetometer. The magnetic moments of the virgin MWCNTs were then subtracted from those of the irradiated samples. The measured magnetization, which is similar to that of the conventional ferromagnetic materials, strongly indicates the presence of ferromagnetic moments in the irradiated MWCNTs. We have further performed x-ray photon spectroscopy on the virgin and irradiated MWCNTs. It is observed that the percentage of sp^3 bonded carbon atom increases with irradiation fluence. The mixing of sp^2 and sp^3 bonds gives further evidence for magnetic ordering in the defected carbon nanotubes. In order to verify our experimental results we have performed *ab initio* simulations using density functional theory (DFT). Our results show a small net magnetic moment in the defected carbon nanotubes. By investigating the σ-π orbitals admixture, we attribute the origin of magnetism in MWCNTs to the presence of topological defects and the attendant mechanical strain introduced by ion irradiation.

Valence band of graphite oxide

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We investigated the valence band structure of graphite oxide by photoelectron spectroscopy at the Pohang Accelerator Laboratory, Korea.The typical sp^2 hybridization states found in graphite were also seen in graphite oxide. However, the π state disappeared near the Fermi level because of bonding between the π and oxygen-related states originating from graphite oxide, indicating electron transfer from graphite to oxygen and resulting ina downward shift of the highest occupied molecular orbital (HOMO) state to higher binding energies. The band gap opening increasedto about 1.8 eV, and additional oxygen-related peaks were observed at 8.5 and 27 eV.The electronic states of graphite were also found in graphite oxide. Thus, graphite oxide has an electronic structure similar to that of pristine graphite except for the states near the Fermi level and oxygen-related states.

Mechanical Characterization of Ultra Thin Membrane Made Up of Well Aligned Carbon Nanotubes

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A, high-frequency, capacitive, micro-machined, ultrasonic transducer based on a membrane of densely well aligned carbon nanotubes is currently being developed. Our study consists first in making very thin membranes made up of well aligned carbon nanotubes. Our nanotubes are single walled, both metallic and semiconductors. The nanotubes are suspended over a micron wide trench. An actuation electrode is lying at the bottom of the trench. A technique for mapping the spring constant and extracting the mechanical properties of the suspended membrane, namelylocal thickness and Young modulus, through AFM characterization has previously been described[1]. The thicknesses of our membranes are in the tens nanometer range, down to monolayer. Our present work focuses on the capacitively induced vibrations of these membranes. Using Doppler laser vibrometer, and thanks to the high density of the nanotube alignment, vibrations of the membranes can be observed. We apply an alternative and biasing voltage between the membrane and the bottom electrode to create an electric force attracting the conductive membrane. The membrane is thus vibrating around an equilibrium position. Our present set up limits the experiments at frequencies lower than the membrane resonance frequency. Membrane displacement up to 5nm peak to peak has been obtained at a few MHz [2]. We currently study the measurements conditions, data analysis and treatment related to this experiment, as rough data have to be extracted from actual set up, namely laser spot size regarding to the micrometric width of the vibrating area. This use of Doppler laser vibrometer for measurements on this type of devices needs care but appears liable to provide key information regarding to the micron sized membrane mechanical behaviour. We use this experimental technique to study the link between vibration amplitudes and membrane morphology, and the influence of the anchoring stress on both edges of the membrane. Experimental protocol and results will be presented and discussed.

[1]B. Lebental, A. Ghis, E. Delevoye, J-M. Caussignac, F Bourquin.*EJECE* n° 4 (2011)
[2] B. Lebental, PhD thesis, Université Paris-Est, France, 2010. http://pastel.archives-ouvertes.fr/pastel-00574780/fr/

Solvents for Nanotubes and Graphene – Why the Difference?

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The effective dispersion of nanomaterials is universally acknowledged to be critical when one wishes to harness their full potential in devices or applications. Over the past number of years much work has been carried out on overcoming the inherent difficulties associated with producing high quality dispersions of both single walled carbon nanotubes (SWNTs) and graphene. Liquid-phase exfoliation of these intractable materials in organic solvents offers high quality dispersions from a relatively simple processing route. Whilst work by these authors has discovered and chararacterised families of new solvents for both SWNTs and graphene there remains outstanding questions as to why certain solvents work and others do not[1-2]. Herein, I shall present recent findings on the critical components necessary for solvents to debundle SWNTs and/or exfoliate graphite to produce graphene. Whilst these two materials have very similar surface energies (a critical component when considering suitable solvents for materials), the set of effect solvents for both are not identical. Reasons for this variation will be presented.

1. Bergin, S.D., et al., *ACS Nano*, 2009. **3**(8): p. 2340-2350.
2. Hernandez, Y., et al.,. *Langmuir,* 2010. **26**(5): p. 3208-3213.

Gold Nanoparticles Containing Carbon Nanotubes-Polyelectrolyte Multilayer Thin Films via Layer-by-Layer Self-assembly

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Multi-walled carbon nanotubes (MWCNT)/polyelectrolyte (PE) hybrid thin films were fabricated by alternatively depositing negatively charged MWCNT and positively charged (diallyldimethylammonium chloride) (PDDA) via layer-by-layer (LbL) assembly technique. The stepwise growth of the multilayer films of MWCNT and PDDA was characterized by UV-vis spectroscopy. Scanning electron microscopy (SEM) images indicated that the MWCNT were uniformly embedded in the film to form a network and the coverage density of MWCNT increased with layer number. Au nanoparticles (NPs) could be further adsorbed onto the film to form Au NPs/MWCNT composite films. The electron transfer behaviour of multilayer films with different compositions were studied by cyclic voltammetry using $[Fe(CN)_6]^{3-/4-}$ as an electrochemical probe. The results indicated that the incorporation of MWCNT and Au NPs not only greatly improved the electronic conductivity of pure polyelectrolyte films, but also provided excellent electrocatalytic activity towards the oxidation of nitric oxide (NO).

Melt Processed Polymer - Carbon Nanotube Composites as Materials For Liquid Sensing Applications

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Polymer/Carbon Nanotube (CNT) composites show improved mechanical, thermal, and electrical properties, and also sensitivity to external stimuli.CNT composites prepared by different mixing methods can be used to detect mechanical strain, temperature changes, different chemicals in form of gases, liquids, vapours, or tastes. A detection of environmental condition changes is only possible, if it affects the electrically conductive CNT network inside the insulating polymer matrix. Such changes of the CNT network structure result in changes of the electrical resistivity of the composite material that can be designated as the sensing behaviour. In order to use the full potential of CNT in composite materials, good nanotube dispersion and an established percolated nanotube network inside the polymer matrix are crucial. This aim is challenging, as nanotubes tend to form aggregates and agglomerates, which have to be dispersed and distributed within the polymer matrix during processing.

In this study the possibility to use melt prepared composites containing multiwalled carbon nanotubes (MWCNT) for liquid sensing purposes was examined. As examples polylactic acid (PLA)/MWCNT [1-3] and polycarbonate (PC)/MWCNT composites exhibiting good CNT dispersion were compression moulded to thin films. For PLA based composites, also melt spun fibres were prepared using different take-up velocities. In addition, polymer blends consisting of polycaprolactone (PCL) having different MWCNT contents and either polypropylene (PP) [4] or PLA were investigated using varied phase fractions. For the latter, textiles were woven from melt spun multifilament fibres. The electrical resistance changes caused by contact with different solvents like n-hexane, toluene, chloroform, tetrahydrofuran, dichloromethane, ethanol, and water were recorded for immersion/drying cycles. The resistance of melt pressed films and textiles reversibly changed upon the cycles with good reproducibility. The sensitivity towards resistance change during solvent contact decreased with increasing MWNT content, with increasing difference between the solubility parameters of solvent and polymer, and in the fibres with higher orientation of the MWCNTs due to increased take-up velocity.

Such sensory CPC films and textiles can be for example applied for leakage detection in building construction and industrial plants, where pipings and tanks have to be monitored.

[1] K. Kobashi, T. Villmow, T. Andres, P. Pötschke. *Sensors and Actuators B: Chemical*, **134**,787-795, (2008).
[2] K. Kobashi, T. Villmow, T. Andres, L. Häußler, P. Pötschke, *Smart Materials and Structures*, **18**, 035008, (2009).
[3] P.Pötschke, T. Andres, T. Villmow, S. Pegel, H. Brünig, K. Kobashi, D. Fischer, L.Häussler, *Composites Science and Technology*, **70**, 343–349, (2010).
[4] P. Pötschke, T. Villmow, T. Andres, K. Kobashi, R. Rentenberger, H.Brünig, D. Fischer, L. Häussler, *Polymer Preprints*, **50**, 419-420, (2009).

High Conductive Tranaparent Ultrathin Single-Walled Carbon Nanotube Films

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Single-walled carbon nanotube (SWNT) films are of great importance to a number of applications such as optical and electronic devices. Here, we describe the discovery that we can fabricate free-standing highly-conductive transparent nanometer-thick (~10-250 nm) SWNT films by using improved floating-catalyst CVD SWNTs (F-SWNTs). Dipping the HNO_3-treated F-SWNT films on glass substrates prepared by spray-coating from a surfactant-dispersed aqueous solution resulted in quick and nondestructive self-release to form free-standing nano-SWNT films on the water, maintaining the original sizes. The films have sufficiently high transmittance (75-95 %), a very low sheet resistance (~120 ohm/sq), and a small average surface roughness (~3.5-7.0 nm). More importantly, the films on the water can be transferred onto flexible polyethylene terephthalate (PET) films and the transferred films are mechanically flexible, which is a great advantage over conventional indium-tin oxide (ITO) and therefore strongly promise to be "post ITO".

[1] Q. Liu, T.Fujigaya, H.-M. Cheng, and N. Nakashima, *J. Am. Chem. Soc.*, **132**, 16581–16586, (2010).

Terahertz Response of Anisotropic CNTs/Polystyrene Composite Films

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Interaction between terahertz electric field and carbon nanotubes (CNTs) have attracted much attention because of their unique structural and electronic properties. A film of highly oriented single-walled nanotubes attenuates electric field parallel to the tube axis and can acts as excellent linear polarizer [1]. It can be proposed that anisotropic terahertz response have remained for composite films with preferred orientation of CNTs.
Anisotropic composite materials have been prepared by repeated forge rolling of polystyrene contained CNTs with a length of 60 µm. The nanotube loading was 0.5 wt.%. We suggested that direction of the forge rolling coincides with a predominant orientation of CNTs in composite. The transmission and reflection spectra of the composites were recorded for two polarizations of electric field vector. Reflection signal for parallel polarization was twice higher than the signal for perpendicular polarization. A strong anisotropic effect in transmission coefficient for composite film was found in the range from 15 to 400 µm for parallel polarization.
CNT can be represented as thin metallic wire. In the presence of parallel polarized external terahertz electric field such system will play the role of antenna with maximum emission perpendicular to the tube axis for specific relation between CNT length and wave length. Thereby absorption of electric field will obtain resonant character. Absorption spectrum of film was deconvoluted on contributions from nanotubes of certain length. Strong absorbance at low wave length is associated with a high contamination of short nanotubes (about 88 %), content of initial tubes is about 10 %. We propose that forge rolling of composite results in destruction of nanotubes and appearance of high content of shorter CNTs than initial one. Agglomeration of CNTs or their segments into spread aggregates (100-200 µm) causes absorption in the wave length region from 100 to 400 µm.

[1] Z. Wu, et. al, *J. Appl. Phys.*, **103**, 094324, (2008).

Thermal Stability of Triple-Walled Carbon Nanotubes

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Triple walled carbon nanotubes are predicted to show fascinating properties because of wall-wall interactions could make physical and chemical stable. Therefore, it is very interesting to compare thermal stability of TWNTs to SWNTs and DWNTs. In this study, we investigate structure stability and changes of TWNTs after high temperature thermal treatment above 1500°C by TEM, Raman, and UV.

Electrical Properties Of CNT-Based Polymeric Matrix NanoComposites

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NanoComposites (NCs) are a class of materials widely investigated in the last decade. NCs properties depend not only on the characteristics of their individual elements but also on their morphology and interfacial behavior. Large interface area between matrix and nano filler is a key issue for NCs.

NCs fillers comprise the large family of Carbon nanomaterials, which include: fibers, nanotubes, fullerene, nano-diamonds, etc.

Carbon Nanotubes (CNTs) are one of the most popular and intensively studied Carbon based nanomaterials.

Several studies demonstrate how just a small percentage of CNTs loading can improve the material properties [1], still maintaining the polymers plasticity.

The most accessible near-term application for CNTs-polymer composite involves their electrical properties. The intrinsic high conductivity of CNTs makes them a logical choice for tuning the conductive properties of polymers, as demonstrated by MacDiarmid [2]. Depending on the specific application of CNT-based NCs, it is possible to create either an isotropic or an anisotropic material, by orienting preferentially the CNTs [3]. In the case of NCs prepared for electrical applications, it is desirable to create a homogeneous polymer composite. Carboxylic functionalized CNTs (-COOH groups) for their well known easy dispersion in polymers [4] are the ideal candidate. In fact the modification of their surface decreases their hydrophobic nature and improves interfacial adhesion to a bulk polymer through chemical attachment. Easy and good dispersion of CNTs in the polymer matrix is essential to obtain a homogeneous final product. Small diameter CNTs, providing a uniform dispersion, means more CNTs per volume unit and as a consequence a more capillary distribution in the polymer matrix at the same weight percentage. Following these reasoning the choice of CNTs has been done on a commercial product (Nanocyl™ NC3101) ready to our purposes.

The choice of the polymers has focused on low cost materials, commercial products featuring good affinity with selected CNTs:a thermoplastic polyolefine normally used in the area of glass gluing; a syloxane and two thermoset commercial epoxy resins, used in the automotive and in the aerospace field.

A detailed study is presented, on the experimental conductivity and scaling laws thereof, for each of the four polymeric matrices above mentioned, as a function of the CNTs volume fraction. It will be shown that, depending on the polymer choice, it is possible to obtain NCs having a DC conductivity either showing a huge dependence on the volume fraction of CNTs or a less marked one. A Finite Element Method (FEM) simulation was performed on a composite material slab characterized by different resistivities, with the aim of evaluating the volume interested by the higher fraction of current density and estimating the penetration depth of DC currents into the sample thickness.

[1] O.Breuer, U.Sundararaj, *Polymer Composite,* **25**, 630-645, (2004).

[2] A.G.MacDiarmid, *Synthetic Metals*, **125**, 11-22, (2002).
[3] A. Chiolerio, et al, *Diamond and Related Materials*, **17**, 1590-1595, (2010).
[4] Gao Guan-hui, et al, *Advanced Material Research*, **79-82**, 609-612, (2009).

Hydrogen Production via Partial Oxidation of Methanol over Cu Thin Films Electrodeposited on TiO_2/CNTs Nanocompoistes

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Selective production of hydrogen by partial oxidation of methanol ($CH_3OH + (1/2)O_2 \rightarrow 2H_2 + CO_2$) over carbon nanotubes (CNTs) supported Cu-TiO_2 catalysts was studied. First, CNTs were directly grown on carbon papers via thermal chemical vapor deposition under Ar-NH_3-C_2H_2 atmosphere at 750 ºC. Thin films of TiO_2 nanoparticles were then deposited on the surfaces of the CNTs by liquid phase deposition [1] toact as test electrodes. The deposition process was conducted at 60 ºC for 1.5 hr, and the electrodes were later calcinated at 400 ºC under air atmosphere for 1 hr. Cu catalysts for hydrogen production were deposited on the prepared TiO_2/CNTs electrode via an electrodeposition technique in an Ar saturated 0.1 M sulfuric acid aqueous solution with 2 mM $CuSO_4$. Further investigations by X-ray diffractometer and energy dispersive spectrometer, accompanied by scanning electron microscopy and transmission electron microscopy on the structural and electrochemical characteristics will be presented. In addition, the effects of different Cu loadings will be investigated, loadings of Cu will be determined via inductively coupled plasma-mass spectroscopy.

[1] J.G. Yu, H.G. Yu, B. Cheng, X.J. Zhao, J.C. Yu, W.K. Ho, *Journal of Chemistry B*, **107**, 13871-13879, (2003).

Effects of Acid Treatment of Carbon Nanotube on the Mechanical Properties and Fracture Process of Carbon Nanotube/Alumina Composites

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Recently, researchers have focused on carbon nanotubes (CNTs) which have outstanding mechanical properties, motivating their use in ceramic composites as a fibrous reinforcing agent. However, as reported in the previous studies, the improvement in the mechanical properties of ceramic composites has been limited due to the inhomogeneous dispersion of CNTs in the matrix [1]. It is a prerequisite for the fuller utilization of CNTs to achieve their homogeneous distribution in the CNT/ceramic composites. It is well known that acid treatments produce negatively charged functional groups on the surface of CNTs [2]. The functional groups make the CNTs easily dispersed in polar solvents, such as water and ethanol [3]. The objective of this work is to evaluate the effects of the duration of acid treatment by H_2SO_4/HNO_3 on the fracture process and the mechanical properties of the alumina composites.

The CNTs used in this study were multi-walled carbon nanotubes (MWCNTs). MWCNTs were refluxed in 3:1 (volume ratio) concentrated H_2SO_4/HNO_3 mixtures for 0, 0.5, 1, 2, 3 and 4 h at 70°C. MWCNT/alumina composites were prepared by spark plasma sintering, and bending strength and fracture toughness of the composites were measured [4]. Aluminum hydroxide powders were used as the starting material for the alumina matrix. The aluminium hydroxide, pristine MWCNTs and acid-treated MWCNTs were subjected to zeta potential measurements to characterize their surface properties.

It was found that there was an optimal acid treatment time for the improvement of the mechanical properties of the composites. The experimental results revealed that the composite made with MWCNTs treated for 2 h gave the highest mechanical properties. The measured bending strength and fracture toughness of the composite with 0.9 vol.% MWCNTs treated for 2 h were 689.6 ± 29.1 MPa and 5.90 ± 0.27 $\mathrm{MPa \cdot m^{1/2}}$, respectively. With increasing the acid treatment timefrom 0 to 2 h, the zeta potential values of the MWCNTs powders were markedly increased, and then decreased from 2 to 4 h. SEM observations of the fracture surfaces revealed that the longer acid treatment time tended to produce more uniform and homogeneous distribution of MWCNTs in the composites, and the number of tiny agglomerations (probably consisted of fragmented MWCNTs) was observed to increase as the treatment time increased. TEM observations also showed that outer-layers of the MWCNTs were exfoliated and peeled for the longer acid treatments of 3 and 4 h. In addition, our previous study has indicated that the tensile strength of heavily acid-treated MWCNTs was lower than that of the pristine MWCNTs [5]. The improvement in the mechanical properties due to the acid treatments up to 2 h may be attributable to the better dispersion of the MWCNTs in the matrix. On the other hand, the reduction in the mechanical properties measured for the longer acid treatments may be due to the lower tensile strength of the damaged MWCNTs and the increased number of the inhomogeneous agglomerations. The present experimental results suggest the usefulness of the acid treatment by H_2SO_4/HNO_3 mixtures for the preparation of homogeneous MWCNT/ceramic composites.

[1] J. Cho et al., *J. Mater. Sci.*, **44**, 1934-1951, (2009).
[2]K.A. Wepasnic et al., *Carbon*, **49**, 24-36, (2011).
[3] Y. Liu et al., *Carbon*, **43**, 47-52, (2005).
[4] G. Yamamoto et al., *Nanotechnology*, **19**, 315708, (2008).
[5] G. Yamamoto et al., *Diam. Relat. Mater.*, **19**, 748-751, (2010).

Structure and Properties of Yarn-like Carbon Nanotube Fibres

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As a consequence of their size and atomic structure, nanomaterials have a range of unique properties often not found or difficult to realise in the bulk. Examples of these are: boron nitride (BN) nanotubes with stiffness of ~ 1 TPa[1], carbon nanotubes (CNTs) with thermal conductivity of ~ 3000 W/mK [2] and an electrical conductivity close to that of copper [3], graphene layers with an estimated specific surface area of 2630 m^2/g. These properties are exceptional; however, the challenge is to produce macroscopic materials that exploit the outstanding properties of these individual 'molecules'. For nanotubes, their elongated shape and axial properties suggest that the optimal arrangement is a fibre, with the nanotubes aligned parallel to each other and to the fibre axis. This route is consistent with traditional methods for making strong/stiff fibres based on long backbones of carbon-carbon bonds extended along the fibre axis and parallel to each other, as proposed some eight decades ago [4].
Carbon nanotube fibres can be spun directly from the reactor by drawing them out of the hot-zone during CNT growth by chemical vapour deposition (CVD) [5]. This process is continuous and allows production of CNT fibres at rates of 10 – 100 m/min. The fibres have typical tensile strength and stiffness of 1.5 GPa and 100 GPa, respectively; although values as high as 9 GPa and 360 GPa have been observed [6]. The material is also thermally and electrically conductive, with present values at 100 W/mK and 8×10^{-5} S/m [7]; has similar chemical and thermal resistance to graphite; and shows high resistance to cutting and exceptional tolerance to bending[8].
The structure of CNTs fibres is unusual for a high-performance fibre. Rather than solid, its structure resembles that of a yarn like cotton [8], with the small subfilaments being the nanotube bundles. The strength of the fibre can be related to the characteristics of the basic fibrous elements, their surface area per unit mass, their contact area with neighbors, their length and the strength of the interface between them in shear [9].

[1] Song, J., Huang, J., Hwang, K. C. & Jiang, H., *J. Nanosc. and Nanothecnol.*, **8**, 3774 – 3780, (2008).
[2] Berber, S., Kwon, Y. & Tomanek, D., *Phys. Rev. Lett.*, **84**, 4613 – 4616, (2000).
[3] Benedict, L. X., Crespi, V. H., Louie, S. G. & Cohen, M. L., *Phys. Rev. B*, 52, 14935 – 14940, (1995).
[4] Carothers, W. H. & Hill, J. W., *J. Appl. Chem. Soc.*, **54**, 1579 – 1587, (1932).
[5] Li, Y. L., Kinloch, I. A. & Windle, A. H., *Science*, **304** (5668), 276 – 278, (2004).
[6] Koziol, K. K. et al., *Science*, **318**, 1892-1895, (2007).
[7] Stano, K. L. et al., *Direct Int. J. Mater. Form.*, **1**, 59 – 62, (2008).
[8] Vilatela, J. J. & Windle, A. H., Adv. Mater., **22**, 4959 - 4963 ,(2010).
[9] Vilatela, J.J., Elliott, J. A. & Windle, A. H. *ACS Nano*, **5**, 1921–1927, (2011).

Carbon nanotube surface modifications revealed by solid sample electrokinetic measurements

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Thanks to their specific properties, carbon nanotubes (CNT) give rise to a wide scientific production and are very promising for many applications (nano-electronics, nano-composites, nanoporous membranes, …). In order to tailor their properties, their surface have to be well known and controlled.

A large number of works [1-3] have already investigated the CNT electrokinetic potential (zeta potential) in colloidal system in order to study the CNT dispersion. However, these studies are limited to a few types of CNT surface modifications and the electrolytes in use vary from a paper to another. Therefore, it is hard to have an overall view of CNT surface properties with respect to the applied post-treatments.

The scope of the lecture is to present a large investigation of CNT surface modifications followed by zeta potential measurements. Experiments are performed on aligned multiwalled carbon nanotubes (MWCNT) synthesized by aerosol assisted catalytic chemical vapor deposition [4]. Starting from a single sample batch, we study as-synthesized MWCNT as well as samples subjected to post-annealing treatment [5], acid treatment, UV irradiation, bulk photopolymerization and diazonium salt grafting technique [6].

The effects of these treatments are discussed with the help of complementary characterization techniques such as microscopic observations (SEM, TEM), thermogravimetric analyses (TGA) or elementary composition by EDX. This work underlines the great interest of the electrokinetic measurements on CNT solid samples to follow their surface state. We show that the surface modification has a major influence on zeta potential curves with drastic changes of isolectric points (IEP). These changes are illustrated by the IEP tendency of polymer grafted MWCNT to move towards the bulk polymer resin one. We will also present example for which the observation of the surface grafting is rather difficult to perform, while solid sample electrokinetic measurements rapidly indicates the success of surface modification. In the context of the development of aligned MWCNT-based materials or devices the use of such measurements contribute to have a rapid insight of the surface state of CNT.

[1] Y.-T. Shieh et al., *Col. Polym. Sci*, **288**, 377, (2010).
[2] M. U. Khan et al., *Carbon*, **48**, 2925, (2010).
[3] P. Azadi et al., *J. Phys. Chem. A*, **48**, 3962, (2010).
[4] M. Pinault et al., *Nano letters*, **5**, 2394, (2005).
[5] M. Pinault et al., *Diam. Relat. Mater*., **13**, 1266, (2004).
[6] V. Mevellec et al., *Chem. Mater*., **19**, 6323, (2007).

Dispersion of Carbon Nanotubes in Polystyrene/Siloxane Blends

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Carbon nanotube (CNT) based nanocomposites have attracted much interest, owing to the conductive properties and mechanical reinforcement CNTs may transfer to the bulk material. When using CNTs as a filler material for the development of (polymer) nanocomposites, a key element is the dispersion of the CNTs. This will strongly influence at what point a 3D percolating CNT network is formed, also known as the percolation threshold. For various reasons, the percolation threshold should be as low as possible. However, due to the strong interactions between CNTs, achieving good dispersion in the matrix can be problematic. For this purpose, specialized dispersion techniques are used in the preparation of CNT nanocomposites, such as latex technology, where surfactants are used to form aqueous polymer and nanotube emulsions, which are subsequently mixed, freeze-dried and compression-moulded [1]. A complementary approach for lowering the percolation threshold is limiting the volume of the material that is accessible to CNTs. Here a phase separated morphology is desired, with CNTs ideally only found in one of the phases, leading to volume exclusion or double percolation [2].

In this work a polystyrene (PS) / polymethylphenylsiloxane (PMPS) blend system was studied as a matrix for CNT nanocomposites. The study of these polymer blend nanocomposites was performed using thermal analysis techniques, such as DSC, as well as surface characterization and rheology. While an excellent dispersion of CNTs by polydimethylsiloxane (PDMS) was reported before [3], this is to our knowledge the first study on the related PMPS, which seems to show similar CNT-dispersing properties. Unlike the strongly immiscible behaviour known for PS/PDMS blends however [4], the PS/PMPS system showed partial miscibility. While this means that phase separated morphologies can still be attained, which can be used for volume exclusion, this also makes it possible to develop homogeneous blends where PMPS seems to act more as a CNT compatibiliser. Clear proof of mechanical percolation was found for such systems, and conductivity studies are underway [5].

[1] N. Grossiord, J. Loos, O. Regev, C. Koning, *Chemistry of Materials*, **18**, 1089-1099, (2006).
[2] A. Göldel, G. Kasaliwal, P. Pötschke, *Macromolecular Rapid Communications*, **30**, 423-429, (2009).
[3] A. Beigbeder, M. Linares, M. Devalckenaere, P. Degee, M. Claes, D. Beljonne, R. Lazzaroni, P. Dubois, *Advanced Materials*, **20**, 1003-1007, (2008).
[4] M. Maric, C. Macosko, *Journal Of Polymer Science Part B-Polymer Physics*, **40**, 346- 357, (2002).
[5] N. Van den Brande, C. Koning, P. Geerlings, G.Van Lier, G. Van Assche, B. Van Mele, Journal of Thermal Analysis and Calorimetry - 10th European Symposium on Thermal

Analysis and Calorimetry (ESTAC-2010) special edition, (accepted for publication).

A Novel Electrode Arrangement for Alignment of Carbon Nanotube in Large- sized Composite Film

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In this study, a novel electrode arrangement was proposed to align multi-walled carbon nanotubes (MWCNT) in epoxy resin to fabricate a large-sized nanocomposite film. It has been reported that alignment of MWCNT in a matrix can improve electric and mechanical properties in aligned direction compared to random disperse of MWCNT. In the preceding studies, however, the size of composites was smaller than a few centimeters because the size was limited by a distance between a pair of parallel electrodes, in which the composite was inserted to apply a high electric field for MWCNT alignment. The conventional one pair of parallel electrode arrangement has an advantage of simplicity, but limited output voltage of high voltage source does not allow application to large-sized composite fabrication such as a few tens of centimeter, which will be necessary for industrial mass production of nanocomposite. To address this issue, a multiple array of parallel electrodes was designed and tested. A thin wire electrode was employed instead of a plate electrode, which was commonly used in the conventional one pair of parallel electrode, so that composite material was spread over a thin dielectric plate (glass) placed on the multiple pair of wire electrodes rather than being inserted between a space between two facing plate electrodes. This arrangement has the following features.

1) High electric filed region can be extended over wider area just by increasing the number of wire electrode pair without increasing electrical potential difference between the wire electrode pair energized by a high voltage source. This feature realizes fabrication of large-sized nanocomposite films in which nano-sized filler is oriented under action of the high electric field.

2) The composite film can be easily flattened and smoothed on the solid dielectric plate.

3) As the conduction current becomes negligible due to high resistance of the dielectric plate inserted between the electrode array and the composite material, possible Joule heating of the composite film during the electric field application can be suppressed.

A drawback of proposed electrode arrangement, discrete electric field distribution bordered by the wire electrodes, was effectively avoided by linearly oscillated motion of composite material and the dielectric plate over the wire electrode array, which could realize spatial averaging of the electric filed.

For a demonstration of validity of proposed electrode arrangement, MWCNT/ UV-cured epoxy composite film with the size of 15 cm × 15 cm was fabricated. MMCNT filler was uniformly oriented along the electric filed direction over the entire area of the film. The electrical resistivity of the composite film reached approximately 105 Ωm in parallel direction to the MWCNTs alignment (for MWCNT filler loading of 0.05 wt.%), which decreased about three orders of magnitude than that of without electric filed application.

Electrical and Thermal Conductivity in an Epoxy Resin-Carbon-Based Materials Composite

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The effective utilization of Carbon BasedMaterials (CBM) in composite applications depends strongly on their ability to be dispersed individually and homogeneously within a matrix. To maximize the advantage of CBMs as effective reinforcement for high strength polymer composites, they should not form aggregates and must be well dispersed to enhance the interfacial interaction within the matrix. Several processing methods are available for fabricating CBM/polymer composites. Some of them include solution mixing, in situ polymerization, melt blending and chemical modification processes.

Our protocol for solution processing method includes the dispersion of CBMs in a liquid medium by vigorous stirring and sonication, mixing the CBMs dispersion solvents in a polymer solution and controlled evaporation of the solvent with or without vacuum conditions.

A thermoset commercial epoxy resin (Epilox™), used in the automotive field, has been chosen for this study together with 16 different kinds of Carbon based materials: 13 different commercial Carbon NanoTubes (CNTs), including Single and Multi-Walled CNTs both as grown and functionalized, carbon beads and powders.

Different weight % (wt.-%) concentrations of CBMs in polymer resin were tried to study the electrical and thermal behaviors of the polymer Nano-Composites (NCs).

A detailed electrical characterization [1][2], made making use of sophisticated Finite Element Method (FEM) simulations and a careful realization of a measurement setup, allowed to collect confident estimates for the resistivities and to apply physical models such as the percolation theory and the fluctuation-mediated tunneling theory. Several conduction behaviors have been found: from highly conductive NCs, which showed linear Ohmic curve, to non-linear diode-like trend up till completely insulating one. Parameters extracted from the model fitting allowed us to conclude that the lowest percolation threshold may be found.

Furthermore a laser flash technique was applied to measure the thermal diffusivity [3], using a pulsed laser in order to realize non-contact heating while the temperature variations were recorded by an infrared detector. The solution of the heat diffusion equation has been made by considering the sample made of a solid, homogeneous, isotropic and opaque materials [4].

[1] A. S. Grove, Physics and Technology of Semiconductor Devices, Wiley & Sons, (1993).
[2] D. K. Schroder. *Semiconductor Material and Device Characterization, Wiley Inter- Science Publications*, (1990).
[3] W. J. Parker, et al, *Journal of Applied Physics*, **32**, 1679, (1961).
[4] H. Mehling, et al, *International Journal of Thermophysics*, **19**, 941, (1998).

(PU/Nylon 6)/MWNT composite nanofibers produced by coaxial and side-by-side (coaxial/single) electrospinning: Preparation, characterization, and mechanical properties

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This paper presents the preparation, characterization, and mechanical properties of polymer/MWNT composite nanofibers by coaxial electrospinning, and coaxial/single side- by-side electrospinning. Polyurethane and nylon 6 are used as model polymers for either the sheath and core of coaxial configuration and their combinations in the side-by-side electrospinning at different tip angles. Acid-treated multiwalled carbon nanotubes (MWNT) were loaded into the polymers at different concentrations from 0.1 to 5 wt%. The distance between the spinneret and the collector was maintained at 150 mm, and the voltage varied from 15 to 25 kV. The characterization of the electrospun composite nanofibers includes FESEM, EDS, TEM, thermogravimetric analysis (TGA), FTIR, Raman spectroscopy, and UV-visible light spectroscopy. The mechanical properties of the nanofibers are investigated using Instron Tensile Tester according to ASTM D882-10 by testing at least 4 specimens for each sample. Preliminary results showed around 30 – 70% improvement in tensile strength of the carbon nanofibers as compared to the neat polymer nanofibers depending on the MWNT loading. Other tests are still on-going.

Electrical Conductivity and Tensile Property of Carbon Nanotube-Polyisoprene Composite Prepared with a Rotation/Revolution Mixer

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Polymer composites containing inorganic fine particles as fillers are widely used in various industrial fields as structural and functional materials. For example, carbon black (CB) has been practically used to improve reinforcement and/or electrical conductivity of elastic materials. Among a lot of carbon fillers, carbon nanotubes (CNTs) have attracted a great deal of attention for extended nanotechnological applications because of their peculiar structure, multifunctionalities, large specific surface area, and high aspect ratio. However, it is difficult to disperse CNTs in polymer matrices because they make highly entangled agglomerates owing to strong *van der Waals* interaction and graphite-like surface. Usually a twin-screw (Banbury) mixer or an extruder has been used to knead fillers in elastomers. However, the conventional mixing methods bring about a collapse of CNTs due to strong mechanical shear, which results in high electrical percolation threshold and low electrical conductivity or poor mechanical properties. The present study demonstrates a novel mixing technique consisting of an ultrasonic pretreatment and a rotation/revolution (R/R) mixing without mechanical shear [1]. Multi-walled carbon nanotubes (MWNTs) and isoprene rubber (IR) composites were prepared by the R/R mixing technique, and the effects of the incorporation of MWNTs into IR on the electrical conductivity and tensile strength of the composites were investigated. As a result, the percolation threshold of the MWNT/IR composite was reduced to one-thirteenth by using the R/R mixer, compared to the conventional Banbury mixer. TEM micrographs showed MWNTs were individually dispersed in the composite prepared with the R/R mixer, whereas a lot of fragments like CB were observed in the composite with the Banbury mixer. Furthermore, resonance Raman spectra showed the area ratio of D-band to G-band of MWNT/IR composites prepared by the R/R mixer was about three times smaller compared to the composites with the Banbury mixer. These results revealed the strong mechanical shear by the conventional mixing method resulted in a collapse of MWNTs followed by a high percolation threshold. The tensile strength of the composites prepared with the R/R mixer was increased with increasing MWNT content (at least up to 1.77 wt.%). On the other hand, when the Banbury mixer was used, the tensile strength was independent of MWNT content. ESR measurements showed the amount of radicals generated by heating was decreased with an increase in MWNT content, which suggested the addition of MWNTs to IR inhibited the degradation of the rubber. This is probably ascribed to a radical scavenging capacity of MWNTs as well as fullerene. However, the other species of CNTs such as single-walled carbon nanotubes (SWNTs) or MWNTs with different structural properties from the foregoing MWNTs incorporated into IR indicated an opposite behavior that the amount of radicals were increased with increasing CNT content. At present, further study with regard to this radical behavior is under progress. The present results led us to the conclusion the R/R mixing technique was expected to be a promising procedure for the preparation of various polymer composites containing CNTs.

[1] K. Tsuchiya et al., *Compos. Sci. Technol.* in press

Tailoring Temperature Invariant Viscoelasticity of Carbon Nanotube Material

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Viscoelasticity describes the ability of a material to both dissipate energy (viscous) and reversibly deform (elastic) and permeates all levels of our lives from human tissue, shoe soles to vibration isolators. Tailoring viscoelasticity is of practical importance because the required mechanical properties can greatly differ with application. Over the long history of viscoelasticity development, thousands of materials have shown the disadvantage that the stiffness (storage modulus) and viscosity (damping ratio) are difficult to be simultaneously improved. It is this reason why a strong and highly viscous material is rare, which is yet highly required.

By using carbon nanotube (CNT) as building blocks, we fabricated a viscoelastic CNT material composed of long and entangled CNTs. The inherent thermal resistance of CNTs provided temperature invariant viscoelastic properties from -196-1000°C, far exceeding the operational range of conventional viscoelastic material [1]. Here, in contrast to existing conventional materials, the stiffness and viscosity of this material could be simultaneously improved. This allows for fabricating both highly elastic and highly viscous materials. We demonstrated that, over one order increase in density (3.3-36 mg/cm^3), the storage modulus was increased one-order from 0.11 MPa to 1.05 MPa (similar to polymeric foams-like to soft rubbers), while the loss modulus was increased 30-foldfrom 0.0105 MPa to 0.322 MPa. It is in terms of 30-fold increase in the amount of dissipative energy. As a result, the damping ratio was increased from ~0.1 to 0.32[2]. This unique phenomenon was explained by the zipping and unzipping of carbon nanotubes at contacts as the cause of the viscoelasticity. The storage and damping ratio were supposed to scale as the contact density and the contact length, both of which were observed to be increased with the material density. This could be the reason for the increases in the elastic and viscous aspects in tandem. Furthermore, the thermal stability of CNTs and working mechanism created a new group of materials on the Ashby map which is compliant (soft) and yet operates at high and low temperatures. These results represent important and significant improvement in the well-established field of viscoelasticity, which is promising to unlock possibilities by overcoming the obstacles of conventional materials.

[1] M. X., D. N. F., T. Y., M. Y., K. H., *Science*, **330**, 1364-1368, (2010).
[2] M. X., D. N. F., M. Y., K. H., Submitted

Improved Properties of Adhesives By Integration Of Carbon Nanotubes

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To achieve special electrical and mechanical properties of carbon nanotubes in other materials a preferably homogenous dispersion of the nanofiller within the polymer is required. At a given concentration the increase of the CNT dispersion can have a positive effect on the electrical conductivity. Different authors report about the behavior of CNTs in polymeric matrices and about their tendency to form micrometer sized bundles or agglomerates that negatively affect the mechanical properties of the composites because they act as imperfections in mechanical tests. In case of a homogenous dispersion an improvement of the mechanical properties can also be achieved. In this study we dispersed CNTs into epoxy resins and acrylates. Furthermore we compared different types of nanotubes. The aim was to improve the property balance of the entire system and to compare the influence of different types of nanotubes. Such composites may be used to enhance the cohesion and to achieve flexible and more stable bondings of metals, glass, plastics and textiles. Different methods are used commonly for inserting carbon nanotubes into adhesives with high or low viscosity. We chose methods such as calendering and high pressure dispersing to integrate nanoparticles within the matrices and to achieve homogenous and stable dispersions. Using light microscopy and SEM the distribution of the particles within the matrix and the quality of the dispersions were investigated. Furthermore to characterise the quality of the dispersions oscillatory measurements were performed. Curing tests were performed to demonstrate the changing behaviour of the adhesive dependent from the filler content. Measuring electrical conductivity resulted in the electrical percolation starting underneath 0.1 wt.-%. Further with increasing CNT content at about 3 wt.-% conductivity increases to values in the conductive range (>10-1 S/cm). Between 0.01 and 0.5wt.-% the materials exhibit antistatic behaviour. Through this we demonstrated that filling epoxies with Carbon Nanotubes improves the conductivity. Mechanical test of the composites have been done for investigations of reinforcement by the nanoparticles. Adhesion tests were done for characterization of the adhesion and cohesion between adhesive and adherend.

Electrical Properties of the Composite Consisted of Multi-Layer Graphene and Multi-Walled Carbon Nanotubes

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A novel carbon structure composed of multi-layer graphene and aligned multi-walled carbon nanotubes (MWNTs) has been discovered and reported previously [1]. This unique structure has multi-layer graphene spontaneously grown on the top of aligned MWNTs. The top film-like part has a flat surface, implying that the composite may have a better electrical contact with an electrode than a bundle of MWNTs when used as vertical interconnect for LSI [2]. In this work, we have investigated the electrical properties of the composite and the electronic structures of the interface between the composite and metal electrodes.

The composite was obtained by chemical vapor deposition (CVD), as described elsewhere in detail [1]. As the carbon source, a mixture of acetylene and argon gases was introduced into the CVD chamber. The substrate temperature was 510 °C during the CVD process. The current-voltage measurements of the composite were done for vertical interconnects (vias) connecting the upper electrode (Cu/Ti) and lower electrode (TiN/Cu). For comparison, similar measurements for vertical interconnects made of a bundle of MWNTs were also performed. The average electrical resistance of >10 composite vias was found to be one third of that of MWNTs. To understand this difference, the interface between the upper flat part of the composite and the electrode (Ti) was investigated by using hard x-ray photoemission spectroscopy (PES). The PES measurements were performed at the BL47XU in the SPring-8 (2007A1912). The PES spectra of the composite indicate that the titanium carbide (TiC) was formed at the interface, although the Ti film was partly oxidized. On the other hand, the Ti film deposited on the usual MWNTs was mostly oxidized. Taking into account the fact that TiC is known to form ohmic contact with nanotubes, the result indicates that the composite has better electrical contact with the metal electrode, which supports the results for the electrical resistance.

[1] D. Kondo, S. Sato, and Y. Awano, *Appl. Phys. Express*, **1**, 0740031, (2008).
[2] M. Nihei, A. Kawabata, D. Kondo, M. Horibe, S. Sato, and Y. Awano, *Jpn. J. Appl. Phys.*, **44** 1626, (2005).

Studying Chiral Selective Reactivity of SWNTs

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Individual semiconducting Single-Walled Carbon Nanotubes (SWCNTs) emit band-gap photoluminescence (PL) in the near-infrared (NIR). [1] This fact is particularly interesting for biosensing because NIR radiation is not absorbed by biological tissue, and hence can be used for biosensing within biological samples or organisms. However, a strong suppression of PL has been observed when SWNT sidewalls are perturbed by chemical reactions. [2] Although this quenching phenomenon has hampered the use of covalently derivatized SWNTs as near-infrared (near-IR) fluorophores, it can also provide a method for sensing and studying single-molecule chemical reactions with individual SWCNTs. [3]
In this study we present preliminary results that show changes in the optical properties of the tubes related to the type of chemical reaction that introduces the sidewall electronic perturbation. Different SWCNT derivatives have been synthesized using two synthetic processes: 1,3-dipolar cycloaddition and radical addition of anilines. These reactions were carried out under microwave irradiation. [4] The series of derivatives have been characterized using TGA analyses, Transmission Electron Microscopy and Raman spectroscopy. With the aim of studying the optical properties of these materials Fluorescence and Raman measurements were performed. Interesting results are noticed: Cycloaddition and radical addition may show different chiral selectivity.

[1] M. J. O'Connell, S. M. Bachilo, C. B. Huffman, V. C. Moore, M. S. Strano, E. H. Haroz K. L. Rialon, P. J. Boul, W. H. Noon, C. Kittrell, J. Ma, R. H. Hauge, R. B. Weisman, R. E. Smalley, *Science*, **297**, 593-596, (2002).
[2] M. L. Usrey, E. S. Lippmann, M. S. Strano, *J. Am. Chem. Soc.*, **127**, 16129-16135, (2005).
[3] L. Cognet,D. A. Tsyboulski, J. D. R. Rocha, C. D.Doyle, J. M. Tour, R. B. Weisman, *Science*, **316**, 1465-1468, (2007).
[4] a) F. G. Brunetti, M. A. Herrero, J. de M. Muñoz, S. Giordani, A. Díaz-Ortiz, S. Filippone, G. Ruaro, M. Meneghetti, M. Prato, E. Vázquez, *J. Am. Chem. Soc.*, **129**, 14580- 14581, (2007); b) N. Rubio, M. A. Herrero, A. de la Hoz, M. Meneghetti, M. Prato, E. Vázquez, *Org. Biomol. Chem.*, **8**, 1936-1942, (2010).

Surfactant Screening for Metal/semiconductor Separation of Carbon Nanotubes

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There are two electric types of single wall carbon nanotubes (SWCNTs), metallic (M) and semiconducting (S) ones. Among the M/S separation methods using surfactants in an aqueous solution, sodium dodecyl sulfate (SDS) plays a key role in density gradient ultracentrifugation (DGU) [1] and agarose gel separation [2-4]. In this study, we screened various surfactants for the M/S separation and newly found a few surfactants which can be used for DGU and agarose gel separation. Gel centrifugation method using agarose was applied for the high-throughput screening because the method was suitable for multiple and micro separation. From 96 kinds of amphiphiles in the first screening, two surfactants were found to show a slight M/S separation. From the common feature of these surfactants and SDS, i.e. straight alkyl tail and charged head group, several kinds of surfactants were selected and used for the second screening, resulting that three kinds of surfactants were newly discovered. Especially, the M/S purity after the separation using sodium dodecanesulfonate was almost same with the case of SDS. Some of these surfactants could also be used for the M/S separation by DGU.

[1] M. Arnold et al., *Nature nanotech*, **1**, 60-65, (2006).
[2] T. Tanaka et al., *Appl. Phys. Express*, **1**, 114001-1-3, (2008).
[3] T. Tanaka et al., *Nano Lett.*, **9**, 1497-1500, (2009).
[4] T. Tanaka et al., *Appl. Phys. Express*, **2**, 125002-1-3, (2009).

Displacement Measurement of a Carbon Nanotube Cantilever in Liquid for Protein Interaction Force Sensing

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We demonstrated the displacement measurement of cantilevered nanotubes, and performed the measurement of interaction forces between proteins using optical detection technique under light microscopy.[1] Since the typical spring constant of the nanotubes synthesized by chemical vapor deposition is around 10^{-4} N/m, ultrasensitive force detection is expected using a nanotubes cantilever. However, cantilevers with low spring constant suffer from the thermal vibration in an aqueous solution, causing the instability and thus less sensitivity of the measurement. Therefore, prior to the force measurement between proteins, we estimated the detection sensitivity and stability of cantilevered nanotubes by our optical detection system. The measurement of the nanotube displacement was performed by irradiating the nanotube tip with a laser, and by capturing the scattered light from the tip with a CCD camera. The Gaussian peak of sectional profile of the nanotube tip with respect to the video frame showed the standard deviation of 14 nm, indicating that the resolution for the deflection detection can be achieved to be more than 14 nm in our setup in water. The measurement of interaction forces between proteins were measured by using proteins attached to the tungsten tip and di-imide-activated nanotube tip. [2] The proteins crosslinked between the tungsten and nanotube tips were pulled to measure the interaction force by retracting the tungsten tip. The displacement of the nanotube tip was 156±14 nm when the nanotube detached the tungsten tip. By using the parameters of 9 µm and 70 nm as the length and diameter of the nanotube used in this study, the spring constant was calculated to be 1.0 mN/m. Taken these together, the force was estimated to be 150 pN,

indicating the force required to break weak bonds such as ionic bonds between proteins, since the force required to break the covalent bond of crosslinked proteins is much greater (~6.5 nN) than the interaction force obtained in the experiment.[3]

[1] S. Sawano et al., *Nano Lett.* **10**, 3395, (2010).
[2] W. J. Huang et al., *Nano Lett.* **2**, 311, (2002).
[3] H. Maruyama et al., *J Appl. Phys.*, **102**, 094701, (2007).

Optical Properties of Few-walled Boron Nitride Nanotubes by Photoconductivity Measurements

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Boron nitride (BN) nanotubes have been considered as wide band gap semiconductors mostly insensitive to diameter and chirality change. They exhibit strong luminescence spectra in the spectral range of 200 to 250 nm [1]. These characteristics are promising for various optoelectronic devices in the deep ultraviolet range, namely in the field of photo-detection or light-emitting sources [2].

In this presentation, in addition to previous works [3, 4], hBN, multi-wall and well-crystallized few-walled BN nanotubes are studied through photoconductivity experiments in the UV spectral range. The morphology and structures of the samples were characterized by high-resolution transmission electron microscopy (HR-TEM, Zeiss Libra FE). Results of photoconductivity are interpreted with the help of photoluminescence (PL) and excitation of photoluminescence (PLE) experiments performed on the same samples. PL measurements were using a dedicated PL set up with an excitation at 193 nm and PLE experiments were performed at Bessy synchrotron facility. The experimental setup of the photoconductivity experiments consists in exciting the sample using an UV lamp coupled to a monochromator in order to tune the output excitation wavelength (spectral resolution of 1 nm at best). The sample consists in a film of few-wall BN nanotubes deposited on an electronic device with interdigited electrodes ranging from 1 to 10 μm. The photocurrent induced in the material by the excitation light is recorded by a sourcemeter, which also apply a constant bias voltage through two tungsten tips onto the sample.

It will be shown that photoconductivity experiments provide indirect measurements of the sample's optical absorption, which allow complementary interpretation of the optical transitions in BN nanotubes since the exact band gap and optical properties of BN nanotubes are still in dispute.

[1] P. Jaffrennou,J. Barjon,T. Schmid,L. Museur,A. Kanaev,J.-S. Lauret,C. Y. Zhi,C. Tang,Y. Bando,D. Golberg,B. Attal-Tretout,F. Ducastelle, and A. Loiseau, *Phys. Rev. B*, **27**, 235422, (2008).

[2] L. H. Li, Y. Chen, M.-Y. Lin, A. M. Glushenkov, B. M. Cheng, and J. Yu, *Appl. Phys. Lett.*, **97**, 141104, (2010).
[3] G. Brasse, S. Maine, A. Pierret, P. Jaffrennou, B. Attal-Trétout, F. Ducastelle, A. Loiseau, *Phys. Status Solidi B*, **247**, 3076, (2010).
[4] K. Watanabe, T. Taniguchiand H. Kanda, *Nature Materials*, **3**, 404, (2004).

Growth And Phase Composition Of Iron-Filled MWCNT Obtained By Thermal Decomposition Of Ferrocene

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Iron-filled multiwall carbon nanotubes were produced by pyrolysis of a C_{60} fullerene and ferrocene ($(C_5H_5)_2Fe$) mixture. X-ray diffraction analysis has shown that, together with the more common α-Fe, Fe_2O_3, C (graphite) and Fe_3C, an unknown phase is present. Indeed three unlabeled peaks are present at low angles($2\theta < 22^o$).These three peaks seem to correspond to the fullerene C_{60} and it would be easy to think that they can be due to the residue that was not consumed in the CNT formation; although no evidence of C_{60} was found during the TEM analysis. Furthermore an attempt was made to match the unlabeled peaks with the less stable iron carbides, including the known, but rarely observed, Fe_5C_2 and Fe_7C_3. None of these correspond to the values observed. Detailed elemental analysis revealed the presence of 5 main elements: Fe, C, O, Si; however it seems clear that Si and O are not in the core of the carbon nanotubes. In fact, in the majority of cases the percentage of O and Si is similar to the percentage that was found in the carbon film on the top of the Cu grid used for the preparation of the TEM samples. We also observed that iron oxides are not in the cores of the nanotubes but, more interestingly, seem to grow from metal particles that were not covered with graphite shells. Furthermore, carbon shells provide protection against oxidation, so an iron particle without graphite shells will be easily exposed to oxidation conditions. In agreement with previous reports, it is apparent that some intermediate iron carbide phases seem to play an important role in the growth mechanism [1-2]. Moreover TEM analysis reveals important information related to the morphology of the nanotubes. Together with the more common straight nanotubes, filled carbon nanoparticles were observed in the sample. Interestingly in 1998 P.J.F. Harris [3] described a method to obtain filled carbon nanoparticles carrying out high-temperature heat treatments on microporous carbons, which had been impregnated with molybdenum, uranium and cobalt. Curiously, in addition to the combined growth mode, in many cases is possible to see the formation of branches commonly referred to as the open growth mode. Departing from the formation of a single nanotube, iron particles seem to catalyze the growth of more nanotubes connected to each other in a branch like structure.

[1] D. Golberg et al. *Acta Materialia* **54**, 2567-2576, (2006).
[2] C. Müller et al. *Phys. Stat. Sol. (a)* **203**, 6, 1064-1068 (2006).
[3] P.J.F. Harris, S.C. Tsang *Chemical Physics Letters*, 293,53-58, (1998).

A Test Vehicle for RF/DC Evaluation and Destructive Testing Of Vertically Grown Nanostructures (VGCNS)

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We have developed an RF test vehicle suitable for measuring DC and microwave performance of vertically grown carbon nanostructures (VGCNS) as via-interconnects. A first version of the interconnect test vehicles devices were designed, fabricated and characterized. The RF small signal (S-parameter) and large signal measurements show that carbon nanofibres can be used as interconnects in microwave circuit, even for power devices.

The design of test vehicle employs a three metal layer concept, forming sequentially the ground, signal and device under test structures for characterization in a microstrip configuration. The structures as such consisted of interconnects of dimensions ranging from 50 nm to 100 µm diameter made of VGCNS. In the first version of the interconnect test vehicles, the interconnects were made of carbon nanofibers grown at 450 C. From SEM measurement we found that the resulting height was around 1.5-2 µm. Epoxy polymer SU-8 was employed by spinning on the device and a subsequent etch back process was carried out to open up the tip of the fibres to connect to consecutive interconnects with the third metallisation layer. After growing the nanofibres, it was observed, using SEM, that interconnect sizes smaller than 10 µm diameter suffered from parasitic growth and therefore the effective device dimension deviated from the initial design.

We carried out small signal measurements using a vector network analyser for frequency ranging from 1 to 25 GHz, in order to characterise the transmission and reflection/absorption of the devices as function of their diameter size. The large signal evaluation was performed by measuring the gain compression of the devices. In addition destructive tests, aiming at testing the current carrying capability of the interconnect, have also been performed.

The resistivity of interconnects was measured to vary varies from 0.2 µΩ·mm-1.3 mΩ·mm. Apparently, the device performance is considerably influenced by the fill factor of the interconnect with VGCNS. Small variations in fill factor (in %) provided a large variations in device resistivity.

Furthermore, it was also observed that the resistance drops at higher power levels. RF conductivity of interconnects ranges from $5x10^3$ S/m to $7x10^5$ S/m.

The average input power before interconnect destruction is larger than 25W with effective device diameter ranging from 3 µm to 100 µm interconnects. In addition, the average gain compression before interconnect destruction was found to be 0.6 dB.

It was not possible to extract the conductivity value of an individual nanofiber using comparison to simulation data, since the devices might have suffered from parasitic growth as well as pinhole metal diffusion during top metal contact formation. This certainly affects the actual device dimension and properties. Nevertheless, the proof of concept of design and manufacturing a test vehicle for RF measurements of vertically grown nanostructures was achieved. We will report the findings and anomalies in the measured devices. Further improvement is expected in the coming test vehicle version.

Control of SWNT Synthesis by Self Assembled Monolayer for Realizing Transistors

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The application of CNTs to nano-electronics requires an ability to control CNTs growth in terms of diameter and chirality, since their electronic properties are determined by the chirality of the tubular structure. In this work, we report a new method to control the surface density of a catalyst nanoparticles using self assembled monolayer (SAM). The catalyst was prepared in two steps: (i) the growth substrate is functionalized by silanisation, leading to the formation of a pyridine terminated molecular monolayer. (ii) Self assembled monolayers (SAM) of metallic complexes (Ru, Co, Fe porphyrin) or salts ($FeCl_3$, $RuCl_3$) are then obtained by coordination between the ions and the pyridine groups pointing outwards the surface. This method allows to control the size and the surface density of the catalytic metallic nanoparticules formed through a subsequently annealing step. Exposing these catalysts to the HFCVD (hot filament chemical vapour deposition) conditions can further allow some control on the SWNTs diameters, their surface density and eventually to a certain selectivity of their chirality.

The SWCNTs growth was carried on Ru porphyrin, $FeCl_3$ and $RuCl_3$ catalysts via HFCVD with two independent W filaments for the carbon precursor (methane) and the hydrogen dissociation respectively. The morphologies of the CNTs on Si substrates were characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and micro-Raman spectroscopy. The results show the formation of high quality SWNTs with a control of their diameters and their surface density. Transport measurements revealed that the SWNTs obtained from Ru porphyrin and FeCl3 are mostly semiconducting behaviour as proven by connecting them into CNT-FET devices which show impressive characteristics with on/of current ratio of $>10^7$. By contrast, SWNTs obtained from $RuCl_3$ salts exhibit mostly as metallic nanotubes without applying any sorting technique.

Dynamical Behaviour Of 5T Molecule Encapsulated In Carbon Nanotubes Observed by Aberration-Corrected HRTEM

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Despite the recent progress in nano-electronics with SWNTs as active material [1], such devices are limited to the near-infrared region due to the intrinsically small band gaps of SWNTs. The encapsulation of molecules (peas) makes SWNTs optically active in the visible spectra range and allows tuning the properties of new hybrids as well as keeping the physical properties of SWNTs. Recently, the very first peapods with photoluminescence (PL) emission in the visible spectral range have been demonstrated by our team [2, 3] by encapsulating α-sexithiophene (6T) inside SWNTs.

Aberration-corrected high-resolution transmission microscopy (AC-HRTEM) is the only direct technique to observe the nanotubes together with the encapsulated molecules. We used FEI Titan 80-300 high- resolution transmission electron microscope equipped with a CEOS-designed hexapole-based aberration corrector for the image-forming lens operated at 80 kV. This way, the electron knock-on damage to the sample was reduced. We present images slightly under-focused in order to enhance the contrast of the molecule inside the SWNT. The results obtained were compared with HRTEM image simulations, which were performed with a standard multislice procedure [4].

Here we present the behaviour of α-quinquethiophene (5T) molecule inside the SWNTs that is representative for series of oligothiophenes, namely, 4T,5T and 6T. Extensive washing followed the peapod synthesis in order to remove non-encapsulated molecules.

AC-HRTEM images revealed successful encapsulation of the oligomers together with the fact two arrays of 5T molecules accommodate along the sidewalls of the tube. Evaluation of time-dependent micrograph series shows that the distance between the 5T molecules inside the tube varies over the period of observation. However, the distance between the 5T molecule and the tube wall seems to be stable. Image simulations were done for two configurations of straight 5T molecules – parallel and perpendicular with respect to the electron beam. We can conclude that 5T molecules bend and rotate inside the tube during the observation.

[1] J. A. Misewich, R. Martel, Ph. Avouris, J. C. Tsang, S. Heinze, J. Tersoff, *Science*, **300**, 783- 786, (2003).
[2] M. A. Loi, J. Gao, F. Cordella, P. Blondeau, E. Menna, B. Bártová, Cécile Hébert, S. Lazar, G. A. Botton, M. Milko, Claudia Ambrosch-Draxl, *Adv. Mater.*, 22, 1635-1639, (2010).
[3] K. Yanagi, H. Kataura, *Nat. Photonics*, **4**, 200-201, (2010).
[4] Stadelmann P.A., JEMS,

http://cimewww.epfl.ch/people/stadelmann/jemsWebSite/jems.html, EPFL, Lausanne

Strong MWCNT Spun Fibers by Spinning Millimeter Scale MWCNT Array

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Carbon nanotube (CNT) has good mechanical property, for example, reported tensile strength of individual multi walled CNT (MWCNT) is 150 GPa [1]. Therefore, CNTs are expected to be used in light weight and high strength materials, and CNT composites have been researched by many researchers [2,3]. Recently, dry spinning from a MWCNT array has been reported. MWCNT spun fibers are fabricated without using binder materials. One of good things of the method is that large-scale and highly aligned CNT structures are easily formed. Tensile strength of MWCNT spun fibers was reported to be 100-1000 MPa [4-6]. However, according to the theory of fiber spinning [7], MWCNT spun fiber is expected to have higher strength than at least 10 GPa. In the present work, we fabricated MWCNT spun fibers by spinning millimeter scale MWCNT arrays and investigated post-spin processes to improve mechanical properties. Research purpose is to achieve strong MWCNT fibers.

We invented a chemical vapor deposition method to grow ultra-long and highly spinnable MWCNT arrays [8, 9]. This MWCNT growth method uses $FeCl_2$ powder as a precursor for Fe catalyst. The MWCNT arrays were grown at 835 °C. The highly spinnable array of 3 mm in height was grown in 30 min with the high growth rate over 0.1mm/min. Every array is endlessly drawable. It is very easy to draw a long-lasting MWCNT web, which is a two dimensional MWCNTs network. Web length exceeds over 60 m from a 4 cm-long substrate. In the present study, MWCNT fibers were fabricated with twisting webs. To form spun fibers, no binder material was used. To study the relation between tensile strength and aspect ratio of MWCNTs, length of MWCNTs was varied from 1.0 mm to 2.5 mm. The spun fiber diameters were ranging from 20 um to 30 um. With increasing the MWCNT length, tensile strength increased monotonically from 250 MPa to 550 MPa. Longer MWCNTs have an advantage for a strong fiber because large contact areas result in strong Van der Waals connections each other MWCNTs. We achieved high tensile strength of 1.0 GPa and high young's modulus of 60 GPa in this work, with using 2.5 mm-high MWCNT. We found that an as-spun fiber has low tensile strength because of a number of spaces in the fiber, and so post-spin processes which decrease the spaces in the fiber are important to improve the mechanical properties.

[1] B. G. Demczyk et al, *Mater. Sci. Eng,* A334, 173, (2002).
[2] D. Qian et al, *Appl Phys Lett*, **76**, 15, (2000).
[3] E. T. Thostenson et al, *J. Phys. D: Appl. Phys*, **35**, L77-L80, (2002).
[4] K. Liu et al, *Nanotechnology*, 21, 045708, (2010).
[5] C. D. Tran et al, *Carbon*, **47**, 2662-2670, (2009).
[6] M. Zhang et al, *Science*, **306**, 1358, (2004).
[7] J. W. S. Hearle et al, *Structural mechanics of fibers, yarns, and fabrics, Wiley- Interscience, New York*, (1965).
[8] Y. Inoue et al, *Appl. Phys Lett*, **92**, 213113, (2008).
[9] Y. Inoue et al, *Carbon*, **49**, 2437-2443, (2011).

Direct Synthesis of Single-walled Carbon Nanotube Containing Platinum Group Metal

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Owing to its large specific surface area, physical and chemical stability, single-walled carbon nanotube (SWCNT) is one of the most attractive materials. To prepare homogeneous nanoparticles is a key issue for catalytic reaction because it directly connects to the control of the reaction. Using the sidewall of SWCNT as a catalyst supporter, the size of nanoparticle can be controlled, because the particle size should be determined by the interaction between SWCNT and metal species and its curvature. In the meanwhile, because SWCNT has a huge space in itself, the space was expected to be used as hydrogen storage. Referring to the theoretical and experimental study, its absorption ratio seems to be fairly expectant at 77 K; on the other hand, at RT it seems to be far below the goal suggested by DOE. For this matter, metal species are expected to enhance the absorption ratio by inducing a chemisorption. This study focused on the possibilities of synthesizing platinum group metal nanoparticles on/in SWCNT. Even though the case of metal on SWCNT has been reported by dispersion of platinum particles on SWCNT after its synthesis. However, these methods are not suitable for bulk synthesis. Thus, the primary purpose of this study is to examine the effect of platinum group elements on synthesizing carbon nanotubes. Then, another purpose of this study is to investigate how to synthesize SWCNT containing platinum group elements by methane CVD for bulk synthesis. First, we added platinum group elements into Fe/Mo conventional catalyst supported on alumina, and also examined platinum group element itself as a mono catalyst. As a result, adding an adequate amount of platinum group metals into catalysts never disturbs the synthesis of SWCNT. Referring to TGA measurement, the presence of metal attached and/or metal involved SWCNT is suggested. Furthermore, SEM images indicate many nanoparticles are on SWCNT. When ruthenium catalyst is used, ruthenium nanoparticles are observed on the surface of nano carbon materials, which looks like SWCNT. These results indicate the possibility that SWCNT containing platinum group metal nanoparticles may be synthesized by methane CVD.

Effect of Chemical Reduction on the Gas Diffusivity and Solubility of a Polymer/Graphene Oxide Composite Films

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We investigated the oxygen-barrier property of poly(vinyl alcohol) (PVA)/graphene oxide composite films. We employed various analytical techniques, including DSC, XRD, TEM, SEM, XPS, and oxygen transmittance measurement system. We demonstrated that the gas barrier property of GO is drastically modified by the chemical reduction of GO. We also showed that the change of oxygen diffusivity and solubility in PVA/GO and PVA/RGO composites are mainly attributed to the degree of flattening of wrinkled-GO structure which is originated from the degree of C/O atomic ratio.

Electric Field Effect on the Electroluminescence of the ZnS Phosphor-CNT Composite

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Inorganic powder electroluminescence (EL) is considered to be one of potential candidates in future flat panel displays and illumination applications, primarily due to its potential for simple fabricating process, scalability to large size, and low cost [1].In general, EL is defined as emitting light under the high electric field without thermal generation. Although the EL devices have various advantages, the application of AC powder or thick-film EL devices is confined, such as backlighting in cellular phones. Relatively insufficient brightness compared to other kinds of flat panel displays is one of key reasons for the limited application. Many factors for practical applications are required to optimize low brightness, relatively short lifetime, and high operation voltages. A new trial to improve the EL performance through the action of the field enhancement in a device has been exhorted. Bae [2] et al. observed enhancement in the EL emission in ZnS:Cu,Al cathodoluminescence phosphor powder by mixing carbon nanotube (CNT) with phosphor powder. Field enhancement by CNTs could affect the EL performance. CNTs have been considered to be very good field emitter sources for high aspect ratio and unique electric-properties, which yielded to CNT-based field emission displays [3]. To incorporate CNTs as an electrical conducting phase into a polymer was reported for the purpose of improving the dielectric properties by the action of many of microcapacitors in the CNT composite [4]. However, this might easily lead to an electric short or high current flow due to the formation of the CNT network. Consequently, modifying the properties of CNTs is necessary in an emitting layer in EL devices to utilize the electric field around CNTs.ZnS:Cu,Cl powder EL devices were fabricated using CNTs, which were shortened by the cryogenic crushing method [5]. The shortened CNTs were mixed in an emitting layer of the EL device, which might yield to an increase in luminance and efficiency of EL devices through enhanced electron tunneling and acceleration into a ZnS host material [5]. At the driving voltage of150 V, the phosphor-CNT composite EL device after the aging treatment showed a 60% increase inefficiency. The underlying mechanism for the role of CNTs will be explained in the conference.

[1] Y. A. Ono, *Electroluminescent Displays* World Scientific, Singapore, (1995).
[2] M. J. Bae and et. al., *Appl. Phys. Lett.*, **95**, 071901_1-3, (2009).
[3] I.T. Han and et. al., *Appl. Phys. Lett.*, **81**, 2070-2072, (2002).
[4] Z.-M. Dang and et. al., *Appl. Phys. Lett.*,**90**, 012907_1-3, (2007).
[5] J. Lee and et. al.,Carbon, 44,, 2984-2989 (2006).
[6] J.-Y. Kim and et. Al., *IEEE Electron Dev. Lett.*, **31**, 1269-1271, (2010).

Sorting Out Empty and Water-Filled Carbon Nanotubes

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The unusually efficient solubilization of carbon nanotubes using bile salt surfactants (=cholates or steroid surfactants)[1] has enabled major advances in their processing and purification,[2] as well as their spectroscopic study. The regular, unperturbing micellar coating yields much narrower spectral line widths than other surfactants,[1] which has allowed us to resolve the radial breathing modes of empty (end-capped) and water-filled (opened) SWCNTs, thus revealing that both coexist in aqueous solutions.[3,4] Simple chemical treatments (air oxidation and acid treatment) and mechanical treatments (ultrasonication, or even stirring) turn out to yield complete or partial opening of SWCNTs respectively. We now show that empty and water-filled CNTs can be separated, and the empty tubes allow enhanced diameter sorting by density gradient ultracentrifugation (DGU). The empty tubes display a reversed dependence of buoyant density on diameter (with larger diameter tubes floating up) compared to the more commonly used open (water-filled) SWCNTs,[5] thus explaining the counterintuitive order of diameter-sorting in previous DGU work. The newly isolated empty nanotubes turn out to possess far more ideal, unperturbed properties. The pristine empty tubes not only have the largest possible aspect ratios, but also display much more efficient band-gap emission, larger Raman cross-sections, and sharper electronic and vibrational resonances.[5]

[1] W. Wenseleers, I.I. Vlasov, E. Goovaerts, E.D. Obraztsova, A.S. Lobach, A. Bouwen, *Adv. Funct. Mater.*,**14**, 1105, (2004).
[2] M.S. Arnold, A.A. Green, J.F. Hulvat, S.I. Stupp, M.C. Hersam, *Nature Nanotechnol.*,**1**, 60, (2006).
[3] W. Wenseleers, S. Cambré, J. Čulin, A. Bouwen, E. Goovaerts, *Adv. Mater.*,**19**, 2274, (2007).
[4] S. Cambré, B. Schoeters, S. Luyckx, E. Goovaerts, W. Wenseleers, *Phys. Rev. Lett.*,**104**, 207401 (2010).
[5] S. Cambré, W. Wenseleers, *Angew. Chem. Int. Ed.*, **50**, 2764-2786, (2011).

Separation of Single Walled Carbon Nanotubes. A Scalable and Non Destructive Approach.

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The extraordinary electronic and optical properties of single walled carbon nanotubes (SWNTs) are determined by their structure; SWNTs are either metallic or semiconducting depending on their diameter and chirality [1]. Many valuable applications in, for example, transparent conductors, solar cells, biosensors and nanoelectronics, require nanotubes of specific electronic character and purity [2].

Current techniques for the separation of SWNTs into semiconducting and metallic species are only partially successful due to the difficulty in the dispersion of SWNTs [3] and separation occurs only on a limited scale. Before SWNTs can be separated the van der Waals forces that hold them together must be overcome; currently high power sonication is used in all cases to perform this separation. Sonication is known to damage the nanotubes and can destroy their unique properties. Here, using technology exclusively licensed from University College London Business (UCLB), we detail a fully scalable method of SWNT purification and separation based on the different susceptibilities of impurities, metallic SWNTs and semiconducting SWNTs to chemical reduction; involving no sonication.

Transferral of these reduced tubes as a dry powder to an organic solvent allows for the spontaneous dissolution of the most easily reduced fraction. By carefully controlling the metal to carbon ratio in the initial liquid ammonia reduction the spontaneously dissolved fraction can be tailored to contain predominantly metallic SWNTs, predominantly carbonaceous impurities or a representative sample of the raw SWNTs. In cases where the metal to carbon ratio is designed to selectively reduce metallic SWNTs, the remaining, undissolved fraction contains predominantly semiconducting SWNTs. It is important to note once again that no sonication and no centrifugation is used in this process.

[1] M. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, *Physics Reports-Review Section of Physics Letters*, **49**, 409, (2005).
[2] M. Arnold, A. Green, J. Hulvat, S. Stupp, M. Hersam, *Nature Nanotechnology*, **1**, 60, (2006).
[3] J. Bahr, E. Mickelson, M. Bronikowski, R. Smalley, *Chemical Communications*, **2**, 193, (2001).

Generic Techniques for The Large-Scale Integration Of Carbon Nanotubes

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One of the most challenging bottlenecks for the large-scale use of carbon nanotubes (CNT) is they integration. As the temperature required for their in situ growth is generally too high, it is thus mandatory to find efficient ways to pattern and manipulate them at low cost and wafer-scale. We propose here two ways of large-scale integration which have been proved to be useful for a wide range of applications from cell culture to microelectronics.

The patterning of CNT layer at the microscale is required for several engineering purposes. As an example CNT have been proved to be useful for the growth and differentiation of neuronal cells and their spatial localization in well defined areas. The use of microcontact printing has been optimized to create precisely patterned dense layers of double-walled CNT (DWNT)[1] on a flat surface. A microstructured silicone (PDMS) stamps inked (spray coating) with a suspension of DWNT dispersed in water using carboxymethylcellulose (CMC) was used to report DWNT layers on flat surfaces. With this technique a very flat layer of CNT may be deposited at wafer-scale along patterns of arbitrary shapes and dimensions in the micrometric range. When Neuronal cells were cultured on these specific patterns [2], adhesion was enhanced on the DWNT areas, and differentiation lead to neurite outgrowth guided by the DWNT patterns.

For microelectronics purposes, due to their very anisotropic properties, it is interesting to control the orientation of the CNT when deposited on a surface. This achievement cannot be obtained through the previous Micro Contact printing technique. To generate oriented deposition of CNT, a protocol based on dielectrophoresis (DEP) manipulations using buried electrodes and capillary assembly was developed. Electrodes are designed to create strong electric fields at very precise locations and over large arrays. The electrodes are then covered with a thin (300nm) insulating layer (Silicon Nitride). Then, a drop of purified DWNT suspension is deposited and an adapted electrical bias is applied between the electrodes using a function generator. The insulating layer avoids any contact between the CNT and the dielectrophoresis electrodes and prevents CNT to be stuck on the electrodes or to be damaged by a strong current. The next step is a careful pull out of the droplet from the insulating layer to avoid any disorientation of the CNT due to the capillary forces which are quite strong on the triple line (substrate/liquid/air). Using this technique, dense bundles of oriented CNT can be precisely localized and oriented at the wafer scale. Depending on the application, the CNT can then be transferred on another substrate by contact printing or directly used to connect individual pairs of electrodes. Finally, we have demonstrated the possibility to use this technique for the creation of large arrays of oriented DWNT suspended layers.

[1] E. Flahaut, et al., *Chem. Commun.*, 1442-1443 (2003).
[2] A. Beduer, L. Vaysse, E. Flahaut, F. Seichepine, I. Loubinoux, Ch. Vieu *Microelec. Eng., in the press, "Multi-scale engineering for neuronal cell growth and differentiation"*

Deposition of Aligned Carbon Nanotubes Using Fountain Pen Nanolithography

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The ability to controllably deposit aligned carbon nanotubes from solution onto chosen positions on a silicon substrate with sub-micron precision opens possibilities for a new method of creating carbon nanotube-containing electronic devices. One planned application is the study of electrical transport properties with plasmonically enhanced Raman spectroscopy, which requires devices comprising carbon nanotubes interfaced with plasmonic nanoantennas and electrodes. Here, the 'fountain pen nanolithography'[1]technique uses a nanopipette mounted within an atomic force microscope to deliver a solution containing dispersed single-walled carbon nanotubes to a silicon substrate. Different experimental parameters such as tip-speed and nanopipette size affect the deposition occurring when the tip is in contact with the surface. Atomic force microscopy has been used to examine the dimensions of the deposition. Polarised Raman spectroscopy[2] has been performed on the deposited lines containing carbon nanotubes. This has shown that an extremely high degree of alignment can be achieved in the carbon nanotubes deposited by this method.

[1] A. Lewis et al., *Appl. Phys. Lett.*,**75**, 2689-2691, (1999).
[2] J. A. Fagan et al., *Phys. Rev. Lett.*, **98**, 147402, (2007).

Selective Solubilisation and Individualization of Nanotubes in Aqueous Solutions of Inorganic Salts

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Here we show the potential for selective solubilisation and individualization of SWNTs in aqueous solution of an anionic surfactant (sodium cholate, SC) when combined with different inorganic salts, such as sodium sulphate, fluoride, chloride and iodide [1]. We observe that sodium chloride and sodium sulphate enhance the photoluminescence of SWNTs in comparison with the pristine SWNT-SC solution. On the other hand, sodium iodide causes photoluminescence quenching. These effects on SWNT solubilisation are tube diameter dependent. We attribute this to the water-mediated interactions between hydrophobic solutes and salt ions being sensitive to the solute size and shape and ion charge density [2,3]. In particular, small ions of high charge density are hydrated in solution and, as a result, interact unfavourably with hydrophobic solutes [2]. In contrast, large ions of low charge density associate with hydrophobic solutes to reduce the nanotube-surfactant hydrophobic interactions.

[1] F.Bonaccorso et al. Submitted, (2011).
[2] K.Collins, M.Washabaugh, *Quarterly Reviews of Biophysics*, **18**, 323-422, (1985).
[3]M. G. Cacace, E. M. Landau, and J. J. Ramsden, *Quarterly Reviews of Biophysics*, **30**, 241-277, (1997).

Self Assembly Of Lipid Nanostructures In Aligned Carbon Nanotubes

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Lipids, like other amphiphilic molecules, show a tendency to self-assemble into more or less complex aggregates when their concentration exceeds the critical micelle concentration. They are the main structures forming the cell membranes and their self assembly is crucial for the appropriate function of living organisms.
At the attempt of stabilizing carbon nanotube (CNT) suspensions, the adsorption of amphiphiles on the CNT surface has been studied before, particularly with the anionic surfactant SDS [1]. It was shown that their self-assembly on the CNT surface can follow the carbon pattern [1]. This suggests that – apart from stabilizing suspensions - CNTs could be used as orientation inducing substrates or templates for amphiphilic molecules. In this work we have investigated the self assemblies of biological lipid molecules in the presence of aligned arrays of carbon nanotubes, which include the surface adsorption as well as the assembly in the narrow channels between the nanotubes. We have observed various lyotropic nanostructures that are found for corresponding lipids in the bulk under dry and hydrated conditions. The structural studies were performed using small and wide angle X-ray scattering techniques. This work is most desirable for designing the nano-micro-fluidic architectures, novel composites, nanoscale devices, platforms for ultra-sensitive recognition of antibodies and supported model membranes.

[1] a) C. Richard et al., *Science*, **300**, 775-778, (2003); b) K. Yurekli et al., *JACS,* **126**, 9902-9903, (2004).

Electrochemically Functionalized Carbon Nanotubes and Graphene : From Device Applications to On-chip Nanobiosensors

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Carbon in both its one-dimensional (carbon nanotubes - CNTs) and two-dimensional (graphene) allotropic forms is emerging to be a major candidate for a number of on-chip device applications. Chemical functionalization routes designed to expand the spectrum of realizable applications bring in specialized properties that are unattainable in these systems in their pristine form. Our focus is on the use of electrochemistry both as a preparative and as an analytical tool for the design and operation of devices based on single-wall CNTs (SWCNTs) and graphene. The devices comprise of individual or few SWCNTs or reduced graphene oxide flakes contacted by electrodes working in a field-effect transistor configuration.

The first part will focus on the use of electrochemistry as a preparative tool, to functionalize the surface of contacted SWCNTs and graphene flakes. We have designed a generic route to attach a wide spectrum of receptors on to the surface of carbon nanostructures either in a covalent or non-covalent manner [1]. The receptors range from simple organic moieties through nanoparticles to biomolecules. In comparison to other approaches electrochemical modification (ECM) offers the specific advantage that the energy level of the chosen carbon nanostructure can be selectively tuned, allowing one to chemically or biologically tailor their surface properties in a very controlled manner [2]. The extent of functionalization can be controlled in situ by monitoring its conductance while performing ECM. In addition, only the addressed nanotubes are functionalized giving a very high site-specificity. Deploying this principle we demonstrate controlled modification of carbon nanotube networks resulting in purely semiconducting device characteristics. The advantages of using electrochemistry to modify electronic structure will be highlighted here in the context of other chemical functionalization methods.

The second part will deal with the use of functionalized carbon nanostructure devices as highly sensitive analytical tools for the detection of gaseous, chemical and biological species. Representative sensing paradigms will be presented : (a) hydrogen sensors based on Pd-nanoparticle decorated SWCNTs or graphene [3] (b) pH sensors with aniline moieties and (c) enzyme-free sugar sensors based on boronic acid receptors on the CNT surface [4]. The focus here is on the ability to tune the chemical nature of the receptor coupling to the carbon nanostructure and thereby have a good control over the functional interface. Electrochemistry allows us to switch this coupling between covalent and non-covalent without altering the binding characteristics of the receptor. For example, with covalently and non-covalently attached boronic acid receptors we corroborate in detail the transduction mechanism of our CNT sensors. The talk concludes with implications for future on-chip SWCNT chemical and bio sensors.

[1] K. Balasubramanian and M. Burghard, *J. Mater. Chem*, **18**, 3071, (2008).
[2] K. Balasubramanian, M. Burghard and K. Kern, *Phys. Chem. Chem. Phys*., **10**, 2256, (2008).
[3] R.S. Sundaram, C. Gomez-Navarro, K. Balasubramanian, M. Burghard and K. Kern, *Adv. Mater*. **20**, 3050, (2008).
[4] A. Vlandas, T. Kurkina, A. Ahmad, K. Kern and K. Balasubramanian, *Anal. Chem*., **82**, 6090 (2010).

Energetics and Electronic Structure of Encapsulated Single-Stranded DNA in Carbon Nanotubes

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Nanometer-scale tubular-spacing inside single-walled carbon nanotubes (SWCNTs) is inherently capable of accommodating foreign atoms molecules, leading to novel one-dimensional phases with unusual physical properties. Recently, single-stranded DNA (ssDNA) has been experimentally demonstrated to be encapsulated into the inside of SWCNTs. ssDNA is an amphiphilic biopolymer consisting of aromatic bases polymerized via hydrophilic backbone of sugar-phosphate groups. The energetics and electronic structures of the ssDNA-SWCNT hybrid systems are, however, still unclear. In order to provide theoretical insight into this novel bio/nano hybrid material, we here study the energetics of encapsulation of ssDNA in SWCNTs and electronic structures of the resulting ssDNA- SWCNTs hybrid systems on the basis of the density functional theory (DFT) [1].

As a structural model for the hybrid system, we consider infinite length of ssDNAs (poly-adenine, poly-guanine, poly-thymine, and poly-cytosine) encapsulated into SWCNTs.

Our DFT calculations clarify that the encapsulation reaction is exothermic for nanotubes with diameters greater than 1.33 nm. The energy gain is calculated to be in the range of 0.8–1.5 eV/nm, depending on tube diameter, base sequences, and ssDNA structure. In optimal ssDNA-SWCNT hybrid-system geometries, the polar groups of ssDNA, i.e. the POH moiety in its backbone, are located adjacent to the wall of the nanotube. The electronic structure of the hybrid system is qualitatively similar to a simple sum of those of an isolated ssDNA molecule and an empty SWCNT. However, detailed analysis of the electronic structure of the hybrid system reveals that the encapsulation of ssDNA into a SWCNT affects the electronic structures of both the ssDNA and the SWCNT.

[1] K. Kamiya and S. Okada, *Phys. Rev. B* , in press.

Carbon Nanomaterials as Catalysts for Hydrogen Desorption from Complex Metal Hydrides

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A key issue of complex metal hydrides for their application as hydrogen storage materials is the requirement of a catalyst to facilitate hydrogen uptake and release. One promising new class of such catalysing agents is constituted by carbon nanomaterials, in particular nanotubes and fullerenes. In a close collaboration with experimentalists, we have explored [1] how carbon nanostructures can act as catalysts for hydrogen release in the complex metal hydride sodium alanate ($NaAlH_4$). The stability of the AlH_4 moiety is due to the charge transfer from Na, resulting in an ionic bond between Na^+ and AlH_4^- and a strengthening of the covalent bond between Al and H. Interaction of $NaAlH_4$ with any electronegative substrate, such as a carbon nanotube or fullerene, affects the amount of charge donated from Na to AlH_4 and thus weakens the Al–H bonds, causing hydrogen to desorb at lower temperatures.
Further experiments [2] concentrated on the catalysing effects of fullerenes (C_{60}) for the hydrogen uptake and release in lithium borohydride ($LiBH_4$). In an effort to better understand the involved mechanism, we have carried out a detailed computational study of the interaction between $LiBH_4$ and C_{60}. Considering a stepwise removal of the hydrogen from $LiBH_4$, we find that the presence of C_{60} can lead to a substantial reduction of the involved H- removal energies. This effect is explained as a consequence of the interaction between the negatively charged borohydride complex and the C_{60} entity [3].
Finally, graphitic nanofibres (GNFs) represent another new promising class of materials for catalysing the dehydrogenation and rehydrogenation process in complex metal hydrides. Experiments considering both planar GNFs (PGNFs) and helical GNFs (HGNFs) have been carried out [4–6] and the results show that HGNFs posses superior catalytic activity over other carbon nanomaterials in improving the desorption kinetics and decreasing the desorption temperature of certain H-storage materials. We are again employing density functional theory calculations in an attempt to better understand this catalysing effect from first principles.

[1] P. A. Berseth, A. G. Harter, R. Zidan, A. Blomqvist, C. M. Araújo, R. H. Scheicher, R. Ahuja, and P. Jena, *Nano Lett.* **9**, 1501-1505, (2009).
[2] M. S. Wellons, P. A. Berseth, and R. Zidan, *Nanotechnology* **20**, 204022, (2009).
[3] R. H. Scheicher, S. Li, C. M. Araúo, A. Blomqvist, R. Ahuja, and P. Jena, *Nanotechnology,* under review, preprint arXiv:1102.2435
[4] M. S. L. Hudson, H. Raghubanshi, D. Pukazhselvan, and O. N. Srivastava, *Int. J. Hydrogen Energy* **35**, 2083-2090, (2010).
[5] H. Raghubanshi, M. S. L. Hudson, and O.N. Srivastava, *Int. J. Hydrogen Energy* **36**, 4482-4490, (2011).
[6] M. S. L. Hudson, H. Raghubanshi, D. Pukazhselvan, and O. N. Srivastava, *Int. J. Hydrogen Energy*, in press, DOI:10.1016/j.ijhydene.2011.03.006

Graphene Bubble as Adaptive Focus Lens

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Conventional zoom and focus optical systems require the precise mechanical movement of their components. Thus, these systems are complex, expensive, bulky and high power- consuming. Graphene is a two-dimensional material with unique properties. Most of the research has been concentrated on its electronic properties [1]. However, this material shows further remarkable properties: graphene is impermeable to every gas, it is very elastic, robust and optically transparent [2].

Here we investigate graphene bubbles as adaptive focus lenses. The bubbles are typically formed after graphene deposition and they have been characterized by Atomic Force Microscopy and Raman Spectroscopy. The bubbles have been also used as a prototype to study the Raman spectrum of graphene under biaxial strain: the G peak does not show any splitting, no large variation in the FWHM of the 2D peak is observed, or dependence in the Raman intensity on the light polarization [3], in contrast to uniaxial strain [4].

We show that it is possible to control the curvature of the bubble by applying a gate voltage. This makes graphene bubbles perfect candidates as lenses in mobile phone cameras, space-based camera systems and cheap devices.

[1] A. K. Geim, K. S. Novoselov, *Nature Mat.*, **6**, 183 (2007).
[2] A. K. Geim, *Science*, **324**, 1530, (2009).
[3] J. Zabel, R. R. Nair, T. Georgiou, P. Klar, K. S. Novoselov, C. Casiraghi, submitted
[4] T. M. G. Mohiuddin, A. Lombardo, R. R. Nair, A. Bonetti, G. Savini, R. Jalil, N. Bonini, D. M. Basko, C. Galiotis, N. Marzari, K. S. Novoselov, A. K. Geim and A. C. Ferrari, *Phys. Rev. B*, **79**, 205433, (2009).

Highly Efficient Exfoliation and Sorting of Graphite flakes

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We demonstrate high yield production of graphene in liquid phase [1] via low power sonication of graphite in sodium deoxycholate (SDC) followed by a separation in preparative ultracentrifugation. There are two main approaches to ultracentrifugation: sedimentation-based separation (SBS) and isopycnic separation. The former discriminates particles by their difference in mass. The latter exploits subtle density differences between particles in a density gradient medium [2,3]. A fracture mechanics model is presented to explain the exfoliation process. During sonication, the bubbles implosion imposes an inward radial fluid flow, which induces viscous forces on the graphite flakes [4]. Such forces must be sufficiently high for exfoliation, but low enough to avoid in-plane fracture, in order to produce large graphene flakes. Our results suggest that graphite exfoliation via sonication produces on average flakes with lateral sizes that increase with the number of layers. Thus the exploitation of SBS permits to obtain a separation based on the number of layers other than on their mass [5]. TEM and Raman spectroscopy indicate that ~65% of the flakes produced by SBS are monolayer with average size~600nm^2 [6,7]. Isopycnic separation, besides number of layers sorting, allows us to obtain larger flakes than SBS. The sorting strategy relies on the creation of density differences between graphite flakes with different number of layers. Surfactants provide this density variation [8]. We show that sorting by number of layers is strongly affected by the flakes surface/volume ratio and the coverage and clustering of the surfactant molecules. SDC is the most effective surfactant for exfoliation and sorting of graphite flakes, with ~60% of the flakes in the topmost fraction being monolayers, with average size 1μm^2.

[1] Y. Hernandez et al. *Nature Nano*, **3**, 563, (2008).
[2] M. S. Arnold et al., *Nature Nano*, **1**, 60, (2006).
[3] F. Bonaccorso et al., *Journal of Physical Chemistry C*, **114**, 17267, (2010).
[4] R. W. Fox, A. T. McDonald, P. J. Pritchard, *Introduction to Fluid Mechanic*, Wiley, 6 Edition ISBN 0471202312, (2003)
[5] F. Bonaccorso et al., submitted (2011).
[6] O.M. Marago’ et al., *ACS Nano*, **4**, 7515, (2010).
[7] F. Bonaccorso et al., *Nature Photonics*, **4**, 611, (2010).
[8] A. A. Green et al, *Nano Lett*. **9**, 4031, (2009).

Electrically Switchable, Flexible Smart Windows Using Graphene-based Transparent Conductors

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Scarcity, brittleness, processing limitations and fabrication costs of Indium Tin Oxide (ITO) are crucial limiting factors towards the development of flexible displays and electronics requiring flexible, transparent conducting electrodes (TCEs). Carbon nanotubes (CNTs) and graphene offer ideal TCE alternatives[1,2,3,4]. Both CNT and graphene liquid dispersions can be used in roll to roll (R2R) processing. The performance of CNT networks is limited by inter-tube junction resistance. This can be reduced by interspersed graphene flakes. A solution processable hybrid CNT-graphene conducting film is therefore an attractive proposition for R2R manufacturability of electronic devices requiring flexible TCEs.
Electrically switchable smart windows (ESSWs) employ liquid crystal (LC) droplets embedded in a polymer, sandwiched between two TC electrodes. An electric field controls the overall alignment direction of LC molecules, allowing light modulation through the device[5]. The TCE requirements for ESSWs is high transmittance (>80%) and low sheet resistance, typically in the range of ~1kΩ/□ or smaller [6].Here, we demonstrate an up- scalable CNT-graphene hybrids TCE for a smart window. We employ wire-wound rod coating for the liquid dispersions of CNTs and graphene on a polyethylene terephthalate (PET) substrate. The CNT-graphene hybrid coating has 1kΩ/□ sheet resistance, 94-97% transparency in the visible spectrum with <2% standard deviation in optical uniformity across ~200cm^2. The TCEs exhibit ~15% change in resistance when bent to a radius of 3.5mm in 10 cycles, far surpassing the ~25000% increase in a 60 Ω/□ ITO sample. A 120cm^2 flexible smart window is then fabricated. The device exhibits excellent electric field induced light transmittance (~60%) even under flexion. When OFF, the device transmits <0.25%, giving a >230 contrast ratio.

[1] F. Bonaccorso, et al., *Nat Photon*, **4**, 611, (2010).
[2] S. Bae, et al., *Nat Nano*, **5**, 574, (2010).
[3] G. Gruner, *J. Mater. Chem*. **16**, 3533, (2006).
[4] S. De, et al., *Small*, **6**, 458, (2010).
[5] J.L. Fergason US Patent 4435047, (1984).
[6] C.M. Lampert, *Sol. Energy Mater. Sol. Cells*, **52**, 207, (1998).

Wideband Tunable, High-power Ultrafast Lasers Mode-locked By Graphene

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Ultrafast passively mode-locked lasers with spectral tuning capability and high output power have widespread applications in biomedical research, spectroscopy and telecommunications [1,2]. Currently, the dominant technology is based on semiconductor saturable absorber mirrors (SESAMs) [2,3]. However, these typically have a narrow tuning range, and require complex fabrication and packaging [2,3]. A simple, cost-effective alternative is to use single wall carbon nanotubes (SWNTs) [4-9] and graphene [9-14]. Wide- band operation is possible using SWNTs with a wide diameter distribution [5,9]. However, SWNTs not in resonance are not used and may contribute to unwanted insertion losses [9]. The linear dispersion of the Dirac electrons in graphene offers an ideal solution for wideband ultrafast pulse generation [9-13,15].

Here, we report graphene saturable absorbers (GSA) for wide band tunable and high power ultrafast laser sources. Tunable ultrafast pulses are generated with an Erbium-doped fiber laser mode-locked byGSA [11]. The output wavelength is tunable from 1525nm to 1559nm.Even wider range tunability is feasible with broader filters[11]. The full width at half maximum (FWHM) spectral bandwidth is ~3nm. The output pulse duration is ~1ps. High power ultrafast pulses are generated using a solid-state laser. A Nd:YVO_4 crystal is employed as gain medium. The peak output wavelength is ~1064nm. The FWHM of the output spectrum is ~0.17nm. The average output power of the laser increases almost linearly with the pump power. The maximum average output power is ~1W at 2.6W pump power. The corresponding pulse energy is ~14nJ.

[1] Martin E. Fermann et.al., *Ultrafast Lasers Technology and Applications*, (2003).
[2] U. Keller, *Ultrafast solid-state lasers*. (Elsevier, Amsterdam, 2004).
[3] U. Keller, *Nature*, **424**, 831, (2003).
[4] S. Y. Set et al., in *Optical Fiber Communication Conference (OFC)*, (2003).
[5] F. Wang et al. *Nat. Nanotechnol*., **3**, 738, (2008).
[6] Z. Sun et.al., *Appl. Phys. Lett*., **95**, 253102, (2009).
[7] V. Scardaci et al.,*Adv. Mater*., **20**, 4040, (2008).
[8] E. J. R. Kelleher et al., *Appl. Phys. Lett*., **95**, 111108, (2009).
[9] T. Hasan et.al., *Adv. Mater*. **21**, 3874, (2009).
[10] Z. Sun et.al., *ACS Nano*, **4**, 803,(2010).
[11] Z. Sun et.al., *Nano Res*., **3**, 653, (2010).
[12] F. Bonaccorso et.al., *Nat. Photonics*, **4**, 611,(2010).
[13] D. Popa et.al.,*Appl. Phys. Lett*., **97**, 203106, (2010).
[14] D. Popa et al., *Appl. Phys. Lett*. **98**, 073106, (2011).
[15] A. K. Geim et al., *Nat. Mater*., **6**,183, (2007).

Functionalized Carbon Nanotubes: Comparative Study of Quantative Characterization Methods

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The use of carbon nanotubes (CNTs) in different applications is now still limited due to nonreactive nature of nanotubes surface and due to their agglomeration into micron-size structures during the growth. To overcome these problems, a functionalization of CNTs by changing their surface composition via introduction or addition of other elements or groups of elements has proved to be efficient. The functionalization can improve solubility and processibility of CNTs, and, so, allows combining of the unique properties of nanotubes with those of other types of materials.

An identification of the nature and the amount of functional groups introduced in CNTs is one of critical steps for the development of large scale application of functionalized nanotubes. This characterization is generally performed using Raman spectroscopy, X-ray photoelectron spectroscopy, electron microscopy combined with electron energy lost spectroscopy. These methods have high resolution, but they are costly for routine examination and their results sometimes are difficult to apply to the bulk material in general. Some of chemical methods such as titration and spectrophotometric methods are also applied in this field, but their using is often limited by physical adsorption of reagents by CNTs surface.

In the present work the comparison of the results of several methods in quantitative determination of functional groups has been performed to investigate their advantages and limitations. Multi-walled CNTs functionalized with N- and/or O-containing groups were characterized with using both physical and chemical methods to find the correlation between the results of different techniques.

Highly Conductive, Long-Range SWNT Network Structure Made by Wet Shear Dispersion

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Carbon nanotubes (CNT) have been studied as fillers in diverse multifunctional composites due to a wide range of the excellent properties. Dispersion technology of CNTs is challenging to realize commercial products such as coatings, heat sink, and structural members. Much efforts have been focused on dispersing CNTs individually into matrices, however, deterioration in CNT quality by damaging the surface and shortening was an inevitable problem [1].
Here we present long-range SWNT network structures comprised of long (hundreds of microns), flexible nanotubes, which can reach the electrical, thermal conductivity and mechanical robustness throughout matrices like polymers and metals. The SWNT network structures were made by dispersing as-grown SWNT forests in solvent through a shear from wet-jet mill, where mostly keeping the SWNT quality. The SWNT forests were synthesized by water-assisted CVD method ‘Super Growth’. First, the SWNT forest was suspended in solvent showing the configuration like trunks of a tree. To control the SWNT network structure, we applied different shears at 20-120 MPa on the wet dispersion. By the shear dispersion with vortex flow, the trunks (big nanotube bundles) were transformed into fine meshes. To observe the structure, the SWNT ensembles were discretely laid on a flat substrate. An SEM observation revealed that nanotubes spread continuously in each ensemble, which differs from a network through contacts of individually-dispersed nanotubes. The trunks from the starting SWNT forest were unravelled widely with the increased jet pressure, resulting in more SWNT ensembles as well as a reduction in the ensemble size. The SWNT ensembles ranged tens of microns to 1 mm in size. A digital microscope enabled the 3D analysis of SWNT ensemble in solution, which is indicative of a randomly spreading network structure. Entanglement of these SWNT ensembles in solution caused a high apparent solution viscosity depending on the structure. A wide variety of solvents is applicable to fabricate the SWNT ensembles on the wet process, such as organic solvents of methyl isobutyl ketone, ethanol, DMF, and even water without surfactants. These SWNT suspensions from many solvents are stable for several months without precipitation at the concentration any higher than 0.3 mg/mL, where the SWNT ensembles intertwine.
Buckypapers made from these SWNT ensembles showed a high electrical conductivity of 60-90 S/cm. In contrast to the long-range SWNT network structure, Buckypapers from ultrasonication-processed, shortened SWNTs gave a low conductivity of ~50 S/cm.
In this study, we propose a novel SWNT network structure, which stretches hundreds of micron long to deliver the excellent properties in matrices. The SWNT ensembles were recently utilized for SWNT rubber wire [2] and SWNT Buckygel actuator [3], yet, the detail was unclear.

[1] P. M. Ajayan, J. M. Tour, *Nature*, **447**, 1066-1068, (2007).
[2] T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, T. Someya, *Nature Mater*., **8**(6), 494-499, (2009).

[3] K. Mukai, K. Asaka, T. Sugino, K. Kiyohara, I. Takeuchi, N. Terasawa, D. N. Futaba, K. Hata, T. Fukushima, T. Aida, *Adv. Mater.*, **21**, 1582-1585, (2009).

Carbon Fiber – Carbon Nanotube Hybrid

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Since long back, carbon fibers (CF) have been used as a reinforcement material in various polymer matrices. Carbon fibers effectively increase the mechanical strength of polymer composites. However, due to wide gaps between two fibers in the matrix, the electrical conductivity of those composite materials does not improve significantly. Since the mass production of carbon nanotubes (CNT) became possible, CNTs are being used as filler into various CF-polymer composites. The conventional method is to mix 0.5 to 5% CNTs in resin-based composite materials to enhance their electrical conductivity.

In this work, however, instead of mixing CNTs into fiber-resin matrix, we preferred to grow CNTs directly on CFs. This proved to be easier and more effective in improving the mechanical strength as well as electrical conductivity of the composite, simultaneously. Commercially available carbon fibers were loaded with iron and cobalt catalysts and chemical vapour deposition was carried out at 600°C using camphor as the carbon source. CNTs of different densities were grown on CFs with different camphor feed weights. Controlled mixing of as-grown CF-CNT hybrid to commercial polypropylene (PP) was found to enhance the tensile strength, flexural strength, electrical conductivity and thermal conductivity significantly. This approach offers a convenient way of improving mechanical strength and electrical conductivity of composites at more affordable prices.

Unidirectional MWCNT sheet/epoxy composites

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Since the discovery of carbon nanotube (CNT), high mechanical properties of CNTs are intensively researched. So far, CNTs has been regarded as short fibers with the length of several tens micro-meters, and so it has been commonly used as filler to reinforce matrices for light-weight structural components [1]. Recently, we established a chemical vapor deposition growth method of ultra-long and highly spinnable multi-walled carbon nanotube (MWCNT) arrays [2]. From the highly spinnable arrays, unidirectionally aligned MWCNT paper sheets were formed [3]. The aligned MWCNT sheet is suitable to reinforce composite materials. In this study, we fabricated unidirectional MWCNT sheet/epoxy composites and investigated mechanical properties.

MWCNT arrays were grown by chloride assisted chemical vapor deposition. $FeCl_2$ is used as precursor of Fe catalyst. MWCNTs grow with a high growth rate over 0.1 mm/min up to 2 mm and the array is highly spinnable. By pinching and pulling out the edge of the MWCNT array, a MWCNT web, which is a two dimensional MWCNT network, is drawn. Then a unidirectionally aligned MWCNT sheet paper was fabricated by winding MWCNT webs on a drum, and the rolled MWCNTs structure was cut opened. MWCNTs are connected by van der Waals and no binder material is used. Since MWCNTs are aligned in the drawn direction in the web, the alignment is maintained in the web and thus MWCNTs are highly aligned in the sheet. The MWCNT sheet shows highly anisotropic features in electrical and thermal conductivity and mechanical properties [3].

Unidirectionally aligned MWCNT/epoxy composites were fabricated by a hand lay-up method. Epoxy was well impregnated into the MWCNT sheet. MWCNTs are well aligned in the composite. By this procedure, highly aligned MWCNT composites are formed very easily in a short time. MWCNT volume fraction was 14 %. Tensile tests of unidirectional MWCNT/epoxy composites were carried in the aligned direction.Young's modulus increased from 3GPa for pure epoxy to 31GPa for composite, and tensile strength increased from 81MPa to 137MPa.The present large reinforcement was surely due to a high degree of alignment and ultra-long MWCNTs.

[1] D. Qianet al., *Appl Phys Lett.*, **76**, 15, (2000).
[2] Y. Inoue et al., *Appl Phys Lett.* **92**, 213113, (2008).
[3] Y. Inoue et al., *Carbon*, **49**, 2437, (2011).

Electronic State of Polyaniline Deposited on Carbon Template and Supercapacitor Performance of Composite

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Polyaniline (PANI) is a conducting polymer, which is actively studied as a material for chemical sensing, high-power energy-storage devices, variety of biomedical applications, and so on. One is the most attractive property of PANI is a realization of the different redox states: a fully reduced state having only benzenoid moieties (leucoemeraldine base), a fully oxidized form with only quinoid nitrogen (pernigraniline base), and a half oxidized/half reduced state (emeraldine base). The latter state being protonated or doped is highly conducting, that makes PANI attractive as electrode material of supercapacitors. However, through the big volumetric change in the doping/dedoping process the PANI has poor cycling stability. One of the ways to solve this problem is a creation of composite with conducting carbon material possessing high surface area. Recently, it has been shown that the composites of PANI with carbon nanotubes (CNTs), graphene, or ordered mesoporous carbon (OMC) material have the high specific capacity and long-term stability when they were tested as electrode material in an electrochemical cell. The forms of deposited PANI depend on the synthetic method as well as structure of the initial template material.

Here we use methods of X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy for probing the electronic structure of composites from PANI and array of aligned multiwall CNTs, vertically grown on silicon support, or OMC material, fabricated using periodic silica template. PANI has been deposited on a carbon template in the result of chemical oxidation of aniline chloride in acidic aqueous medium using sodium persulfate as oxidant. The calculated fraction of PANI was 70 and 68% in composite with OMC and CNTs, respectively. The interpretation of experimental data was done based on quantum-chemical calculations different forms of PANI using B3LYP method. It was found that the protonated forms of PANI developing on the surface of CNTs, while PANI deposited in porous of OMC contains a marked amount of imine (=N-) nitrogen. The supercapacitor measurements were carried out in a standard three-electrode cell using cyclic voltammetry (CV) in a 1M sulfuric acid aqueous solution. The composites showed the increased specific capacity as compared with unsupported PANI and pristine carbon materials. The capacity of the PANI/CNT and PANI/OMC electrodes was ~510 and ~85 F/g at the sweep rate of 5 mV/s. These value correlates with the increased fraction of the doped PANI in the first composite.

Enhanced Hydrogen Storage Capacitance of Graphite Oxide Intercalated by Poly (sodium 4-styrensulfonate)

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Molecular hydrogen (H_2) sorbents are appealing materials for storing hydrogen fuel onboard vehicles. To use the H_2 sorbents at near ambient conditions, the binding energy of H_2 in sorbent materials must be within certain range (e.g., 20-40 kJ/mol). For achieving high H_2 adsorption capacity are several conditions, which is high surface area substrate material, fluent of H_2 intimate functional group and appropriate binding energy with H_2. Graphite oxide(GO) is not well matched with this condition but polymer intercalated GO shows good candidate for hydrogen storage materials.
The GO was produced by a modified Brodie method using precursor graphite as a starting material. The GO was mixed with poly(sodium 4-styrensulfonate)(PSS) by stirring for 24 hr. Subsequently, The GO/PSS mixed solution was sprayed on the quadruple quartz crystal microbalance(QCM).The QCM was loaded on the vacuum chamber and measure H2 storage capacity by frequency shift [1].The PSS/GO shows the high H_2 storage capacity over than 1.7 wt% at RT and 0.5 MPa. However, with increasing the cycle of hydrogen adsorption and desorption capacity was decreased due to some amount of H_2 was still remain in the PSS/GO. After heating the chamber over than 100 °C, the PSS/GO H_2 storage capacity was perfectly recovered. Reproducible experiments shows that the similar shape with first cycle of H_2 storage capacity around 1.5~1.8 wt%.

[1] S. C. Lim, K. K. Kim, S. H. Jeong, K. H. An, S. B. Lee, Y. H. Lee, *Int J Hydrogen Energy*, **32**, 3442-3447, (2007).

Electrochemical Capacitance of PAN-based and CNT/PAN Nanofiber Papers in Organic Electrolyte

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Electrospinning of polymers is a very successful method for preparing fibers with diameters from submicro- to nanometer sizes. In particular, the electrospinning of polyacrylonitrile (PAN) followed by stabilization and carbonization results in fine carbon nanofibers. In the present study, a promising porous electrode for electrochemical capacitors has been prepared in single-step approach by using PAN and carbon nanotubes (CNT). The addition of CNT to the PAN solution for electrospinning contributes to increase the electrical conductivity and shape retention of the resulting nanofiber papers [1]. Porous carbon nanofiber papers were obtained by simultaneous carbonization/activation of PAN-based and CNT/PAN nanofiber papers at 1000 °C in CO_2 atmosphere. The papers can be applied to capacitor electrodes without any binder or percolator. The characterization using N_2 adsorption indicated that the one-step carbonization/activation developed subnanometer pores in the PAN-based and CNT/PAN nanofiber papers, and the BET specific surface areas were not so high, remaining in SBET = 705 m^2/g and 975 m^2/g, respectively. Despite the moderate surface area, however, the electrochemical evaluation in organic electrolyte showed that the capacitance values reached higher than 100 F/g. Furthermore, the carbon nanofiber papers have outperformed the energy-density retention of activated carbon (Norit Super 50) at a high power-density region. The high power capability of the electrodes is attributed to the high intrinsic electrical conductivity and to the high diffusion rate of ions assumed by the opened mesopore structure.

[1] E. J. Ra, K. H. An, K. K. Kim, S. Y. Jeong, Y. H. Lee, *Chem PhysLett*, **413**, 188-93, (2005).

Growth of Adhesion-Improved CNT Forests on Carbon Fibers for Composites

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We report a method for growing tightly bounded carbon nanotube (CNT) forests on the surface of carbon fibers (CFs) for their composites. The mechanical strength of the hierarchical CNT-CFs composite laminates strongly depends on the adhesion between CNT and CFs at the interface. We achieved improvement in the adhesion between the vertically-aligned CNT forest and the CFs. The degree of adhesion was qualitatively assessed using the Scotch-tape test. Epoxy composite was fabricated with the adhesion- improved CNT-CFs specimen for characterizing CNT-CFs sample. The CNT-CFs composite shows 60 times and 1.5 times increase in the electrical conductivity and the fracture toughness over the baseline (CF-only) sample, respectively.

Transparent and Conductive Thin Films of Graphene/Polyaniline and Carbon Nanotubes/Polyaniline Nanocomposites

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The combination of carbonaceous nanostructures (as graphene and carbon nanotubes) and conjugated polymers (as polyaniline) offers the possibility of exploring new materials presenting novel eletrical, optical and electrochromic properties, arising from the interaction between the two components. Nanocomposites between polyaniline and carbon nanotubes or more recently polyaniline and graphene have been prepared by in situ polymerization of aniline over a CNTs or a chemical reduced graphene dispersion. This route yields powder materials that are not possible to be processed in transparent films, which makes impossible their utilization as active component in several devices. In this work we report a very versatile and efficient method to obtain homogeneous and transparent thin films of graphene/polyaniline [1] and CNTs/polyaniline [2], through a chemical polymerization of aniline at an aqueous-organic interface. The nanocomposites are obtained only at liquid water/toluene interface as a free standing, transparent and self-assembled films. The films can be easily removed from interface and deposited over any substrate, which represent a good advance in order to build efficient and reproducible devices. Different carbonaceous nanostructures/polymer ratios have been employed. All the materials have been characterized by Raman, FT-IR and UV-Vis spectroscopy, XRD, SEM, TEM, cyclic voltammetry and conductivity measurements. Results indicate an efficient carbon nanostructures/polymer interaction. Several properties have been explained based on these interactions. A model to the self-standing film occurrence, based on interface stabilization, has been also proposed. Films presenting transmittance of 90% and resistivity lower than 50 ohm/square have been obtained, indicating that these materials are very useful for transparent electrodes replacing ITO-based films.

[1] DOMINGUES, S. H., SALVATIERRA, R. V., OLIVEIRA, M. M., ZARBIN, A. J. G., *Chemical Communications*, **47**, 2592-2594, (2011).
[2] SALVATIERRA, R. V., OLIVEIRA, M. M., ZARBIN, A. J. G., *Chemistry of Materials*, **22**, 5222-5234, (2010).

Transparent and Conductive Thin Films of Carbon Nanotubes/Prussian Blue Nanocomposites: Preparation, Characterization and Application as Electrochromic Material and H2O2 Sensor

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Nanocomposite materials formed by the combination of Prussian Blue (PB) and carbon nanotubes (CNTs) present several interesting properties. PB has a general formula $Fe^{III}_4[Fe^{II}(CN)_6]_3.nH_2O$ and presents important redox, ferromagnetic and multi- electrochromic properties. We recently developed an innovative route to prepare a CNT/PB composite paste electrode (with high sensitivity to H_2O_2 detection), based on an in situ electrochemical reaction between the iron-based compounds present in the cavities of carbon nanotubesand the ferricyanide ions in solution [1]. Here we demonstrate that this route can be extended to other kind of electrodes, and show by the first time the electrochemical preparation of thin and transparent CNT/PB electrodes, starting from a transparent film of Fe-filled CNTs. The CNT films were prepared by deep-coating and showgood homogeneity and a transmittance at 550 nm varying from 81 to 87%. After the electrochemical reaction with the ferricyanide ions, the gray-black films became blue, and the transparence at 550 nm varies from 58% to 80%. The films were characterized by cyclic voltammetry, UV-Vis spectroscopy, XRD, SEM and Raman spectroscopy. A strong interaction between the PB and the CNTs was detected through these techniques. The electrochromic performance of these films have been evaluated, and compared to PB films prepared electrochemically in the conventional way. The nanocomposite films presented excellent electrochemical stability. The films were employed as amperometric sensor for hydrogen peroxide. The sensors demonstrated very low detection limits (4.60×10^{-9} mol L^{-1}) and very high sensitivity (97.2 A cm^{-2} M^{-1}), which represents one of the best response ever described in the literature for this kind of sensor.

[1] NOSSOL, E., ZARBIN, A. J. G., *Advanced Functional Materials*, **19**, p.3980, (2009).

Multifuncional Nanocomposites Obtained Between Iron-Filled Carbon Nanotubes and Polymeric Latexes

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The present study describesthe synthesis, characterization and study of properties of multifunctional nanocomposite materials obtained by two different polymeric latexes ((poly(styrene-co-butyl acrylate) and natural rubber) and carbon nanotubes (CNTs). The CNTs used in this work have their cavities filled by magnetic species, mainly iron and iron oxide1. In order to prepare stable aqueous dispersions of CNTs, two different approaches have been employed: 1) mixture of the surfactant sodium dodecyl sulfate (SDS); 2) previous treatment of the CNTs with a mixture of nitric and sulfuric acid solution. Several nanocomposite samples were prepared containing different amount of CNTs (from 0.01 to 10 wt%). The nanocomposites have been characterized by X-ray micro-tomography, transmission and scanning electron microscopy, atomic and magnetic force microscopy, Raman and infrared spectroscopy. The thermal, electrical and mechanical properties have been evaluated by thermogravimetric analysis, resistivity measurements (four-points) and stress-strain tests. The obtained data demonstrated that the amount of CNTs affect the structure of the nanocomposites. A good adhesion between the CNTs and polymer matrices was revealed by AFM images. Raman and infrared spectroscopy revealed that the incorporation of CNTs didn't change the polymers structures. The occurrence of networks of CNTs in the polymeric matrices provided significant increases in electrical properties and in the resistance to solvent sorption of the nanocomposites, in comparison to the unfilled polymer. The mechanical properties of the polymers were improved in both classes of nanocomposites. Thermal properties of the materials not changed with the CNTs presence. Due the magnetic species encapsulated into CNT cavities, ours nanocomposites present magnetic behavior, confirmed by magnetic force microscopy, resulting in novel kind of multifunctional materials with a great potential for further applications.

[1] M.C. Schinitzler, M.M. Oliveira, D.M. Ugarte,A.J.G. Zarbin, *Chem. Phys. Lett.*, **381** 541, (2003).

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Study Of Carbon Nanotubes And Functionalized-Carbon Nanotubes As Substrates For Flow Injection Solid Phase Extraction. Application To Cd Monitoring In Solid Environmental Samples

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A research was performed to evaluate the capabilities of carbon nanotubes (CNTs) and modified CNTs for preconcentrating Cd using an on-line ultrasonic nebulization (USN) – inductively coupled plasma optical emission spectrometry (ICPOES) system.

Cadmium is a heavy metal, known to be extremely toxic and occurs in almost all soils, surface waters and plants being readily mobilized by human activities [1]. In this context, Cd has been named as a potential health threat moreover is considered as a priority pollutants bynational and international organizations.

Nowadays, trace elemental determination can be efficiently performed in association with solid-phase extraction (SPE)/preconcentration techniques. It is basically aiming at the enrichment of metallic species and/or matrix separation with the advantages of achieving high concentration factors, simple operation, the ability to handle large volume of samples in systems free from contamination, rapid phase separation, and the possibility of coupling with different analytical techniques. The combination FI-SPE-ICPOES does not only provide improvements in detection limits but also leads a noticeably enhancing in the analytical performance of the methods.

The choice of a suitable adsorbent for on-line column preconcentration systems is a critical factor to obtain full recoveries and high enrichment factors. Since its discovery [2], carbon nanotubes (CNTs) have been proposed and used as a novel solid phase extractant for inorganic and organic compounds/elements at trace levels [3]. Considering the unique physical and chemical properties of these carbonaceous materials and their potential applications they have come under intense multidisciplinary study. Their large sorption capacity is linked to well-developed internal pore structures, a large specific surface area, and the possibility of binding a wide variety of functional groups to their surface.

Considering the above advantages, it was deemed of interest to further investigate the capabilities of these new substrates. In this case, a SPE system was coupled on-line to USN-ICP OESfor Cd detection.

The on-line solid phase extraction of Cd on carbon-base materials named, carbon nanotubes (CNT), oxidized-carbon nanotubes (ox-CNT) and L-alanine-carbon (ala-CNT) was studied systematically. Our studies evidenced that ox-CNT exhibited the best analytical performance for Cd preconcentration and determination. The main factors that influenced the preconcentration and determination of Cd were examined thoroughly, and they included sample pH, sample flow rate and volume, and eluent concentration and flow rate. Under optimal conditions, the adsorption capacity on ox-CNTs was found to be 130 µmol g^{-1} and the detection limit (3) achieved was 1.03 g L^{-1}.The conditions were established and Cd determination in sediments and sludges was successfully carried out.

[1] J.R. Larison, G.E. Likens, J.W. Fitzpatrick, J.G. Crock, *Nature*. **406,** 181-183 (2000).
[2] S. Iijima, T. Ichihasi, *Nature*. **363**, 603-605 (1993).
[3] R.A. Gil, S. Cerutti, J.A. Gásquez, R.A. Olsina, L.D. Martinez, *Talanta*. **68,** 1065-1070, (2006).

Highly Elastic Transparent SWCNT - Polymer Electrodes With Excellent Robustness And Long-Term Stability

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Transparency, elasticity, flexibility, all combined with good electrical conductivity, robustness and long-term stability are key properties for transparent and / or flexible electrodes. Applications include biochemical devices, displays, solar cells, tactile dis- playsand organic light emitting diodes [1]. Especially attractive are electrodes allowing both, flexibility and transparency.

Transparent electrodes are in great demand nowadays. Most often, Indium Tin Oxide (ITO) is used here. However, due to its brittleness, lacking corrosion resistance, a world-wide Indium shortage, and a demanding ITO film preparation (leading to high overall costs), efforts are underway to look for alternative electrode materials and cost-efficient electrode preparation methods. Flexible electrodes on the other hand usually consist of thin opaque metal layers which must be sputtered. While being highly conductive, an inherent insufficient long-term stability (mechanical, electrical, chemical) of such flexible devices results in the need for alternative solutions.

Single-Walled Carbon Nanotubes (SWCNT) are promising candidates for a replacement of ITO for transparent electrodes as well as for a replacement of metal thin films for flexible electrodes due to their electrical, mechanical and chemical properties combined with their unique low dimensionality making them strong but (almost) in- visible and highly conductive 1D-wires [2]. SWCNT were applied on silicone films via a modified spraying / airbrush method, a method allowing cost-efficient and large-area roll-to-roll technologies, with the nano- tubes being modified and p-doped in order to increase the conductivity. Sandwiched silicone electrodes with a sheet resistance of 100 / 1200 / 9000 Ω/sq with 80 / 90 / 95 % transparency (@ 550 nm) for standard purified-IWS-SWCNT have been obtained.

Stretching these films up to 250% of their length did not result in catastrophic degradation of the resistance. Any shape and resistance change of these films was fully reversible up to a linear strain of 70%. By proving the long-term stability of a sheet 200x200mm² wide, 10^6 cycles of an applied linear elongation of 10% did not result in any electricalresistivity change nor any electrical and mechanical degradation.

[1] S. De, T.M. Higgins, P.E. Lyons, E.M. Doherty, P.N. Nirmalraj, W.J. Blau, J.J. Boland, J.N. Coleman, *ACS Nano*, **3**, 1767–1774, (2009).
[2] M.S. Dresselhaus, G. Dresselhaus, P. Avouris, Carbon Nanotubes: “Synthesis, Structure, Properties and Applications”, vol. 80 of Springer Series in Topics in Appl. Phys., Springer-Verlag, Berlin, (2001).

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Metallic And Semiconducting Single Wall Nanotube Based Transparent Conductors.

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Highly enriched metallic (m-) SWNTs are ideal to replace contacts and brittle and expensive transparent conductive oxide electrodes, while semiconducting (s-) SWNTs can be used, for example, as channel material in transparent and flexible transistors. Density gradient ultracentrifugation (DGU) is a well-established tool to sort nanotubes by diameter [1], chirality [2], length [3] and to separate m- and s-SWNTs [2,4,5]. To date the m/s separation requires co-surfactant mixtures with different relative concentration [2,4,5]. Here we show that the optimization of the density profile, based on a Sodium Cholate and Sodium Dodecyl Sulfate mixture, can produce highly enriched s- and m-SWNT samples in the same process.
From optical absorption spectroscopy we estimate final yields of ~95% for both m- and s-SWNTs in the same DGU run. This result does not require iterative procedures for the separation, speeding up the process and preventing waste of material. The highly enriched sorted m- and s-SWNTs, as well as the starting material, are used for the production and characterization of transparent thin films with different electronic properties. SWNT transparent films are deposited via vacuum filtration [6,7], followed by transfer process to a quartz substrate and subsequent annealing at 250 °C in N_2. A sheet resistance of 150Ω/□ is achieved for metallic films at 70% transmittance in the visible range, whilst several kΩ/□ are measured in the case of semiconducting films with similar transparency.

[1] M. S. Arnold et al., *Nano Lett.*, **5**, 713, (2005).
[2] F. Bonaccorso et al., *J. Phys. Chem. C,* **114**, 17267, (2010).
[3] J. A. Fagan et al., *Langmuir*, **24**, 13880, (2008).
[4] M. S. Arnold et al., *Nat. Nano.*, **1**, 60, (2006).
[5] K. Yanagi et al., *Appl. Phys. Express*, **1**, 034003, (2008).
[6] Z. C. Wu et al., *Science*, **305**, 1273, (2004).
[7] A. A. Green, M. C. Hersam, *Nano Lett*., **8**, 1417, (2008).

The effect of MWNT content and functionality on PMMA mechanical properties

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Poly methyl methacrylate (PMMA) is a highly used transparent thermoplastic polymer which is used as a structural material in various applications. In order to improve the mechanical properties such as stiffness, toughness and strength, multi wall carbon nanotubes (MWNT) were incorporated into the PMMA matrix. The incorporation was performed using a twin screw extruder, followed by hot pressing.

Both pristine and functionalized MWNTs were used in three different concentrations. For comparison carbon black was added into PMMA as a reference. The composites were examined using high resolution scanning electron microscopy (HR-SEM) to evaluate the MWNT dispersion. The MWNT content in the composite was determined using thermal gravimetric analysis (TGA). Furthermore, the effect of the MWNT concentration and functionalized groups added to the MWNT was investigated in respect to the mechanical properties by means of tensile and fracture toughness tests.

Carbon Nanotubes For Enhanced Physical Property And Chemical Reactivity - Thermal Conducting Soft Polyol Composites And Their Production -

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Since carbon nanotubes became commercially available due to their large scale industrial production for competitive prices, the production of CNT-based composites for different applications is brought increasingly into focus of activity. Carbon nanotubes are generally known, due to their rigid sp^2-carbon skeleton, for their outstanding high mechanical strength and excellent thermal conductivity. Already early theoretical calculations predicted outstanding thermal conductivity [1].Measurements of individual tubes demonstrated thermal conductivity values up to 3000 W/mK [2]. These predictions provide the motivation for the development of carbon nanotube-based composite materials with improved thermal conductivity. Some possible examples are metal composites with improved thermal conductivity or lower thermal expansion coefficient. Others are lightweight polymers with enhanced mechanical strength and increased thermal conductivity or semi-fluid (pastes) mouldable composite compounds for bridging of gaps between rigid elements. Commonly those soft composites, so-called thermal interface materials (TIMs), consist of a liquid matrix and solid fillers. The efficiency of TIMs is affected by two factors: the gap filling ability of the matrix and the thermal conductivity of the filler. The matrices used in this approach are based on natural oils, including sunflower and soybean oil. Known to have good lubricating properties they form the base for a good gap filler. For the improvement of the thermal conductivity, which is generally low for all kind of fluids, CNTs were used as filler.

To prevent phase separation of the liquid binder and the carbon aggregates, the oil was polymerised. During the thermal polymerisation oil monomers connect, building a long molecular chain. With increased molecular weight the matrix viscosity grows. The polymer forms a network in which deagglomerated CNTs are stabilised. The kinetic of the polymerisation reaction was studied. The data show an interesting effect of the carbon nanotubes on the polymerisation reaction. In comparison to the polymerisation reaction without CNTs a catalytic effect of the CNT can clearly be demonstrated. Comparative investigations with a conventional catalyst (anthrachinone) and at different temperature or with altering CNT concentration verify the catalytic influence of tubes on the reaction. Catalytic effects based on CNTs have been reported earlier, including detailed studies of gas- phase reactions [3]. Only recently a CNT catalysed polymerisation has been reported [4], but none in which the remaining catalyst has an additional benefit to the product.

The utilisation of CNTs in this case has two major advantages for the entire process. On one side the thermal conductivity of the CNT-based composite is improved leading to a sufficient thermal interface material; on the other hand the reaction time is shortened due to the catalytic effect of CNTs.

[1] S. Berber, Y.K. Kwon, D. Tománek, *Phys. Rev. Letters*, **84**, 20 (2000)
[2] P. Kim, L. Shi, A. Majumdar, P.L. McEuen,*Phys. Rev. Letters,* **87**, 21, (2001).
[3] J. Zhang, X. Wang, Q. Su, L. Zhi, A. Thomas, X. Feng, D. S. Su, R. Schlögel, K. Müller, *J.*

Am. Chem. Soc. **131**, 32, (2009).
[4] A. Fainleib, L. Bardash, G. Boiteux, *eXPRESS Polymer Letters*, **3**, 8, (2009).

Surface modification of Cu plates with CNT/Cu powder composites through the application of cold gas dynamic spray for the enhancement of boiling heat transfer

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In this study, the enhancement of boiling heat transfer through surface modification of heat transfer materials by surface coating is being explored. Specifically, the study evaluates the integrity of Cu plate substrates coated with carbon nanotube (CNT)/Cu powder composites in terms of their boiling heat transfer performance.

The raw materials of the surface coating are composite powders, which are fabricated by mechanical alloying using an attrition mill. The fabricated surface coating is done through the cold gas dynamic spray method.

Boiling heat transfer test of coated Cu plates is done in a pool of R134a to evaluate their heat transfer performance. The effects of the mechanical alloying parameters such as composition, temperature, milling speed and milling time on the integrity of the coating in terms of its heat transfer performance and strength are investigated. Furthermore, the fabrication parameters for the modified surface with the use of the cold gas dynamic spray method are also being investigated.

The characteristics of the CNT/Cu powder composites and the microstructures of their coatings are being investigated using optical microscopy and scanning electron microscopy.

Photo-actuating CNT Composites for Tactile Display Applications

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The class of materials termed 'Liquid Crystal Elastomers' (LCEs) can reversibly change their shape in response to an applied stimulus. Most LCEs discussed in previous studies can actuate either upon heating or upon irradiation with ultraviolet light (wavelength 300-400 nm). For most practical applications, the use of UV light is problematic due to considerations of cost and of safety; in order to sensitise LCE materials to light of higher wavelengths, another light-absorbing component must be added to the material. In previous work, it has been shown that it is possible to make composites containing well-dispersed carbon nanotubes (CNTs) embedded in an LCE matrix[1]. CNTs will absorb light over a range of wavelengths, and convert that light into local heat, thus allowing phase changes in the LCE material to take place.

In this work, we develop further the concept of LCE-CNT composite materials, and show that adding a low concentration of CNTs to an LCE matrix sensitises the material to Infra-red/visible light while the structure and thermal actuation of the LCE material remains unaffected. We discuss potential applications for these composite materials, with a particular focus on their use in 'haptic' technologies, for example in dynamic Braille displays whose Braille dots could be raised or lowered to allow a user to read text or graphical output in real time. The use of optically actuated components in such displays could overcome several of the limitations inherent in the use of other actuating soft materials, such as the need for a high driving voltage [2], [3].

[1] Y. Ji et. al., *Adv. Mater.*, **22**, 3436-3440, (2010).
[2] S.W. Lee, K.M. Jung, J.C. Koo, S.G. Lee, H.G. Choi, J.W. Jeon, J.D. Nam, H.R. Choi. *Proc. SPIE*, **5385**, 368–379, (2004).
[3]I. M. Koo et. al., *IEEE Transactions on Robotics*, **24**, 549 -558, (2008).

A Single-Walled Carbon Nanotube-Enabled Conductive Aerospace Adhesive

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While rivets remain the only accepted method for long-term electrical bonding of aerospace materials, adhesive bonding is becoming more important with the advent of current-generation aircraft that employ more composite materials, primarily carbon-fiber reinforced polymers, in the airframe construction. Other industries already apply adhesives for electrical bonding. Electrically conductive adhesives have been used as an alternative to solder in electronics. However such adhesives, which are typically composed of silver particles in an epoxy matrix, have poor mechanical strength due to the high filler content required to achieve electrical percolation. Individual single-walled carbon nanotubes (SWCNTs) possess among the highest electrical conductivity of any material and, due to their high aspect ratio, the addition of CNTs to polymers routinely results in electrical percolation and corresponding, dramatic improvements in conductivity with a relatively small amount of filler (< 1 wt% CNTs). For this reason, CNT/epoxy systems are considered a potential solution to allow electrical adhesive bonding without degrading the mechanical strength of adhesive joints required in aerospace applications. In this study we explore the electrical conductivity and joint strength obtained with composites containing SWCNTs in an aerospace grade epoxy system, with the goal to develop a conductive adhesive that retains the structural bonding ability of the baseline adhesive. The composites are prepared using solvent processing methods and characterized for their conductivity, dispersion quality, tensile properties, and joint strength. The strengths are compared to the baseline adhesive and the conductivities are evaluated in terms of electrical requirements for aerospace applications.

Synthesis of Polyaniline - Carbon Nanoribrons Composites

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This work presents the synthesis of composites of polyaniline (PAni) and carbon nanoribbons. The carbon nanoribbons were obtained by opening multiwall carbon nanotubes (MWNT) through an intercalation-exfoliation process from exfoliated multi wall carbon nanotubes. Carbon nanoribbons were then functionalized with aniline by a reductive alkylation reaction. Then, PAni-CNR composites were synthesized by an in situ interfacial polymerization of aniline, using ammonium persulfate and ferric chloride as oxidant agents of aniline monomer. As comparison, composites were prepared with unfunctionalized carbon nanoribbons, and multiwalled carbon nanotubes.

Composites were characterized by electronic microscopy (SEM and TEM). Raman Spectroscopy, XRD, and Four Point Probe were used to evaluate their structure, crystallinity and electrical conductivity, respectively. Our results suggest a stronger nanoribbon-polymer interaction in composites prepared with aniline-functionalized nanoribbons. The electrical conductivity was not significantly different between the different composites although it was approximately one tenth of those of PAni-MWCNT composites.

Preparation and Characterization of Actuators from Carbon Nanstructures- PAni Composites

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In this work, we present the synthesis and characterization of actuators made from composites of polyaniline (PAni) and carbon nanostructures; including: multiwalled carbon nanotubes (MWNT), nanoribbons (CNR), carbon nanofibers (GANF) and graphene oxide (GO). Composites were synthesized by an in situ interfacial polymerization of aniline. Then, composites were dispersed in n-methyl-pyrrolidone (NMP) and 30 – 60 µm films were obtained by casting on a glass substrate. Actuators of these films were tested in electrolyte solutions 1M of HCl, dodecylbenzensulfonic acid and 2-acrylamido-2-methyl-1-propanesulfonic acid. Composites were characterized by electronic microscopy (SEM and TEM). Raman Spectroscopy, XRD, and Four Point Probe were used to evaluate their structure, crystallinity and electrical conductivity, respectively. Our results indicate that HCl solutions are the best electrolytes for actuation, and GO and MWNT work better that the GANF in the process of distending and contracting the actuators. It was found that composites prepared with GO present a higher conductivity that the other composites.

Boron Nitride Nanotubes Chemically Modified By Sulfur

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The field of nanotechnology research involves theoretical and experimental study of physical and chemical properties of nanomaterials, which are different from their bulk equivalents. This information is needed before the nanomaterials can be used for certain applications, most likely as parts of the nanocomposite which promises a combination of properties unachievable with traditional materials. Specifically for NASA, when designing a spacecraft structural material, one need to know if a proposed nanocomposite has the multifunctionality of being light weight and able to protect the spacecraft from extreme heat in the surrounding atmosphere, pressure or vacuum, radiation, meteoroids, and many other environmental phenomena that the spacecraft will encounter. Boron nitride nanotube (BNNT) is currently being considered as the likely nanomaterial in the nanocomposites for spacecraft material application. However, the chemical properties of BNNT that may be used as part of the nanocomposite are incomplete at best. Specifically, the reaction between BNNT and sulfur has not been reported and is not well understood. This reaction is of interest because the multiple bonds of sulfur may potentially be useful in connecting the interfaces between structurally and chemically dissimilar nanomaterials during nanocomposite synthesis. In this research, the BNNT was exposed to sulfur at its liquid state to experimentally observe the results. Considering that carbon nanotube (CNT) can be thiolated (to form –SH bond), carbon-based polymer can be cross-linked by sulfur to form rubber, and understanding the similarity between carbon and boron nitride, some reactions between BNNT and sulfur were expected, and were confirmed by the experimental results. After sulfur exposure, the BNNT gained mass and became more chemically reactive. In some of the BNNT-sulfur reactions, the sulfur in the product can be recovered by high temperature exposure in inert environment. More characterization of the sulfur-exposed BNNT will be presented.

Fluorination of Carbon Nanotubes and Graphene.

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There exist few techniques to date that allow selective modification of regions of a graphene surface, or variation of the properties of single carbon nanotubes along their length in a controlled manner. Of the different chemical modification techniques available, fluorination takes a special place as it can provide for full outer wall functionalisation up to CF for graphene and C_2F for nanotubes,[1] and a range of functionalisation methods is available.[2] In particular radio-frequency (RF) plasma functionalisation is easy, fast, and upscalable to industrial levels with good control over the fluorination degree [3]. There has been a long- time interest in graphite fluorination for lubricant applications [4]. For carbon nanotubes, fluorination is used for debundling and dispersion, enabling their solubilization in e.g. alcohols, and potential applications for fluorinated nanotubes include the use in Lithium-ion batteries, supercapacitors and as lubricants [5].

In this work, the reaction mechanisms and electronic properties for graphene fluorination are explored, and compared to carbon nanotube fluorination using Density Functional Theory calculations. Also, the transport properties of hetero-structures containing various domains (pure C, C_2F and C_4F stoichiometry) are determined. These ab initio studies have been carried out with the Gaussian and SIESTA codes, and the conductance has been calculated using the usual Green functions formalism. Analysis of the addition patterns shows that contrary to graphene, experimentally observed fluorine banding on carbon nanotubes is not formed by fluorine addition in bands directly but by fluorine arranged in a spaced (1,4) addition pattern followed by migration over the surface.

Controlling the fluorination process and subsequent processing can result in hybrid fluorinated materials with unexplored electronic and chemical properties. Partially fluorinated graphene and banded nanotubes should have many interesting properties, since the fluorinated regions will have a different electronic structure than the pristine segments, raising the intriguing possibility of introducing quantum wells on the graphene surface or along the nanotube length via fluorine banding.

[1] C.P. Ewels, G. Van Lier, J.-C. Charlier, M.I. Heggie, P.R. Briddon, *Phys. Rev. Lett.* **96** 216103, (2006).
[2] L. Bulusheva, Yu. Fedoseeva, A. Okotrub, E. Flahaut, I. Asanov, V. Koroteev, A. Yaya, C. P. Ewels, A. Chuvilin, A. Felten, G. Van Lier, D. Vyalikh, *Chem. Mater.* **22** (14), 4197,(2010).
[3] A. Felten, C. Bittencourt, J.-J. Pireaux, G. Van Lier, J.-C. Charlier, *J. Appl. Phys.* 98 074308, (2005).
[4] M. Glerup, V. Krstic, C.P. Ewels, M. Holzinger, G. Van Lier, Doping of Carbon Nanotubes in Doped Nanomaterials and Nanodevices, W. Chen ed., *American Scientific Publishers*, (2007).
[5] S. Osuna, M. Torrent-Sucarrat, M. Sola, P. Geerlings, C.P. Ewels, G. Van Lier, *J. Phys.*

Chem. C **114** 3340, (2010).

Advantages of High-k Dielectric Layer Passivated CNT-FETs for pH Detection

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Carbon nanotube field-effect transistors (CNT-FETs) have a high potential for chemical and biological sensing devices. The CNT-FETs have been successfully applied for sensing protein, DNA, inorganic molecules and pH [1-3]. The detection is usually performed by exposing the CNT channel to the chemical or biological environments to allow direct interaction with chemical or biological molecules and pH solution. The nanotube-molecules interaction has been considered to give rise the conductance changes of the CNT-FET sensors, however, the origin of nanotube-molecule interactions and their role in the conductance changes remain under debate. The CNT-FET sensors have proved to have a high sensitivity for chemical and biological molecules, however the 30 mV/pH sensitivity was much lower compared to 55 mV/pH sensitivity of Si-based FET sensor [2]. We report the use of CNT-FETs in a similar way to the conventional Si-based FET sensors, i.e. ion sensitive FET for pH detection. The CNT-FETs have been fabricated in a conventional way. The CNT-FETs then finally covered by a high-k dielectric layer grown by atomic layer deposition as an ion sensitive layer. The pH detection capability of CNT-FETs with three different high-k dielectric layers, i.e. HfO_2, Al_2O_3 and ZrO_2 were investigated. All layers have the same thickness of 20 nm. The pH measurements have been performed with a poly (dimethylsiloxane) fluidic channel placed over the CNT-FETs. A leak-free Ag/AgCl reference electrode was used to apply a gate voltage. We found that these three high-k dielectric layer are useful as ion sensitive layers for pH detection. HfO_2 layer have the highest sensitivity approaching 55 mV/pH, a value that comparable to the sensitivity of Si-based ion sensitive FETs. Since the CNT channel is not exposed to the pH solution, they are advantages in the stability, reproducibility and lifetime. In addition, similarly to ion sensitive FET sensor they have the well-known pH sensing mechanism.

[1] R. J. Chen et al., *PNAS* **100**, 4984, (2003).
[2] B. L. Allen et al., *Adv. Mater.* **19**, 1439, (2007)
[3] J. H. Back and M. Shim, *J. Phys. Chem B*, **110**, 23736, (2006)

Tunable Chemistry of Multi-wall Carbon Nanotubes as a Route to Non-toxic, Theranostic Systems

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One of the most promising exploitation areas of multi-wall carbon nanotubes (MWNTs) is nanomedicine [1]. Extensive studies have been devoted to application of MWNTs as non- viral vectors in gene and drug delivery [2,3,4]. Particularly, drug delivery vehicles steerable by an external magnetic field seem to be a promising targeted system [5]. Moreover, chemically modified MWNTs may serve potentially as contrastive agents in Magnetic Resonance Imaging (MRI). Our previous work has shown a decreased cytotoxicity for chemically modified (nitrogen-doped and oxidised)MWNTs as compared to their pristine analogues/precursors [6]. Herein, these nanotubes of 'needle-like' morphology, containing various concentrations of encapsulated ferromagnetic iron nanoparticles, were studied in the context of their chemical reactivity. As model chemical reactions leading to anchoring of synthetic nucleosides molecules to nanotubes–transformations of carboxylic groups (O- MWNTs) or 1,3-dipolar cycloaddition (MWNTs and N-MWNTs) were applied.

[1] D. L. Harris, R. Bawa, *Expert Opin. Ther. Patents*, **17**, 1-11, (2007).
[2] N. W. Shi Kam, H. Dai, *Physica Status Solidi (B)*, **243**, 3561-3566, (2006).
[3] W. Cheung, F. Pontoriero, O. Taratula, A. M. Chen, H. He, Adv. Drug Deliv. Rev., 62, 633-649, (2010).
[4] Zh. Liu, K. Chen, C. Davis, S. Sherlock, Q. Cao, X. Chen, H. Dai, Cancer Res., 68, 6652-6660, (2008).
[5] P. Malhotra, A. Singh, JKScience, 12, 3-5, (2010).
[6] S. Boncel, K. Müller, J. Skepper, A. Gondela, K. Walczak, K. K. K. Koziol, Eleventh International Conference on the Science and Application of Nanotubes NT10, Montreal, Canada, p. 26, (2010).

Molecular Magnet And Carbon Nanotubes Interactions For MOLECULAR Spintronic Applications

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Creating new molecular objects which can be used as memory devices is an important challenge. Conceiving such systems and integrating them into physical systems is done with the use of several scientific techniques which cannot be grouped in only one discipline. Here, metallic compound synthesis (transition metals and lanthanides), carbon material purification, experimental measurement of magnetic properties, solid physics and electronic transfers are necessary for a full understanding and study of the subject. This particular one is composed of carbon nanotubes bridging two electrodes and molecules for which magnetic properties are entirely known. These two are interacting by non-covalent interactions.
The final aim is to study the possible coupling between an ideally polarised current flowing through the tube and the spins carried by the metals of the inorganic molecules. In order to do so, each sub-system characteristics must be known perfectly.
The synthesied inorganic molecules can be either paramagnetic or act as nanomagnets, and must stack on carbon nanotubes without losing their magnetic properties (low spatial disorder, absence of covalent bonding).
Carbon nanotubes (HiPCO) are purified by oxidation so as to get rid of the catalyst (which is necessary for their synthesis) and to avoid any magnetic disturbance of the system during the grafting process. It is also very important to be able to realize and characterize the desired circuit, which requires surface physics strategies.

[1] G. Charron, et al., *New J. of Chemistry* **33**, 1211, (2009).

Analysis of Water Adsorption Effects on SWNTs by the Simultaneous Measurements of Photoluminescence and Raman Scattering

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Photoluminescence (PL) spectroscopy and resonant Raman scattering spectroscopy are the most important measurement techniques to characterize single-walled carbon nanotube (SWNT) properties. In this study, we developed a simultaneous PL and Raman scattering measurement system and performed the measurement of PL and Raman scattering spectra from a singly suspended SWNT. Laser beam from a Ti:sapphire laser (690 to 850 nm in wavelength) was used for excitation. Suspended SWNTs were grown between a pair of silica pillars [1]. The pillar spacing and height were 7 and 10 μm, respectively, and the diameter of the pillars was 2 μm. Since an address number was assigned to each of the pillars, we were able to measure each spectrum from the same suspended SWNTs, repeatedly. SWNTs were synthesized by chemical vapor deposition(CVD) method. Ethanol vapour and cobalt nano- particles were used as the carbon source and the growth catalyst.

For simultaneous measurement of PL and Raman scattering spectra, the excitation laser wavelength was only 785 nm. PLand Raman scattering emission light from a SWNT were separated with a dichroic mirror and introduced into each monochromator. The advantage of using a suspended SWNT is that the surrounding atmosphere of the SWNT is easily controlled from vacuum to gas phase, even to liquid phase in an environmental cell.

Furthermore, molecular adsorption on SWNT can be probed by PL spectroscopy [2].

By using the simultaneous PL and Raman scattering measurement system and the environmental cell, we investigated the effect of water molecular adsorption on the optical properties of SWNTs. In the environmental cell, the water vapor pressure and SWNT temperature were controlled. PL spectroscopy elucidated that the optical transition energies in water vapor were lower than those in vacuum, because water molecules adsorbed on SWNT surface and they increased the dielectric constant surrounding SWNTs. On the other hand, the G-band peak in Raman scattering spectra did not change, while RBM peaks showed a slight shift. It indicated that the adsorbed water molecules on SWNTs affected the specific phonon frequency. Especially, it was likely that the frequency of the RBM could be affected by the adsorbed water molecules on SWNTs geometrically.

[1] J. Lefebvre, Y. Homma and P. Finnie, *Phys. Rev. Lett.*,**90**, 21740, (2003).
[2] S. Chiashi, S. Watanabe, T. Hanashima and Y Homma, *Nano Lett.*, **8**, 3097, (2008).

Sensitivity of Boron Nitride Nanotubes toward Biomolecules

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Interfacing biomolecules with nanomaterials and understanding the applicability of bio-conjugated nanostructured materials in technologically important areas are forefront research activities. There exist numerous studies that have focused on carbon-based nanostructures, addressing the challenges to interface biomolecules with nanomaterials, e.g., non-uniformity and instability of carbon nanotubes in solutions. Semiconducting boron nitride nanotubes (BNNTs) which possess morphology similar to that of carbon nanotubes (CNTs), but with distinct properties on their own, appear to be more appropriate candidates for bio-medical applications. Recent experiments report that functionalized BNNTs with biological epitopes can mediate protein and cell binding, and also deliver DNA-oligomers to the interior of cells with no apparent toxicity. We investigated the electronic response of BNNT in the presence of the DNA and RNA nucleobases adenine (A), guanine (G), cytosine (C), thymine (T) and uracil (U)- and the amino acids – arginine (Arg), tryptophan (Trp) and aspartic acid (Asp). Trp is a non-polar aromatic amino acid whereas Asp and Arg are polar amino acids. The results obtained from density functional theory calculations show that molecular interactions between BNNT and nucleobases are mainly governed by van der Waals (vdW) forces [1]. The calculated order of the binding energy is predicted to be $G > A \approx C \approx T \approx U$, implying that the interaction strength of the high curvature BNNT with the nucleobases is very similar, G being an exceptional case. The higher binding energy for the G-BNNT conjugate appears to result from hybridization of the molecular orbitals of G and the BNNT. For the case of amino acid molecules, the calculated results find Asp and Arg to be closer to the tubular surface relative to Trp. Negligible charge transfer is found for the Trp-BNNT complex suggesting the dominance of non-covalent interactions. An occurrence of a relatively large charge transfer from the polar amino acids to the tubular surface of BNNT suggests stabilization of the bio-conjugated complex due to electrostatic interactions. The results find modulation of the band gap of pristine BNNT by Trp, though no change in band gap is seen for polar conjugates. A relatively large binding energy of the Arg-BNNT complex may suggest the possibility of Arg to be the amino acid that can facilitate a direct link to BNNT. Thus, the results suggest BNNTs to be candidate nanomaterials for design and development of a new class of biological probes at the nanoscale.

[1] S. Mukhopadhyay, S. Gowtham, R. H Scheicher, R. Pandey, and S. P. Karna; *Nanotechnology* **21**, 165703, (2010).

Visible Photoluminescence From Copper Nanoparticle/ Multiwall Carbon Nanotube Nanohybrid

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Since their discovery, carbon nanotubes (CNTs) have continuously attracted attention due to their exceptional structure dependent mechanical, chemical and electronic properties [1]. Noble metal nanoparticles on the other hand exhibit interesting properties, specially the optical properties associated with the excitation of surface plasmons. CNTs decorated with metal nanoparticles bring a new category of nanomaterials into focus [2] due to the combined properties of nanoparticles and nanotubes. Such CNT/metal nanohybrid may find wide applications in sensor devices, catalysts for fuel cells, solar cells, hydrogen storage devices and as fillers etc. In this article we report a lucid chemical technique to intercalate multi-walled carbon nanotubes (MWCNTs) with Cu nanoparticles. The hybrid product has been characterized by high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and Fourier transform infrared spectroscopy (FTIR). MWCNT/Cu nanomaterial has shown photoluminescence emission in the range of 550-650 nm when excited in the plasmon absorption region. Among the noble metals, CNT/ Ag hybrid achieved significant attention owing to their potential applications as optical limiter [3], catalyst etc. Cu being comparatively cheaper and easily available material, can be used to replace Au, Ag, Pt etc. in CNT/metal nanohybrids which can also find applications in optoelectronic devices. This type of emission from Cu nanoparticles intercalated MWCNTs has rarely been reported.

[1] C.N.R. Rao, B.C. Satishkumar, A. Govindaraj, M. Nath, *Chem. Phys. Chem*. **22**,78–105, (2001).
[2] M. A. Correa-Duarte, L. M. Liz-Marzan, *J Mater Chem* **16**, 22-25, (2006).
[3] K. C. Chin, A. Gohel, W. Z. Chen, A. I. Elim, W. Ji, G. L. Chong, C. H. Sow, A.T.S. Wee, *Chem. Phys Lett* **409**, 1-3,85-88, (2005).

Photoconductivity And Optical Response Of MWCNT Devices

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Photocurrent measurements derived by light excitation have been reported in different configurations exploiting Carbon Nanotubes (CNTs) [1]. Photoresponse in macro-bundles of Multi-Walled Carbon Nanotubes (MWCNTs) has been observed [2], and a technologically promising high photon-to-current conversion has been demonstrated for MWCNTs by means of an electrochemical method [3]. Studies on large area sheets of MWCNTs grown on sapphire substrate [4] using also pulsed laser beams [5] may provide us opportunities for constructing smart structures with multiple functionalities.

We have grown MWCNTs at 700 °C by thermal Chemical Vapour Deposition (CVD) of acetylene (C_2H_2) gas, in hydrogen (H_2) atmosphere, onto quartz substrates with iron (Fe) catalyst nanoparticles. A Fe thin film (3 nm) has been deposited by thermal evaporation onto masked substrates, in order to obtain different CNT configurations. Gold (Au) electrodes have been evaporated on the ends of each CNTs strip.

These devices have been used in order to investigate photoconductivity properties of MWCNTs under ultraviolet, visible and near-infrared radiation, using a spectrophotometer beam as a light source. The spectral photoresponse of all samples increases with increasing photon energy and very interesting agreement is found between the trends of the photoconductance and the absorbance, demonstrating a strong correlation between optical and electrical properties of our MWCNTs.

We study photoconductivity properties of MWCNTs in order to produce large area light sensors as well as optoelectronic nanodevices.

[1] K. Balasubramanian, Y. Fan, M. Burghard, K. Kern, M. Friedrich, U. Wannek, A. Mews, *Appl. Phys. Lett.*, **84**, 2400, (2004).
[2] J. Wei, J. Sun, J. Zhu, K. Wang, Z. Wang, J. Luo, D. Wu, A. Cao, *Small*, **2**, 988, (2006).
[3] P. Castrucci, F. Tombolini, M. Scarselli, E. Speiser, S. Del Gobbo, W. Richter, M. De Crescenzi, M. Diociaiuti, E. Gatto, M. Venanzi, *Appl. Phys. Lett.*, **89**, 253107, (2006).
[4] M. Passacantando, F. Bussolotti, V. Grossi, S. Santucci, A. Ambrosio, M. Ambrosio, G. Ambrosone, V. Carillo, U. Coscia, P. Maddalena, E. Perillo, A. Raulo, *Appl. Phys. Lett.*, **93**, 051911, (2008).
[5] A. Ambrosio, M. Ambrosio, G. Ambrosone, V. Carillo, U. Coscia, F. Gesuele, V. Grossi, P. Maddalena, M. Passacantando, E. Perillo, A. Raulo, S. Santucci, U. Ugolino, *NIM A*,**589**, 398, (2008).

Novel nanostructure with vertically aligned carbon nanotubes: Synthesis, structural properties and applications

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We present a unique nanostructure with carbon nanotubes (CNTs), which stands out with a special form of the tip growth mode where the top layer is a continuous and smooth bi- metallic film. Such a structure was obtained with catalyst layer stacks like Cr/Ni or Cr/Co, which entirely lift-off from the substrate during the growth. Unlike typical appearance of CNT films, the surface appears remarkably smooth and shiny metallic.

Due to CNT growth between a layer and the substrate the nanostructure was defined as interlayer CNT (ICNT) film**.** The ICNT structure can be obtained in a special thermal CVD process. The CNT film height and structure can be precisely controlled with CVD parameters. Processes are highly reproducible and can be performed on wafer scale.

Extensively characterization with techniques like SEM, AFM, XRD, TEM, and Raman spectroscopy are presented to enlighten the structural composition, growth properties, and growth mechanisms. The role of Cr was identified as a co-catalyst supporting the catalytic function of embedded Ni nanoparticles. This special configuration is the prerequisite for the ICNT growth with multi-walled CNTs which have a higher quality and higher straightness as CNTs grown in conventional processes.

The special structure and properties of the ICNT film facilitate improved fabrication processes and new integration possibilities of CNTs in various applications. Thus, a freely configurable layer stack can be deposited on an ICNT film without intermixing with the CNTs. For instance, this can simplify the CNT via fabrication process in ULSI circuits and improve the electrical/thermal contact at the upper CNT/metal interface.

Moreover, the ICNT growth allows the fabrication of novel nanostructures with interlocking and/or multidirectional grown CNTs in one structure. This can be applied in electronic applications like super capacitors, NEMS, and different sensors. Different integration approaches and first results on those are going to be highlighted.

Perovskite Oxides On MWNTs For Functional Nanoscale Devices

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Perovskite oxides (ABO3) have a broad set of functionalities (i.e., they are piezoelectric, ferroelectric, magnetic and multiferroic), and are used in an entire spectrum of applications. While Carbon nanotubes (CNTs) exhibit remarkable physical properties for applications in nanoelectronic circuits as interconnects and vias. A combination of CNTs with these materials conformaly at their ends could result in an extension of their individual functionalities to create multi-functional 1D perovskite nanostructures that could be easily integrated with conventional microelectronic processes due to compatibility of CNT growth with CMOS processing. Here, we have deposited a range of perovskite type materials like $BaTiO_3$, $BaxSr_{1-x}TiO_3$, and PZT on vertically aligned multiwalled carbon nanotube (MWNT) arrays grown on n-Si by pulsed laser deposition. The as deposited thin films are conformal with high aspect ratios, nano -crystalline and retain their respective 2-D material properties.

We find that the MWNTs are robust and endure the high temperature range ~ 450-700 °C that is a prerequisite for high quality film growth. They also withstand the partial oxygen atmosphere that is required by perovskite oxides in the entire temperature range. As a specific example of functionality, ferroelectric switching from a single $BaTiO_3$ coated vertical MWNT will be presented. These functional nanotubes could be used in a range of nanoscale devices from 3-D ferroelectric and multiferroic memory elements to terahertz emitters, piezoelectric energy generators and high energy density storage devices.

Controlled Synthesis and Macroscale Assembly of Carbon Nanotubes for Nanoelectronics and Macroelectronics

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Carbon nanotubes hold great potential but also face significant challenges for future electronic applications. In this talk, we report our recent progress on type- and chirality- controlled synthesis of massively aligned carbon nanotubes for nanoelectronics. In addition, we will present, for the first time, a monolithically integrated active matrix organic light- emitting diode (AMOLED) based on high-purity semiconducting carbon nanotube thin-film transistors (TFTs).
We have previously reported wafer-scale synthesis and transfer of high-density aligned carbon nanotubes for CMOS integrated circuit applications. However, in order to achieve predictable and uniform device performance for large scale integrated circuits, it is important to control the type and chirality of the carbon nanotubes. To address the problem of coexistence of metallic and semiconducting nanotubes, we have carried out the controlled synthesis of predominant semiconducting nanotubes using chemical-vapor deposition. Under optimized growth conditions, we have observed that more than 90% of the nanotubes are semiconducting, as confirmed by Raman and electrical characterizations. In addition, Rayleigh scattering has been utilized to further confirm the chiralities of the as-synthesized semiconducting nanotubes.
We have also carried out chirality-controlled carbon nanotube synthesis by moving away from metal catalyzed CVD and using chirality-pure nanotube seed instead. Extensive AFM, Raman, Rayleigh, and electrical characterization results will be presented.
Besides aligned carbon nanotubes for nanoelectronics, we have also demonstrated monolithically integrated AMOLED, CMOS integrated circuits, and transparent/flexible electronics using high-performance TFTs with high-purity semiconducting carbon nanotubes. Key technology components including assembly of high-density, uniform separated nanotube networks,high-yield fabrication of devices with superior performance, and n-type nanotube TFTs with air-stable operation will also be discussed.
In conclusion, this work has addressed the challenging task of controlling the electronic type and chirality of carbon nanotubes, and can serve as a critical foundation for future nanoelectronics and macroelectronics.

[1] C. Wang, J. Zhang, K. Ryu, A. Badmaev, L. Gomez, C. Zhou, *Nano Letters,* **9**, 4285- 4291, (2009).
[2] C. Wang, J. Zhang, C. Zhou, *ACS Nano*, **4**, 7123-7132, (2010).
[3] J.Zhang,C. Wang, Y.Fu, Y. Che, C. Zhou, *ACS Nano, ASAP*, (2011).

A Novel Procedure for the Manufacture of Vertical Carbon Nanotube Interconnects

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Carbon nanotubes have outstanding electrical, mechanical and thermal properties that make them potential candidates for next-generation electronic interconnections. Many problems have still to be resolved before this technology becomes main stream. One of these problems is the development of a manufacturing process that is compatible with electronic packaging processing temperatures, that is scalable and able to produce interconnects with low contact resistance and with good adhesion to the substrate. The process suggested here starts from the fabrication of a forest of vertically aligned nanotubes (in the range from 80 µm to 300 µm) on a silicon substrate. The nanotubes are then transferred on a conductive substrate and soldered on both sides with two different types of solder. Initial results show that the described procedure produces interconnects in which CNTs adhere well to the substrate. Raman spectroscopy has shown that the nanotubes are not affected by the manufacturing process. This novel prototype method has been demonstrated to produce electronic interconnects in a relatively simple way, with a process that is industrially scalable and at temperatures compatible with the traditional packaging processes.

Carbon nanotube and graphene-inorganic hybrid materials as next-generation photocatalysts

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Carbon nanotube (CNT) and graphene–inorganic hybrids are an exciting new class of functional materials (D. Eder, *Chem. Rev.* 2010). In contrast to the classical nano- composites, where CNTs are mechanically dispersed in an inorganic matrix, hybrids, in which CNTs are coated by a thin inorganic layer, combine their properties in a way that creates new properties distinct from those of either building block. A considerable synergistic effect originates from the close coexistence of the two phases in the form of interfacial charge and heat transfer processes. As a consequence, CNT-inorganic hybrids have shown increased sensitivities in gas sensors, improved efficiencies in photovoltaics, superior activities in photocatalysts, and enhanced capacities in supercapacitors.

I will present a simple and versatile synthesis route for hybrid materials, and also introduce the first complex hybrids, using a zeolite (i.e. TS-1) as the inorganic compound. I will show that due to their high thermal conductivity, CNTs and graphene can act as heat sinks in stabilising small inorganic particles during calcination treatments. Finally, I will demonstrate the greatly enhanced performance of hybrids over nanocomposites, as well as the superiority of graphene over CNTs in hybrids, for the photocatalytic degradation of organic dyes.

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Chirality-Separation Mechanism of Carbon Nanotubes by Gel Chromatography

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Mono-structured single-wall carbon nanotubes (SWCNTs) are essential in both the scientific research and practical applications such as electronic and optical devices. Recently, we developed simple methods for continuous separation of metallic (M)- and semiconducting (S)-SWCNTs using agarose gel chromatography [1-3]. We found that successively increasing sodium deoxycholate solution concentration during the collection of S-SWCNTs permitted a low-resolution diameter separation [2, 3], but further chirality separation is not possible.
Most recently, we developed single-surfactant multicolumn gel chromatography (SS- MUGEC) for large-scale chirality separation of SWCNTs[4, 5]. In this method, commercial Sephacryl gel (HR S-200 or S-300, GE Healthcare) was used as the medium. Loading excess amount of SWCNT dispersion (that is, overloading) onto a series of gel columns led to selective adsorption of S-SWCNT fractions containing different chiralities in various gel columns. In this manner, large-scale single-chirality separation of nanotubes was achieved. In this study, we will systematically investigate the chirality-separation mechanism of nanotubes by the SS-MUGEC method in which we proposed that the interaction strength between nanotubes and the gel is dependent on the structures of SWCNTs. The structure-dependent interaction of nanotubes with the gel is thought to originate from different surfactant coating coverage on their surfaces. Direct experimental evidences will be shown to demonstrate the proposed separation mechanism.

[1] T. Tanaka et al. *Appl. Phys. Express* **2**, 125002, (2009).
[2] H. Liu et al., *J. Phys. Chem. C* **114**, 9270-9276, (2010).
[3] H. Liu et al., *Phys. Status Solidi B* **247**, 2649-2652 (2010).
[4] H. Liu et al., NT 10, 11th International Conference on the Science and Application of Nanotubes, Montreal, Canada (2010) pp 52.
[5] H. Liu et al., *Nat. Commun.* Accepted.

Preferential Destruction Of Metallic SWCNTs By An RF-Plasma In Inert Gases

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A number of applications ask for purely semiconducting or metallic Single-Wall Carbon Nanotubes (SWCNTs). Of specific interest is the removal of metallic SWCNTs (m-SWCNTs) which is typically easier to obtain than the reverse, the complete removal of semiconducting SWCNTs (sc-SWCNTs) due to the different electronic structure of both nanotube types1. RF-plasma can aid in the preferential destruction of m-SWCNTs in reactive atmospheres.2

Here we report on the preferential destruction of m-SWCNTs deposited on surfaces by a 13 MHz RF-plasma in an inert atmosphere with noble gases. As no reactive chemical species is present, a different reaction pathway than chemical reaction needs to take place, possibly directly by an electron heating process inside the m-SWCNTs.

Interestingly, the strength of the applied electrical field has a minor effect on the success of the removal of m-SWCNTs while the noble gas pressure is key. Reasons for this removal of m-SWCNTs in a non-reactive atmosphere are discussed. Given the relative success, parameter optimizations took place to reach at a selectivity of 100% to get purely sc-SWCNTs on the processed surfaces.

[1] M.S. Strano, C.A. Dyke, M.L. Usrey, P.W. Barone, J.M. Allen, H. Shan, C. Kittrell, R.H. Hauge, J.M. Tour, R.E. Smalley, *Science* **301**, 1519-1522, (2003).
[2] G. Zhang, P. Qi, X. Wang, Y. Lu, X. Li, R. Tu, S. Bangsaruntip, D. Mann, L. Zhang, H. Dai, *Science* **314**, 974-977, (2006).

Diameter And Chiral Selective Purification Of SWNT And DWNT Using CO_2

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High temperature oxidation of carbon nanotubes in air is a well known method to eliminate carboneous impurities from raw material. Recently, it has also been used to selectively remove single-wall carbon nanotubes (SWNT) present in double-walled carbon nanotubes (DWNT) soot [1]. Here, we propose a purification process for both SWNT and DWNT based on a high temperature oxidation in a pure CO_2 gas flow (the so-called inverse Boudouard reaction). This treatment, combined with a standard reflux in nitric acid, provides fast oxidation of amorphous carbon and removal of other impurities without affecting the carbon nanotubes. Because the CO_2 treatment is endothermic, it prevents chain reaction oxidation and allows a better control of the selectivity of the reaction. This feature limits the carbon nanotubes mass loss which is a clear advantage compared to the air oxidation process (~95% mass loss).
Parameterization of the temperature and time of the treatment allowed us to observe both diameter and chirality dependence of the nanotubes reaction rate with CO_2. This selective character was applied to produce high quality thin films of (a) clean and highly enriched DWNT and of (b) highly enriched semiconducting SWNT. The process was used respectively to (a) remove the SWNT present in the initial soot of DWNT and to (b) preferentially oxidize the metallic nanotubes from SWNT samples. The properties of those films will be presented. AFM, TEM, UV-vis-IR absorption and Raman spectroscopy analyses reveal that the thin films treated by this CO_2 process are composed of very high quality carbon nanotubes (micrometers long, very low impurity and catalyst concentration, low Raman ID/IG ratios). Also, no significant nanotube shortening is observed following the different diameter or chirality enrichment treatments.

[1] K. Iakoubovskii, N. Minami, T. Ueno, S. Kazaoui and H. Kataura, *J. Phys. Chem. C*, **112**, 30, (2008).

Non-Destructive And Scalable SWCNT Purification

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Standard wet acidic purification chemistry always attacks the nanotubes to be purified. To avoid excessive damage, the purification conditions (pH-value, concentration, temperature) need to be carefully controlled. This also means that purifying a small amount (grams) of single-walled carbon nanotubes (SWCNTs) requires large reaction bottles with lots of chemicals and acids. This is costly, produces lots of aggressive waste-waters, and is very limited in purifying larger SWCNT quantities. For this reason, economically and cost-efficient and easily scalable, thus attractive ways are explored with a chemistry that does not attack the structural integrity of SWCNTs.
For this reason, different non-oxidative solvents have been under investigation, from size selective solvents (by-products go into solution, SWCNTs go into the sediment) over surfactant-based dispersion experiments (selective dispersion) up to non- oxidizing acids allowing to remove some of the non-carbonaceous by-products while not attacking SWCNTs. The poster shows the different routes and the success accompanied with them. For example, stirring SWCNT in NMP results in a quite good separation of by-products from nanotubes but does not allow up-scaling.

Self-Assembly of Doubly-Clamped/Cantilevered Carbon Nanotube Arrays by a Precise Positioning Method

Ji Cao*, Adrian M. Ionescu

A new method for assembly of doubly-clamped/cantilevered carbon nanotube (CNT) arrays based on our previous work by pre-defined trenches in resist layers is presented. [1] Aligned doubly-clamped/cantilevered CNT arrays with precisely controlled location and density can be achieved on guiding electrodes with arbitrary distance.

Moreover, the fabricated doubly-clamped CNT-clamp pairs are proved to have good conductance. This novel technique provides a more flexible way to fabricate CNT relays or CNT field effect transistors (FETs) on large scale.

It could also enable the mass production of future CNT based complementary logic circuit and NEMS devices. [2]

The process flow is depicted in Fig. 1. First, Ti/Pd electrodes were patterned on a SiO_2 (500 nm)/Si substrate (Fig. 1a), which is then coated with 100 nm LOR/100nm PMMA(Fig. 1b). Unlike the earlier reported ac-dielectrophoresis (DEP) assembly with a critical requirement on the distance between the guiding electrodes, in our method, the distance is arbitrary. Narrow trenches were transferred to the resist layers above the two parallel borders of one of the electrodes (“Electrode A”) by e-beam lithography (Fig. 1c). Then, an ac voltage was applied to“Electrode A”, leaving the other (“Electrode B”) grounded (Fig. 1d). CNTs were attracted to “Electrode A” surface, aligned along the electric field gradient (perpendicular to the borders of “Electrode A”) and further centered into the trenches by the capillary force (Fig. 1e). The clamp windows were defined on a second 50 nm PMMA layer by e-beam lithography (ELB) (Fig. 1f and 1g). Before stripping the resists, single and double clamps were deposited for CNT cantilevers (being dried in critical point dryer) and doubly-clamped CNTs, respectively (Fig. 1h).

Distributions of CNTs on the electrodes without trenches were demonstrated in Fig. 2. CNTs were aligned on the borders of the “Electrode A”, along the electric field. It is shown in Figure 2c that the CNTs on the border are parallel and has distinguishable density, which make it possible for trapping 1 CNT into each trench. Fig. 3 shows that even after long time DEP, CNTs on the borders were assembled only into the pre-defined trenches with little misalignment and impurity. Thus, by adjusting DEP time, number of CNTs in each trench is controllable.

Fig. 4 demonstrates the CNT arrays with one end fixed and the other unclamped, which can be used to fabricate CNT cantilevers if dried in critical point dryer. The length of the CNTs, the thickness of the LOR layer, and the quality of the tubes determine the final suspended height of the free end of the CNTs. Fig. 5 demonstrates the CNT arrays with both ends clamped by defining clamps on both ends during EBL, which can be used to fabricate back-gated CNT FET arrays and so on.

Fig. 6 plots the I-V curve of one of the doubly-clamped CNT-metal pair, after annealing at 200 degree C for 1 hour.

It shows good conductance of the pair and the quality of the contact is approved.

To sum up, self-assembly of both doubly-clamped CNT arrays and CNT arrays with one clamp fixed has been successfully demonstrated, by the proposed method based on trench assisted

DEP on parallel borders of two guiding electrodes with arbitrary distance. Meanwhile, the CNT-metal contacts are proved to be active and robust.
The versatile technique is fully compatible with current CMOS technology, facilitating future electrical connection of CNTs to underlying complex Si circuitry.

[1] J. Cao, A. Arun, K. Lister, D. Acquaviva, J. Bhandari, A. M. Ionescu, Nanotech 2010, June 21-24, 2010, Anaheim, CA, USA.
[2] Z. Hou, D. Xu and B. Cai, *Appl. Phys. Lett.* **89** 213502, (2006).

Fine Patterning of Carbon Nanotube by Electrohydrodynamic Printing

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Single-walled carbon nanotubeline patterns with a width of 10 microns were printed by electrohydrodynamic (EHD) printing method.
Carbon nanotube has many excellent physical properties such as good thermal conductivity, good mechanical strength, and high electric conductivity. Consequently they have a lot of applications like transparent conducting film, field emitter, and sensors. The fabrication of the devices with carbon nanotube requires a fine patterning process of carbon nanotube in general. The patterning of carbon nanotube was demonstrated by using catalyst or chemical vapor deposition but they usually require complex photolithography processes.
Inkjet printing process was one of the candidates to overcome this problem and some groups have shown the pattering of carbon nanotube by thermal or piezoelectric inkjet printing[1]. But the resolution of conventional inkjet printing is limited and the clogging increases dramatically with the nozzle size decreasing for fine patterning.
EHD printing gathered much attention after its high resolution printing capability was demonstrated [2]. Unlike the conventional inkjet printing head, the size of the droplet by EHD printing can be much smaller than the diameter of the nozzle. So we can use a very large nozzle to print small patterns of carbon nanotube, which prevents nozzle clogging problem.
We used a water-based 0.1 wt.% single-walled carbon nanotube suspension as a ink and the ink was injected in the stainless-steel nozzle with a inner diameter of 140 microns and a outer diameter of 340 microns. The nozzle is placed over the glass substrate on the metal chuck connected to the ground while the nozzle is connected to a high voltage supply and several kV DC was applied to the nozzle. The distance between the nozzle and the substrate was about 1 mm. The ejection happens at 2-4 kV with a pulsating conejet mode. The jetting frequency varies with the applied bias voltage. We could get circular pattens whose diameter is about 100 microns at 2-4 kV and observed spray mode at over 4 kV. So the size of the pattern is only one third of the nozzle outer diameter.
We also used commercial glass capillaries with a diameter of 20 microns for finer patterns with similar method while the distance was changed to about 200 microns. We could observe a pulsating mode below 2 kV and continuous conejet mode at a bias voltage from 2 to 4 kV. With a continuous conejet mode, line patterns with a width of 10 microns was achieved at 3.5 kV and the electrical resistance was measured to 2 Mohm for the pattern with a length of 10 mm.

[1] K. Kordas, et. al., *Small*, **2**, 1021-1025, (2006).
[2] J.-U. Park, et. al.,*Nature Materials*, **6**, 782-789, (2007).

Photografting Aligned Carbon Nanotube Networks: Towards Composites and Nanoporous Membranes

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Vertically Aligned Carbon Nanotube carpets (VACNT) are potential candidates for a large range of applications in nanotechnology. Particularly, they can be considered as building blocks for the design of composites containing anisotropic nanomaterials as well as nanoporous membranes exhibiting cylindrical aligned pores composed of the hollow cores of VACNT. The preparation of such materials needs to impregnate VACNT carpets by a polymer resin which fills the inter-tube empty space. Moreover, in order to increase the chemical compatibility between CNT and polymer resins, CNT surfaces have to be functionalized. This two-step process including functionalisation and impregnation has already been reported in the literature [1, 2] but the experiments are often restricted to thin VACNT carpets and the materials obtained after the functionalization and impregnation steps are not fully analyzed.
In this presentation, we will focus both on CNT carpet synthesis by aerosol assisted CCVD [3, 4] and on CNT surface functionalization to obtain nanocomposites and nanoporous membranes. In particular, we will present an original method based on photochemistry which allows both the CNT functionalization and the impregnation of millimeter thick VACNT carpets. We will demonstrate that it is possible to covalently and homogeneously graft styrene through the entire thickness of VACNT carpets. Complementary techniques, such as TGA, SEM-EDX, nuclear microprobe, TEM are used to determine the amount of polymer resin grafted, its thickness on CNT and the polymer distribution all along the VACNT carpet thickness. By changing the photochemical reaction duration, we will also show that it is possible to obtain a complete impregnation of CNT carpets leading to a one-step process to obtain nanocomposites and nanoporous membranes with well controlled CNT/polymer resin interface chemistry. Finally, we will present how to get thin membranes up to hundreds of micrometers from macroscopically thin 1D composite samples.

[1] V.P. Veedu et al., *Nature Materials,* **5**, 457-462, (2006).
[2] J Suhr et al., *Nature Materials,* **4**, 134-137, (2005).
[3] M. Pinault et al., *Nano Lett*. **5**, 2394, (2005).
[4] C. Castro et al., *Carbon,* **48**, 3807-3816, (2010).

The Growth Pattern and Thickness Evaluation of Mesenchymal Stem Cells Cultured on a Variety of Single-Walled Carbon Nanotube

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Since their discovery in 1991, carbon nanotubes (CNTs) have attracted much attention because of their electrically conductive properties and potential for a wide variety of biological applications such as tissue engineering scaffolds, the delivery of drugs, cell tracing and growth platform for neuronal circuits. [1] Mesenchymal stem cells (MSCs) are of special interest because they are self-renewable and multipotent, and can also trans-differentiate into specific tissue cells such as osteoblasts, chondroblasts, adipocytes, and even neuronal cells both in vitro and in vivo.[2] Unlike embryonic stem cells, MSCs are isolated from a variety of tissues, such as bone marrow and adipose tissues. Since MSCs have large differentiation potential, its ex vivo culture expansion and the preservation of stem cell properties have been attracted researcher's attentions. The aim of this study is to evaluate the growth and shape of MSCs cultured on various single-walled carbon nanotube (SWNT) films that have different degrees of thickness and roughness. The thickness, roughness and directional alignment of SWNT films are found to affect the growth pattern of MSCs including their thickness. Our results provided fundamental information on carbon nanotubes for the biocompatibility, and demonstrated that SWNT films can be utilized as substrates for controlling the growth and differentiation of MSCs through the surface modification and the thickness control of the films. Furthermore, to investigate the effect of SWNT films on differentiation property of MSCs, we induced adipogenesis using adipogenic medium, and stained it with oil red O solution. Our results demonstrated that the SWNT Langmuir-Blodgett film and SWNT network film based scaffolds did not show any cytotoxicity, and on the other hand it promoted differentiation property of MSCs comparing to normal culture controls. In addition, lipid vesicles in adipocytes were also differentiated. Our study may suggest for the differentiation to other specific cells by utilizing various SWNT films.

[1] G. Cellot, E. Cilia, S. Cipollone, V. Rancic, A. Sucapane, S. Giordani, L. Gambazzi, H. Markram, M. Grandolfo, D. Scaini, F. Gelain, L. Casalis, M. Prato, M. Giuglizno and L. Ballerini, *Nat. Nanotechnol.*,**4**, 126, (2009).
[2] L. Ferreira, J. M. Karp, L. Nobre and R. Langer, *Cell*, **3**, 136, (2008).

Synthesis, Characterization, and Theoretical Studies of Hybrid ZnO Nanoparticles and Nitrogen-Doped Carbon Nanotubes

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We have synthesized ZnO nanoparticles (ZnO-NPs) anchored on the surface of nitrogen-doped multiwalled carbon nanotubes (CN_x-MWNTs). The anchoring process consisted in adding CNx-MWNTs (previously synthesized using chemical deposition method) in a solution containing dimethylformamide, zinc acetylacetonate, and thiophene. The thiophene solvent was used as a capping agent. Different samples were obtained by varying the thiophene concentration. Scanning and transmission electron microscopy characterizations revealed that ZnO-NPs are homogeneously distributed along the CN_x-MWNTs. X-ray diffraction analysis demonstrated that the ZnO-NPs exhibit a Wurtzite crystal structure with an average diameter equal to 5 nm. We found that the ZnO-NPs does not exhibit a preferential grown direction respect to the nanotube surface, and its growth is controlled by the concentration of passivating agent. First- principles density functional calculations in the local spin density approximation were performed to understand the role of the sulfur atoms (coming from the passivating agent) during the formation of ZnO-NPs and the interaction with CN_x-MWNTs. Our theoretical results on different nanoparticle sizes revealed the presence of unpaired spins on the isolated ZnO-NPs passivated with sulfur. The obtained magnetic moments were located mainly at the surface and on the sulfur atoms. In addition, a ZnO-NP was set on the surface of a N-doped (10,0) single walled carbon nanotubes. After geometry relaxation, the ZnO-NP was attached to the nanotube surface exhibiting a net total magnetic moment. The ZnO-NP was preferentially bonded to the surface of carbon nanotubes via oxygen atoms.

Ab initio simulations of carbon nanotube bundles used as gas sensors

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Carbon nanotubes present great potential for applications due to many interesting properties such as the possibility to be either metal or semiconducting depending on the chiral vector. One could also mention its high surface area to volume ratio which leads to one of the possibilities which raises the highest hopes: the area of nanotube-based gas sensors. One, for instance, envisions the possibility of combining high sensitivity with room temperature operation, surpassing more commonly used semiconductor-based sensors. At the same time, from the technological point of view, one is probably going to use bundles of CNTs instead of a single tube due to commercial viability.

In this work we use density functional theory (DFT) calculations to determine the electronic structure properties of different molecules interstitially positioned between the nanotubes in a bundle. From the most stable structures we couple the DFT calculations to a recursive Green's function method to simulate the electronic transport properties of nanotube bundles containing a large number of molecules randomly distributed along the different tubes forming the ropes. This way one is able to simulate a realistic sensor based on three- dimensional nanotube bundles taking into consideration the effects of disorder. Our results show that both ammonia and CO when trapped between the tube walls show high sensitivity.

The effects of the stiffness of the supported ends on the resonant frequencies of an embedded double-wall carbon nanotube

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This paper studies resonant frequencies and associated vibrational modes for an individual double wall carbon nanotube embedded in an elastic medium with The general form of boundary conditions. The governing equations for free transverse vibration of the model, have been derived using a multiple elastic beam model, based on Euler–Bernoulli beam theory. The effect of the stiffness at the ends and The van-der Waals interaction between the tubes have been calculated. The model supports not only the traditional boundary conditions, such as as free-free, clamped-clamped and cantilever; but also all possible end conditions. The results indicate that the stiffness at each supported ends and the difference between the stiffness of two ends of Carbon nanotube play an important role in resonant frequencies. Detailed results are revealed for aspect ratio, mode number and stiffness of an elastic medium on the vibration of CNTs with general boundary conditions.

Characterisation of Carbon Nanotube Macro-Yarns

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Carbon nanotube fibers produced via The Cambridge Process show attractive mechanical properties such as strengths of up to 2 N/Tex [1] with no loss of strength on knotting [2]. The fibers can be spun in kilometer-lengths via the floating CVD-based method and the scalability of this process has recently resulted in commercial investment by TorTech Nano Fibers Ltd. The company intends to scale up the Cambridge process for the industrial production of hi-tech fabrics for anti-ballistic applications [3].

To enable the exploitation of the intrinsic properties of the fibers they must be spun into macro-yarns for downstream use in composites, cables/ropes and hi-tech fabrics, while transferring the superior mechanical properties of the fibers into the macro-yarn product. Lengths of prototype macro-yarns with diameters typically up to 500 microns, made from up to 600 individual fiber strands, have recently been produced in Cambridge and are undergoing structural analysis and initial tests. Results will be presented comparing the macro-yarn with both the individual fibers and with other high-performance yarns, including an analysis of the effects of knotting and twist angle on the strength of the macro-yarn.

[1] Koziol, K.K. et. al., *Science,* **318**, 1892-1895, (2007).
[2) Vilatela, J. J. and Windle, A. H., *Adv. Mater.*, **22**: 4959–4963, (2010)
[3] http://defense-update.com/wp/20101122_tortech_nano_fibers.html

Novel Testing Method Of Carbon Nanotube-Array Actuators

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Mats of randomly oriented carbon nanotubes, known as Bucky papers, show in contact with an ionic electrolyte an active strain based on the capacitor-like mode of operation [1]. The mats are manufactured by a filtration of an aqueous dispersion. The dispersion is made of commercially available CNT-powder. Various investigations show low reliability and reproducibility of powder-based structures because of the low powder-quality [2].

Furthermore the random orientation of the papers does not allow using the excellent properties of a single CNT. That is the reason why great efforts are made to align the free movable CNTs in the dispersion. Other aligned CNT-based structures like yarns or CNT- array-based papers suffer from low conductibility, low stiffness or bad alignment according to the manufacturing process. The mechanism of strain generation still remains undefined but there is a controversial discussion. Either it is a quantum-mechanical lengthening of C-bonds [3] or an electrostatic repulsion between charged CNTs [4]. Maybe it is a superposition of both mechanisms.

The presented paper focuses on a method for measuring the free strain of as produced vertically aligned CNT-arrays. The advantage of this approach is the analysis of a highly oriented CNT-based structure. The analysed arrays are provided by the working group of Schulte (Polymer Composites, Technical University of Hamburg-Harburg, Germany). The tubes have an average diameter of 20nm therefore they can be identified as multi walled carbon nanotubes (MWCNTs). The average length depends on the CVD-processing time and differs between 500µm and 1300µm. The basic substrate is silicon.

The cell of the set-up is designed for testing small volumes (15ml) of ionic electrolytes. The tested specimens are 10 x 10 mm in size. The specimen used as working electrode is fixed at the bottom of the cell by two PTFE-clamps. The clamps are electrical conductible because of inner Pt-electrodes. A CNT-mat or CNT-arrays positioned in the cell will be used as counter electrode. The calomel-reference electrode completes the three-cell set-up. A glass-cylinder, placed on the top of the CNTs transfers the deflection external of the electrolyte. The deflection of the glass-cylinder is measured by a confocal sensor.

The tests show a similar quadratic correlation between activation voltage and free strain like itis found using CNT-mats within aqueous electrolytes. A maximum strain of 0.14% could be achieved. In comparison the cation-induced strain (negative charged electrode) has a dominant character.

This presented test set-up, the way of analysis and the used specimen avoid on the one hand measuring secondary effects and allow on the other hand recording the reaction of one MWCNT standing in parallel as an array. Therefore the analysed effect must be dominated by a quantum-mechanical character.

[1] R. H. Baughman et al., *Science*, **284**, 1340-1344,(1999).
[2] N. Grobert,*Materials Today*, **9**, 64, (2006).
[3] S. Ghosh, et al., *Chem.Phys. Lett.*, **406**, 10-14,(2005).

[4] D. Suppiger, et al., *Phys. Chem.*, **11**, 5180-5185, (2009).

Carbon Nanoubes as substrates for Surface Enhanced Raman Spectroscopy

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The surface enhanced Raman spectroscopy (SERS) has attracted great attention in the last 30 years. It can increase the Raman signal of molecules by several orders of magnitude facilitating the detection of even trace molecules. In SERS effect, the substrates play a key role, being the responsible for the intensification of the Raman signal. The substrates are obtained by conventional deposition or immobilization of metal nanoparticles on a surface. The current challenge is the gain in performance with the fabrication of nanostructured SERS substrates. Recently, it was shown that if this surface is composed by carbon nanotubes, the effect can be dramatically increased. Also very recently, single or few layers of graphene were seen to work as SERS substrate without even the presence of metallic particles. In this work we investigate the Raman spectra of Raman spectra of octadecilamine molecules bonded to the surface of single- wall carbon nanotubes. Laser excitation energy is changed from 1.92 to 3.81 eV and the dependence of the Raman signal with excitation energy is observed. We note that under special conditions of resonance, the Raman signal of octadecilamine interacting with carbon nanotubes is strongly increased, becoming even stronger than the resonant Raman signal of the carbon nanotubes.

A Simulation Study on the Effects of Shear Flow and Nanotube Shape on the Microstructure and Electrical Properties of Carbon Nanotube/Polymer Composites

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Particle-level simulations are used to simulate carbon nanotube (CNT)/polymer composites in simple shear flow. A resistor network algorithm is used to determine the electrical conductivities.

Effects of different parameters such as nanotube flexibility, aspect ratio, shape and tunneling length and flow fields on the electrical conductivities of the composites can be studied with this method. Results show that using curved nanotubes with high aspect ratio and imposing shear flow reduces the electrical percolation threshold by facilitating the formation of a conductive network. We proved that nanotube agglomeration is beneficial for the electrical conductivity in CNT/polymer composites. In agreement with previous research, we show that the rate of imposed shear flow influences the conductivities of the composites as well as aggregation and orientation of the nanotubes . Flow induced orientation is studied by measuring the anisotropy in the flow-gradient and flow-vorticity planes. The degree of anisotropy is quantified by anisotropy factor and orientation angle measurements. Our simulations show that at high shear rates CNT aggregates are broken down because of the high hydrodynamic forces. Therefore a conductive network cannot be established and conductivity of the composite decreases. Broken aggregates create smaller aggregates or individual nanotubes which then align in the flow direction. Hence the individual cluster number and the anisotropy factor increases. At low shear rates the motion of the nanotubes causes build-up of agglomerates and decrease in orientation factor. Hence when the shear rate is decreased a conductive network can be formed increasing the conductivity of the composites.

Vapor-Solid-Solid Growth Mechanism of Carbon Nanotubes from SiOx Nanoparticles

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Catalyst is very important for the growth of carbon nanotubes (CNTs), especially single-walled CNTs (SWNTs),which can remarkably affect the diameter and wall number of CNTs, and the chirality distribution of SWNTs. Initially, only iron group metals (Fe, Co, Ni) were used as catalysts for SWNT growth via a vapor-liquid-solid mechanism. But recently it has been found that many other metals and some semiconductors are also able to grow SWNTs.
We have recently developed a simple and effective metal-catalyst-free chemical vapor deposition (CVD) method for the growth of SWNTs from SiO_x nanoparticles (NPs),1 and a “scratching growth” approach for the patterned growth of SWNTs on substrates without any metal species.[1] It was also found that SWNTs grow from SiO_x with an extremely slow growth speed of 8.3 nm/s, ~300 times slower than commonly used Co catalyst at the same growth condition.2 Thanks to this slow growth speed of SWNTs from SiO_x NPs, direct length-sorted growth of short SWNTs was achieved. [2]
In this contribution, we will present our recent results on the nature of catalyst (e.g., oxide vs carbide, liquid vs solid) and the growth mechanism of SWNTs in this metal- catalyst-free process by in situ and ex situ transmission electron microscopy (TEM) studies.[3] We first prepared SiO_x-NPs-filled multi-walled CNTs (MWNTs) for the in situTEM observations of the nucleation and growth of CNTs on SiO_x NPs. In such experiments, a SiO_x-filled MWNT was manipulated with a TEM-STM holder and connected with two Au electrodes. When a desired current passes through the MWNT, Joule heating leads to a local high temperature, and thus the MWNT serves as a nano- tubular-furnace. The temperature of this nano-furnace can be tuned by varying the current passed. Carbon atoms generated from the MWNT by electron beam-induced injection and thermal diffusion serve as a carbon source for the nucleation and growth of CNTs from the loaded SiO_x NPs. The in situ TEM studies unveil that the active catalyst for the SWNT growth is solid and amorphous SiOx NPs, suggesting a vapor- solid-solid growth mechanism. Moreover, we have also observed the nucleation of graphene layers on large SiO_x NPs upon heat treatment of SiO_x–filledMWNTs, indicating the ability of SiO_x for graphitization of carbons. The above research demonstrates the ability of oxides for the growth of CNTs and nucleation of graphitic carbon nanostructures, which may guide the designing and exploring of novel catalysts for the controlled and efficient growth of CNTs.

[1]. B.L. Liu, et al., *J. Am. Chem. Soc.*, **131**, 2082, (2009).
[2]. B.L. Liu, et al., *ACS Nano,* **3**, 3421,(2009).
[3]. B.L. Liu, et al., *J. Am. Chem. Soc.*, **133**, 197, (2011).

Sugar & proteins: Nano-Bioconjugates

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Sugars and Post-Translational Modifications are critical biological markers that modulate the properties of proteins. Our work studies the interplay of proteins, sugars and modifications and their utility.

(i) Synthetic Biology's development at the start of this century may be compared with Synthetic Organic Chemistry's expansion at the start of the last; after decades of isolation, identification, analysis and functional confirmation the future logical and free-ranging redesign of biomacromolecules offers tantalizing opportunities. New methods are required: despite 80-years-worth of non-specific, chemical modification of proteins, precise methods in protein chemistry remain rare. The development of efficient, complete, chemo- and regio-selective methods, applied in benign aqueous systems to redesign the structure and function of bioconjugates (proteins, polymers, nanoparticles, viruses, nanotubes) will be presented.

(ii) Bioconjugate Applications: These conjugates find application in: drug delivery, nanomolar inhibitors of bacterial interactions, gene delivery vehicles, probes of *in vivo* function, non-invasive presymptopmatic disease diagnosis, and localized delivery of unprecedented radio-dose.

[1] B.G. Davis, *Chem. Rev.* **2002**, *102*, 579-601.
[2] B.G. Davis, *Science* **2004**, *303*, 480-482
[3] S.I. van Kasteren, H.B. Kramer, H.H. Jensen, S.J. Campbell, J. Kirkpatrick, N.J. Oldham, D.C. Anthony, B.G. Davis, *Nature* **2007**, *446*, 1105-1109.
[4] C. Fleming, A. Maldjian, D. Da Costa, P. Penny, R.C. Noble, N.R. Cameron, B.G. Davis, *Nat. Chem. Biol.* **2005**, *1*, 270-274
[5] S.I. van Kasteren, H.B. Kramer, D.P. Gamblin, B.G. Davis, *Nat. Protoc.* **2007**, *2*, 3185-3194
[6] S.Y. Hong, G. Tobias, B. Ballesteros, F. El Oualid, J.C. Errey, K.J. Doores, A.I. Kirkland, P.D. Nellist, M.L.H. Green , B.G. Davis, *J. Am. Chem. Soc.* **2007**, *129*, 10966-10967
[7] G.J.L. Bernardes, J.M. Chalker, J.C. Errey, B.G. Davis, *J. Am. Chem. Soc.* **2008**, *130*, 5052-5053
[8] S.I. van Kasteren, S.J. Campbell, S. Serres, D.C. Anthony, N.R. Sibson, B.G. Davis *Proc. Natl Acad. Sci. U.S.A.* **2009**, *106*, 18-23
[9] S.Y Hong, G. Tobias, K.T. Al-Jamal, B. Ballesteros, H. Ali-Boucetta, S. Lozano-Perez, P.D. Nellist, R.B. Sim, C. Finucane, S.J. Mather, M.L.H. Green, K. Kostarelos and B.G. Davis, *Nat. Materials,* **2010**, *9*, 485-490.

Small-Sized Aggregates of Carbon Nanohorns Enabling Cellular Uptake Control

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The size of nanocarbons such as nanotubes, nanohorns, and graphene ribbons is a critical parameter for medical applications. The small-sized nanoparticles, especially 30-50 nm, are believed to be helpful to avoid the uptake by reticuloendothelial system (RES) including various macrophage cells and therefore to enhance the targeting ability in drug delivery system (DDS). However, the size control of nanocarbons is not easy especially below 100 nm. Here, we first present our new method to obtain small-sized aggregates (20-50 nm) of carbon nanohorns (S-SWNHs) by an oxidation exfoliation method from normal-sized aggregates (80-100 nm) of single-walled carbon nanohorns (L-SWNHs). The obtained S-SWNHs were large in quantity and high in purity. They had a high ability of material storage. S-SWNHs were hydrophilic and highly dispersed in water. These advantages suggest that S-SWNHs could be more suitable to the medical application than the other nanocarbons examined so far.

We next show superior property of S-SWNH than L-SWNH toward the drug delivery, namely, low uptake by macrophages and high uptake by cancer cells. The cellular uptake was observed with confocal microscopy and quantified by optical absorption measurements, where SWNHs were identified by their black color or strong optical absorption in visible range. No fluorescent label was needed. The results showed that the uptake-quantities of S-SWNHs by macrophage (Raw 267.4) cells were much lower than those of L-SWNHs even without functionalization. By the functionalization with DSPE-PEG (noncovalently), S-SWNHs completely avoided the engulfment by the macrophage cells while the L-SWNHs did not. Folic acid modified S-SWNHs showed a higher uptake by KB cells (folate acide receptor over expressed) than the folic acid modified L-SWNHs. This controllable cellular uptake of S-SWNHs by the functionalization suggests their potential in the realization of ideal drug delivery system, selective delivery of drugs to the specific tissues or cells.

Coronenes Encapsulated Single-walled Carbon Nanotubes for Imaging Probes Targeted to Cancer Cells

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Single-walled carbon nanotubes (SWCNTs) have great potentials for drug delivery and diagnostic imaging agents. One of the advantages of SWCNTs is that the outer surface of SWCNTs can be functionalized covalently or non-covalently, independent of the encapsulated molecules. Proper functionalization of the tube wall leads to a high selective targeting ability to the particular cells or tumours. Furthermore, the encapsulated agents and drugs are isolated from active molecules by the tube wall, which leads to the superior durability of the materials. Here, we demonstrates that fluorescent molecules, coronene ($C_{12}H_{24}$), encapsulated SWCNTs can be used for such nano-carrier type imaging probes targeted to cancer cells. Coronene encapsulated SWCNTs (Coronenes-SWCNTs) were synthesized by sublimation in a vacuum. According to the TEM images, coronene molecules are packed into the SWCNTs and take a one-dimensional stacking structure in high yield [1]. We observed a fluorescence spectrum of Coronenes-SWCNTs micelle solution by 350 nm wavelength excitation. The obtained spectral shape was sharply different from those of the coronene molecules dissolved in an organic solvent and the three-dimensional coronene solid. The difference in the spectral shape suggests that the encapsulated coronenes have unique electronic and optical properties due to the one-dimensional arrangements inside SWCNTs. In order to confirm the uptake of Coronenes-SWCNTs by cells, phospholipid poly(ethyleneglycol)(PL-PEG),which has no cytotoxicity, wrapped Coronenes-SWCNTs(PEG-Coronenes-SWCNTs) was added to macrophage cells (RAW264.7). Confocal microscope images showed that PEG-Coronenes-SWCNTs were successfully internalized inside macrophage cells by phagocytosis. We then carried out similar experiment by using cancer cells. To investigate the targeting efficiency to cancer cells, Coronenes-SWCNTs were wrapped by PL-PEG functionalized with folic acid (FA-PEG-Coronenes-SWCNTs). FA receptor positive cancer cells (KB cell) were incubated with FA-PEG-Coronenes-SWCNTs and the control sample, PEG-Coronenes-SWCNTs, respectively. Confocal microscope images showed that much higher fluorescence signals of coronenes were observed in FA-PEG Coronenes-SWCNTs treated cells. The results suggest that the functionalized SWCNTs encapsulating fluorescent agents are attractive imaging probes targeted to cancer cells.

[1] T. Okazaki, Y. Iizumi, S. Okubo, H. Kataura, Z. Liu, K. Suenaga, Y. Tahara, M. Yudasaka, S. Okada and S. Iijima, *Angew. Chem. Int. Ed.*, in press.

Abstract 477
CNBMT11

Electrochemically Functionalized Carbon Nanotubes and Graphene : From Device Applications to On-chip Nanobiosensors

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Carbon in both its one-dimensional (carbon nanotubes - CNTs) and two-dimensional (graphene) allotropic forms is emerging to be a major candidate for a number of on-chip device applications. Chemical functionalization routes designed to expand the spectrum of realizable applications bring in specialized properties that are unattainable in these systems in their pristine form. Our focus is on the use of electrochemistry both as a preparative and as an analytical tool for the design and operation of devices based on single-wall CNTs (SWCNTs) and graphene. The devices comprise of individual or few SWCNTs or reduced graphene oxide flakes contacted by electrodes working in a field-effect transistor configuration. The first part will focus on the use of electrochemistry as a preparative tool, to functionalize the surface of contacted SWCNTs and graphene flakes. We have designed a generic route to attach a wide spectrum of receptors on to the surface of carbon nanostructures either in a covalent or non-covalent manner [1]. The receptors range from simple organic moieties through nanoparticles to biomolecules. In comparison to other approaches electrochemical modification (ECM) offers the specific advantage that the energy level of the chosen carbon nanostructure can be selectively tuned, allowing one to chemically or biologically tailor their surface properties in a very controlled manner [2]. The extent of functionalization can be controlled in situ by monitoring its conductance while performing ECM. In addition, only the addressed nanotubes are functionalized giving a very high site-specificity. Deploying this principle we demonstrate controlled modification of carbon nanotube networks resulting in purely semiconducting device characteristics. The advantages of using electrochemistry to modify electronic structure will be highlighted here in the context of other chemical functionalization methods.

The second part will deal with the use of functionalized carbon nanostructure devices as highly sensitive analytical tools for the detection of gaseous, chemical and biological species. Representative sensing paradigms will be presented:
(a) hydrogen sensors based on Pd- nanoparticle decorated SWCNTs or graphene [3]
(b) pH sensors with aniline moieties and
(c) enzyme-free sugar sensors based on boronic acid receptors on the CNT surface [4]. The focus here is on the ability to tune the chemical nature of the receptor coupling to the carbon nanostructure and thereby have a good control over the functional interface. Electrochemistry allows us to switch this coupling between covalent and non-covalent without altering the binding characteristics of the receptor. For example, with covalently and non-covalently attached boronic acid receptors we corroborate in detail the transduction mechanism of our CNT sensors. The talk concludes with implications for future on-chip SWCNT chemical and bio sensors.

[1] K. Balasubramanian and M. Burghard, *J. Mater. Chem,* **18**, 3071, (2008).
[2] K. Balasubramanian, M. Burghard and K. Kern*, Phys. Chem. Chem. Phys.***10**, 2256 (2008).
[3] R.S. Sundaram, C. Gomez-Navarro, K. Balasubramanian, M. Burghard and K. Kern, *Adv. Mater.* **20**, 3050 (2008).
[4] A. Vlandas, T. Kurkina, A. Ahmad, K. Kern and K. Balasubramanian, *Anal. Chem.* **82**, 6090 (2010).

Carbon nanotube-mediated siRNA for the therapy of cancer and brain disease

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Carbon nanotubes have been recently proposed as novel nanomaterials that can offer significant advantages for the intracellular delivery of nucleic acids, such as siRNA.
Recently, we have demonstrated in a proof-of-principle study [2] that mino-functionalized multi-walled carbon nanotubes (f-MWNT) can effectively deliver in vivo an siRNA sequence triggering cell apoptosis that results in human lung xenograft eradication and prolonged survival. Moreover, gene silencing has shown to be an effective therapeutic approach in treatment of brain diseases. Ischemic stroke accounts for 80% of all stroke insults and often leads to chronic functional limitations that adversely and long-lastly affect the ability of patients to movement. Physical and pharmacological rehabilitation strategies to reduce chronic impairment are often not sufficient to return to pre-lesion levels of performance of sensory and motor functions. In the past, gene therapy has been suggested to limit stroke derived anatomical and functional damage [1] and viral vector administration of genes into the affected area of the brain has been exploited. We have investigated the use of the amino-functionalized carbon nanotubes material, to design a vector for non-viral delivery of small interference RNA (siRNA) directly into the brain (intracranial administration). This was based on the hypothesis that siRNA against neuronal Caspase-3 could rescue cells from stroke-induced apoptosis after injection of 60 picomoles of endothelin-1 (ET-1). ET-1 is a potent vasoconstrictor that when injected in the motor cortex (M1) induces stroke-like events that cause specific impairments of mobility performance. Using the skilled reaching test in rats, we demonstrate that gene silencing using CNT:siRNA vectors 24hr pre-endothelin administration reduces apoptosis in M1 and enhances motor skill recovery in rats after ischemic stroke. In conclusion, we propose carbon nanotube-mediated RNAi as a novel and effective approach for the therapy of cancer and brain disease.

[1] Tsai, T. H.; Chen, S. L.; Xiao, X. et al. *Methods.*, **2**, 253-258 (2002).
[2] Podesta, J. E.; Al-Jamal, K. T. et al. *Small* **5**, 1176-1185 (2009)..

Biocompatibility And Functionalization Of Isolated, ssDNA Suspended Single- Wall Carbon Nanotubes

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The ability of carbon nanotubes (CNTs) to bind molecules with specific function, such as agents against infectious diseases, provides the opportunity for the use of CNTs as biomedical vectors for drug delivery. Single-wall carbon nanotubes (SWNTs) are known for their capability to transport biologically active cargos into living systems for the purpose of disease diagnosis and therapy [1] . To facilitate biomedical application of CNTs, they need to be solubilized in water, which is typically achieved by non-covalent functionalization with single-stranded DNA (ssDNA). In this study we focus on chirality enriched (6,5) single-wall carbon nanotubes coated with d(GT)16 oligomers as dispersion additive. Studies of nanotube cytotoxicity are often affected by cytotoxic effects of metal contaminants or particle aggregates, which may completely mask the actual cellular response to isolated SWNTs [2]. In this work, samples of well isolated SWNTs with specific diameter and chirality are carefully prepared from CoMoCat starting material by sonication and ultracentrifugation assisted density gradient differentiation. Cytotoxic effects of these nanotube samples are primarily tested on J774.1 murine macrophages. After 24 hours of incubation the number of metabolic active cells is determined by the absorbance of a dye that is sensitive to reduction and therefore an indicator for the effective cell metabolism. The bio-stability of ssDNA-CNT conjugates is also crucial for their potential use as vector. A particular concern is the disintegration of ssDNA-SWNT hybrids under chemical strains inside the cell. Dissociation of ssDNA-SWNT structures is expected to lead to potentially undesirable precipitation and concentration of SWNTs in lipophilic regions of the cell interior. We therefore do not only study the behavior of ssDNA-CNT conjugates in environments with pH varying from 0 to 14 but also their stability with respect to protein mixture and enzyme activity like DNase I. After evaluation of the sample stability and exclusion of cytotoxicity, carbon nanotubes can be functionalized so that they can be used in a drug-delivery system. For this purpose covalent bonds can be formed in specific crosslinking reactions between functional groups in DNA strands and side chains of the agent. In this study we present newly developed successful routes for functionalization of ssDNA-CNT hybrids. A dansyl fluorophore is used as model compound to demonstrate successful functionalization.

[1] N.W.S. Kam, T.C. Jessop, P.A. Wender, H. Dai, *J. Am. Chem. Soc.*, **126**, 6850-6851, (2004).
[2] P. Wick, P. Manser, L.K. Limbach, U. Dettlaff-Weglikowska, F. Krumeich, S. Roth, W.J. Stark, A. Bruinink, *Toxicol. Lett.*, **168**, 121-131, (2007).

Functionalization of Single-Walled Carbon Nanotubes with Ribonucleic Acids

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Optical properties of single-walled carbon nanotubes (SWCNTs) dispersed in ribonucleic acids (RNA), purified from Escherichia coli, were studied using photoluminescence (PL), Raman, and absorption spectroscopy. Isolated SWCNT-RNA hybrids were successfully synthesized. Two distinct PL peaks at 1.248eV and 1.392eV were observed originating from (6,5) and (6,4) SWCNT, respectively. Atomic force microscopy (AFM) images and height profile also showed the evidence of isolated SWCNT-RNA hybrids.

Cationic Carbon Nanotubes for Nucleic Acid Delivery

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Recently, functionalized carbon nanotubes (CNTs) have attracted great interest due to their potential biomedical applications, their improved water dispersibility and their ability to penetrate into the cells. In particular their capacity to complex genetic material has indicated them as promising candidate carriers for plasmid DNA or siRNA both in vitro[1] and in vivo[2]. In this work CNTs have been functionalized with positively charged moieties in order to interact with nucleic acids and permit their delivery inside the cells. For the purpose of directing the delivery specifically inside mitochondria, CNTs have been coupled to a characteristic peptide called mitochondria target sequence peptide (MTS). The final goal of this work is to create a complex between functionalized CNTs and nucleic acids and to selectively target them into mitochondria in order to have the possibility to cure diseases originated from mitochondrial DNA mutation. In this communication, we will present the synthetic strategy to generate the cationic CNTs, bearing ammonium or guanidinium groups and their further modification with MTS peptide. The presence of guanidinium groups will enhance the affinity of CNTs for nucleic acids and will improve the bio-distribution of the final complex. In addition, the cell uptake and sub- cellular distribution of the different conjugates will be discussed.

[1] D. Pantarotto et al., Angew. *Chem. Int. Ed.*, **43**, 5242-5246, (2004)
K. T. Al-Jamal et al., *FASEB J*, **24**, 4354-4365, (2010)
M. A.Herrero et al. *J. Am. Chem. Soc.*, **131**, 9843-9848, (2009)
[2] J. E. Podesta et al., *Small*, **5**, 1176-1185, (2009)

PAMAM Dendrimers Decorating Carbon Nanohorns Surface as Efficient Gene Delivery Materials for Prostate Cancer Cells

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Carbon nanohorns (CNHS) represent a new type of carbon-based nanostructures with interesting properties for applications in materials science, biology and medicine. CNH primary particle consists of a sheet of graphene rolled into a tube (with a structure similar to single-walled carbon nanotubes) of 2-5 nm in diameter with a length of 40-50 nm and with a conically-closed tip. CNHs usually aggregate in assemblies that are reminiscent of dahlia flowers with a diameter that goes from 80 to 100 nm, although they can also constitute buds and seeds. The high purity achieved in the synthesis of CNHs is one of its greatest advantages over carbon nanotubes. CNHs are synthesized in the absence of metal catalyst and thus obtained metal-free. These nano-materials have a high surface absorption and inherent interstitial holes. The size of CNHs aggregates allow their inclusion through endocytosis into the inner cell decreasing the citotoxicity and the globular shape might avoid the asbestos-like toxicity associated to the use of carbon nanotubes. Chemical modification of these materials will allow its manipulation and therefore it allows the synthesis of hybrid nanocomposites with different applications. Thus, anchoring PAMAM dendrimers of different generations renders CNHs with almost unaltered features but significantly enhances its solubility. The presence of a large number of positive charges due to the amino groups located on the PAMAM periphery makes these hybrids ideal for coupling genetic material by means of electrostactic interactions and these materials are therefore suitable for their use as gene carriers into cells. Similarly, the decoration of the CNHs with dendrimer encapsulated nanoparticles (DENs) could allow us monitoring the gene carrier trafficking without the need to use other vehicle markers.

In this work we show the development of a new non-viral vector family for gene therapy that is based on CNHs decorated with PAMAM dendrimers. These hybrid nanomaterials have been applied successfully as small interfering ribonucleic acid (siRNA) transfection agent for gene delivery in prostate cancer cells. Here we report the full characterization of these materials as well as the biological results that clearly demonstrate the potential usefulness of these carriers to deliver siRNA.

Functionalization of Nanodiamond for Biomedical Applications

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Diamond is an attractive material for a variety of biomedical applications due to its inert and biocompatible behaviour. In the past, diamond films have already been used to coat implants, to construct sensor arrays or to deliver drugs. Recently, functionalized nanoscale diamond particles have come into the focus as well. They can be used for drug delivery, for the detection of bioactive molecules or for the *in vitro* and *in vivo* imaging.[1] The latter is closely related to the non-bleaching and basically non-blinking luminescence of lattice defects such as the N-V center.[2]

For most of the bioapplications of nanodiamond a specific surface termination is needed in order to bind biomolecules or other functional moieties. This includes the basic chemistry of atoms directly at the particle surface but also the selective grafting of larger (bioactive) moieties. In this contribution an overview about the recent developments in the field of surface modification of nanodiamond will be given. We will especially focus on reaction schemes leading to highly stable covalent bonds such as C-C bonds.[3,4]

Furthermore, useful techniques such as ultrasonic or mechanochemical approaches for the complete destruction of weakly and strongly bound agglomerates of surface modified nanodiamond will be discussed, leading to colloidal solutions of functionalized nanodiamond – a prerequisite e.g. for an efficient uptake into cells.[5]

Another issue for the assessment of successful surface modification is the analytical characterization of the resulting materials. We will present here a general overview about the chemical and physical methods for the qualitative and quantitative analytics of nanodiamond materials.

[1] E. Osawa, *Diamond Relat. Mater.* **2007**, *16*, 2018; A. M. Schrand, S. A. Ciftan Hens, O. A. Shenderova, *Crit. Rev. Solid State Mater. Sci.* **2009**, *34*, 18; A. Krueger, *Chem. Eur. J.* **2008**, *14*, 1382.

[2] C.-C. Fu; H.-Y. Lee, K. Chen, T.-S.- Lim, H.-Y. Wu, P.-K. Lin, P.-K. Wei, P.-H. Tsao, H.-C. Chang, W. Fann, *Proc. Natl. Acad. Sci.* **2007**, *104*, 727; F. Neugart, A. Zappe, F. Jelezko, C. Tietz, J.-P. Boudou, L. Lu, A. Krueger, J. Wrachtrup, *Nano Lett.* **2007**, *7*, 3588.

[3] T. Nakamura, M. Hasegawa, K. Tsugawa, T. Ohana, M. Ishihara, Y. Koga, *Diamond Relat. Mater.* **2006**, *15*, 678; T. Tsubota, O. Hirabayashi, S. Ida, S. Nagaoka, M. Nagata, Y. Matsumoto, *Phys. Chem. Chem. Phys.* **2002**, *4*, 806; Y. L. Zhong, K. P. Loh, A. Midya, Z.-K. Chen, *Chem. Mater.* **2008**, *20* 3137; Y. Liang, T. Meinhardt, G. Jarre, P. Vrdoljak, A. Schöll, F. Reinert, A. Krueger, *J. Colloid Interface Sci*. **2011**, *354*, 23.

[4] G. Jarre, Y. Liang, P. Betz, D. Lang, A. Krueger, *Chem. Commun*. **2011**, *47*, 544; T. Meinhardt, D. Lang, H. Dill, A. Krueger, *Adv. Funct. Mater.* **2011**, *21*, 494.

[5] Y. Liang, M. Ozawa, A. Krueger, *ACS Nano* **2009**, 3, 2288.

Carbon Nanotubes: Effects of Plasma Protein Binding

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In biomedical applications of carbon nanotubes (CNTs) the CNTs will come into contact with blood and its various components. It has been shown that among the many proteins present in human plasma, only a few bind to various pristine and chemically modified CNTs. We show the binding is highly selective and dependent on the type of nanotubes (single-walled, multi-walled) and the chemical modification, such as dispersant or oxidation. The proteins which bind in largest quantity are human serum albumin and fibrinogen, and also the lipoprotein complex high density lipoprotein (HDL), which contains phospholipids, cholesterol and the apolipoproteins AIV, AI, CIII. Binding most likely occurs at irregularities in the carbon network. In a competition experiment at least two non-overlapping types of binding sites for proteins on carbon nanotubes were identified. Binding of proteins to CNTs was shown to be unstable. Proteins pre-coated onto CNTs can be displaced fairly easily in blood plasma: for example precoated BSA (bovine serum albumin) is replaced by HSA (human serum albumin) when CNTs are incubated in human plasma. Another important group of proteins found to interact with CNTs are innate immune system proteins. The innate immune response plays a key role in protection against pathogens and synthetic particles. By haemolytic assays and western blots we showed CNTs bind C1q, C3 and C4, which are important proteins of the complement classical and alternative pathways. This indicates that the complement system is activated by CNTs and this activation may promote inflammation, granuloma formation and interaction with cells that have receptors for complement proteins. When complement is activated, C3b (the large fragment of activated C3) binds covalently to most targets, via OH or NH_2 groups on the target. The same occurs for C4b. CNTs do not have many available reactive groups of this type, therefore C3b and C4b may bind covalently to other proteins adsorbed to the CNTs; or they may bind by hydrophobic interaction. No evidence was found for covalent binding of C3b to other plasma proteins bound to the CNTs and therefore hydrophobic binding is assumed. We are currently studying interactions of CNTs with red blood cells which may occur by binding of the C3b coated on the CNTs to the receptor CR1 on red blood cells. Furthermore as C3b is a strong opsoniser, a signal for phagocytes to take up C3b-coated particles, we are examining the role of C3 in uptake of CNTs.

Self Assembly of Lipid Nanostructures in Aligned Carbon Nanotubes

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Lipids, like other amphiphilic molecules, show a tendency to self-assemble into more or less complex aggregates when their concentration exceeds the critical micelle concentration. They are the main structures forming the cell membranes and their self assembly is crucial for the appropriate function of living organisms. At the attempt of stabilizing carbon nanotube (CNT) suspensions, the adsorption of amphiphiles on the CNT surface has been studied before, particularly with the anionic surfactant SDS.1 It was shown that their self-assembly on the CNT surface can follow the carbon pattern.1 This suggests that – apart from stabilizing suspensions - CNTs could be used as orientation inducing substrates or templates for amphiphilic molecules. In this work we have investigated the self assemblies of biological lipid molecules in the presence of aligned arrays of carbon nanotubes, which include the surface adsorption as well as the assembly in the narrow channels between the nanotubes. We have observed various lyotropic nanostructures that are found for corresponding lipids in the bulk under dry and hydrated conditions. The structural studies were performed using small and wide angle X-ray scattering techniques. This work is most desirable for designing the nano-micro-fluidic architectures, novel composites, nanoscale devices, platforms for ultra-sensitive recognition of antibodies and supported model membranes.

[1] a) C. Richard et al., *Science*,**300**, 775-778 (2003);
b) K. Yurekli et al., *JACS,* **126**, 9902-9903(2004).

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Antibacterial Activity of Graphite, Graphite Oxide, Graphene Oxide and Reduced Graphene Oxide: Membrane and Oxidative Stress

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Health and environmental impacts of graphene-based nanomaterials need to be thoroughly evaluated before their potential applications. Graphene has strong cytotoxicity towards bacteria. To better understand its antimicrobial mechanism, we compared antibacterial activity of four types of graphene-based nanomaterials (Graphite (Gr), Graphite oxide (GtO), graphene oxide (GO) and reduced graphene oxide (rGO)) towards a bacterial model – Escherichia coli. Under similar concentration and incubation conditions, GO dispersion shows the highest antibacterial activity, sequentially followed by rGO, Gt, and GtO. Dynamic light scattering analysis shows that GO has the smallest average size among the four types of materials. Scanning electron microscope images demonstrate direct contact with graphene nanosheets disrupts cell membrane. No reactive oxygen species (ROS) (e.g. superoxide anion, $O^{2\bullet-}$) production is detected. However, the four types of materials can oxidize glutathione, which serves as redox state mediator in bacteria. Conductive rGO and Gt have higher oxidation capacities than insulating GO and GtO. Results suggest that antimicrobial actions are contributed by both membrane and oxidation stress. We propose that a three-step antimicrobial mechanism, previously used for carbon nanotubes, is applicable to graphene- based materials. It includes initial cell deposition on graphene-based materials, membrane stress caused by direct contact with sharp nanosheets, and the followed ROS-independent oxidation. We envision that physicochemical properties of graphene-based materials, such as density of functional groups, size and conductivity, can be precisely tailored to either lessening their health and environmental risks or increasing their application potentials.

Sensitivity of Boron Nitride Nanotubes toward Biomolecules

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Interfacing biomolecules with nanomaterials and understanding the applicability of bio-conjugated nanostructured materials in technologically important areas are forefront research activities. There exist numerous studies that have focused on carbon-based nanostructures, addressing the challenges to interface biomolecules with nanomaterials, e.g., non-uniformity and instability of carbon nanotubes in solutions. Semiconducting boron nitride nanotubes (BNNTs) which possess morphology similar to that of carbon nanotubes (CNTs), but with distinct properties on their own, appear to be more appropriate candidates for bio-medical applications. Recent experiments report that functionalized BNNTs with biological epitopes can mediate protein and cell binding, and also deliver DNA-oligomers to the interior of cells with no apparent toxicity.

We investigated the electronic response of BNNT in the presence of the DNA and RNA nucleobases adenine (A), guanine (G), cytosine (C), thymine (T) and uracil (U)- and the amino acids – arginine (Arg), tryptophan (Trp) and aspartic acid (Asp). Trp is a non-polar aromatic amino acid whereas Asp and Arg are polar amino acids. The results obtained from density functional theory calculations show that molecular interactions between BNNT and nucleobases are mainly governed by van der Waals (vdW) forces [1]. The calculated order of the binding energy is predicted to be $G > A \approx C \approx T \approx U$, implying that the interaction strength of the high curvature BNNT with the nucleobases is very similar, G being an exceptional case. The higher binding energy for the G-BNNT conjugate appears to result from hybridization of the molecular orbitals of G and the BNNT. For the case of amino acid molecules, the calculated results find Asp and Arg to be closer to the tubular surface relative to Trp. Negligible charge transfer is found for the Trp-BNNT complex suggesting the dominance of non-covalent interactions. An occurrence of a relatively large charge transfer from the polar amino acids to the tubular surface of BNNT suggests stabilization of the io-conjugated complex due to electrostatic interactions. The results find modulation of the band gap of pristine BNNT by Trp, though no change in band gap is seen for polar conjugates. A relatively large binding energy of the Arg-BNNT complex may suggest the possibility of Arg to be the amino acid that can facilitate a direct link to BNNT. Thus, the results suggest BNNTs to be candidate nanomaterials for design and development of a new class of biological probes at the nanoscale.

[1] S. Mukhopadhyay, S. Gowtham, R. H Scheicher, R. Pandey, and S. P. Karna; *Nanotechnology* **21**, 165703, (2010)

Single Nanotube Imaging to Probe Complex Environments

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The optical microscopy of single molecules has recently been beneficial for many applications, in particular in biology. It allows a sub-wavelength localization of the molecules and a subtle probing of the spatio temporal nano-environment of the molecules[1]. For many bio-applications, near infrared nanoprobes and/or more photostable nanoprobes than conventional fluorescent molecules or quantum dots are desirable. In this context, single walled carbon nanotube tubes (SWNTs) are promising. On the one hand, they bear excellent absorption properties which make them suitable for detection at the single particle level using the photothermal heterodyne imaging (PHI) method [2]. PHI is a far-field optical method allowing the ultra-sensitive detection of tiny absorbing individual nano-objects such as gold nanoparticle down to 1.4nm, semiconductor nanocrystals or SWNTs [2]. Approaches were further developed to measure the diffusion of proteins labelled with 5 nm gold nanoparticles in living cells for arbitrary long times opening the route for the detection and tracking of metallic and semiconducting SWNTs in living cells by PHI [2]. On the other hand, the luminescence properties of semiconducting SWNTs are highly sensitive to the nanotubes environment. Single-molecule chemical reactions with individual SDBS wrapped nanotubes could be observed through the stepwise changes of the luminescence intensity within submicrometer segments of nanotubes [3]. For further applications in biology, this sensitivity can either be useful or should be avoided by appropriate nanotube encapsulation [4]. Due to their one dimensional character, understanding the thermal motion of SWNTs in crowded environments is key for applications in biology including sensing, drug delivery etc. SWNTs behave like stiff filaments [5] and despite decades of theoretical study, the fundamental dynamics of such systems remains a mystery. Surprisingly, using highly luminescent SWNTs confined in biocompatible crowed environments (agarose networks), we find that even a small bending flexibility strongly enhances their motion: the rotational diffusion constant is proportional to the filament bending compliance and is independent of the network porosity. This study establishes definitively the reptation dynamics of stiff filaments and provides a framework to tailor the mobility of SWNTs in confined biological environments [6].

[1] M. Heine, et al *Science*, (2008).
[2] L. Cognet, et al *Anal. Chem.*, (2008)
[3] L. Cognet, et al *Science* (2007).
[4] J.G. Duque, et al *JACS* (2008).
[5] N. Fakhri, et al *PNAS* (2009).
[6] N. Fakhri, et al *Science* (2010).

Development of Glucose Sensor Using CNT Compound Materials

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A bio-nanosensor consisting of a silicon-based chip contains a poly[ethylene glycol]- grafted (PEG)-grafted carbon nanotubes (PEG-CNTs) modified with living body materials (ex. enzyme, antibody, and DNA etc.) using plasma ion irradiation (plasma activation) method, developed.[1,2]
We developed a method for measuring changes in the electrical conductivity of a CNT surface reaction, which is a time-based detection method (impedance type). Specifically, we immobilized the glucose oxidase (GOD) on a sensor chip with a CNT base and we then measured changes in impedance caused by the catalyst reaction at the point where the glucose was dripped onto the chip. After evaluating various characteristics, we used PEG to enhance the dispersion of the multiwalled CNTs (MWCNTs) used when the sensor was fabricated. According to evaluation of the glucose sensor manufactured by using glucose oxidase (GOD), impedance revealed an increase due to a catalyst reaction of PEG-CNTs surface. Furthermore, the impedance change which originated in the blood glucose of small animal (rat) was confirmed. The results suggested that a bio-nanosensor made sure concentration dependency of blood glucose.

[1] T. Hirata, S. Amiya, M. Akiya, O. Takei, T. Sakai, and R. Hatakeyama, *Appl. Phys. Lett.*, **90**, 233106-1-233106-3, (2007).
[2] T. Hirata, S. Amiya, M. Akiya, O. Takei, T. Sakai, T. Nakamura, J. K. Tsuzuku, T. Yamamoto, and R. Hatakeyama, *Jpn J. Appl. Phys.*, **47**, 2067-2071, (2008).

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An Optical SWNT Biosensor for Explosives

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A class of peptides from the bombolitin family, not previously identified for nitroaromatic recognition, allows near-infrared fluorescent single walled carbon nanotubes (SWNT) to transduce specific changes in their conformation. In response to the binding of specific nitroaromatic species, such peptide-nanotube complexes form a virtual ‘chaperone sensor’ which reports modulation of the peptide secondary structure via changes in SWNT near-infrared photoluminescence. A novel split-channel microscope constructed to image quantized spectral wavelength shifts in real-time, in response to nitroaromatic adsorption, results in the first single- nanotube imaging of solvatochromic events. The described indirect detection mechanism, as well as an additional exciton quenching-based optical nitroaromatic detection method, illustrate that functionalization of the carbon nanotube surface can result in completely unique sites for recognition, resolvable at the single-molecule level.

Carbon Nanotube Films Preparations for Electronic, Sensors and Bioengineering Application

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Carbon nanotubes films (CNTF) are suggested to be more technological material in production process of devices and systems. It's now considered as radiation resistive transistors and sensors [1], transparent and conductive layers for optoelectronics devices, scaffold material for biological application in tissue engineering. Nevertheless different technological methods of carbon nanotubes films formation biased on chemical vapor deposition, electrophoresis and ink printing are suggested. In this work we describe the development of different methods carbon nanotubes deposition for electronic, sensors and bioengineering with making use of chemical vapor deposition (CVD), dielectrophoresis (DEF) or deposition from surfactant solvents. It was shown the different methods produce different film that can be used or specific applications. CNTF films produced by low temperature CVD demonstrate rather good conductive and transparent properties for nanotubes with diameters 10 – 100 nm. The carbon nanotubes film deposited with making use of dielectrophoresis techniques allow us to control concentration and geometry of nanotubes film. We used DEF for sensor's active layer development based on quasi-one-dimensional structures composite of carbon nanotubes and oxide zinc nanorods. The different surfactants was investigated for CNTF production. To produce biocompatible material we suggested to use bovine albumin (BSA) as surfactant for single-wall carbon nanotubes dissolution. Earlier we used nanotubes-albumin composite as scaffold material for cartilage regeneration [2]. This method was used for transparent conductive film formation by rolling up method on cover slips. We investigated the optical and electrical properties of such film and used them for cell growth electro-stimulation. Thus different methods can be used for CNTF formation. We have shown that method based on carbon nanotubes solution with biological surfactant provide transparent conductive biocompatible films.

[1] D.V. Gromov, V.V. Elesin, G.V. Petrov, I.I. Borinetskii, V.K. Nevolin, *Semiconductors*, **44**(13), 1699–1702, (2010).
[2] S.A. Ageeva, I.I. Bobrinetskii, V.K. Nevolin, V.M. Podgaetskii, S.V. Selishchev, M.M. Simunin, V.I. Konov, V.V. Savranskii. *Semiconductors*, **43**(13), 1714- 1718, (2009).

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Oxidative Stress and Nanoparticles: Badness is Only Spoiled Goodness

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Induction of non-specific (random) oxidative stress is associated with injury by nanoparticles. Is injury the only meaning of oxidative stress after exposure to nanoparticles? Biopersistence of carbon nanotubes (CNT) is viewed as a major stumbling block on the way of their broader applications in biomedicine. Our previous studies discovered an enzymatic pathway of CNT biodegradation by peroxidases – horseradish peroxidaseof plant origin, myeloperoxidase (MPO) of neutrophils and eosinophil peroxidase. Lately, we were able to demonstrate that MPO-driven mechanism is indeed involved in the CNT biodegradation in vivo resulting in delayed clearance of CNT in MPO-/- mice. This emphasizes the necessity to re-assess the role of oxidative stress in pulmonary injury and inflammatory response elicited by CNT. In line with this, lipid peroxidation triggered by CNT exposure in vivo, demonstrates features of enzymatic process participating in regulation of inflammatory response rather than in non-specific oxidative damage. These newly developed concepts on CNT induced oxidative stress will be discussed within the context of their interactions with lipid and protein components of lung surfactant and subsequent recognition by cells of innate immune system.

Synthesis Bombesin-Naphthalenediimide Conjugate Functinalized Single Walled Carbon Nanotubes as a Novel Receptor Imaging Probe

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We hereby report a new cancer probe including carbon nanotube, of advanced purity and with well understood physico-chemical properties and which are wrapped with a cancer cells receptor-binding bombesin-naphthalene diimide conjugate (NDI- bombesin)[1]. Our probes are totally biocompatible and soluble in cell medium which makes them particularly attractive for cancer cells receptor imaging. The specific peptide tag helps carbon nanotubes to target Gastrin-Releasing Peptide Receptor (GRPR) which is highly expressed on prostate cancer cells (PC3) membrane and also helps to ferry carbon nanotube into prostate cancer cells. Therefore, our new bombesin- NDI conjugate functionalized carbon nanotubes(BN-NDI-SWNTs) targeting the GRPR can be viewed as promising tools for the non-invasive diagnosis, monitoring and potential treatment of prostate cancer in future.

[1] Pantos, G. D.; Pengo, P.; Sanders, J. K.,*Angew. Chem., Int. Ed.*, **46**, 1-2, 194-197, (2007).

Biodegradation Of Carbon Nanotubes Investigated Using Raman Spectroscopy

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One of the key expectations of the nascent field of nanomedicine is that in the near future it will be possible to produce new drugs incorporating nanocarriers for use in the human body. It is therefore essential to both understand the ultimate biological fate of these nanocarriers and to develop reliable methods for evaluating their uptake and degradation as many candidate nanocarriers undergo little or no biodegradation. Carbon nanotubes (CNTs) are under extensive research due to their unique mechanical, electrical and magnetic properties. The large surface area to volume ratio of CNTs is attractive for biological applications such as drug delivery and their rich electronic properties have been explored for nanoscale biosensors. However, these attractive characteristics make the biological consequences of CNT largely unpredictable and numerous studies have reported their cytotoxicity. For this reason CNTs were the primary candidate nanocarriers used in this study, which is ultimately concerned with quantifying the degradation of CNTs in cells and tissues using an innovative in vitro approach. Previously we have shown the biodegradation of single- walled carbon naotubes (SWCNT) by human neutrophils using Raman spectroscopy.[1] It was found that there was an increase in the disorder D band relative to the G band with increasing incubation time, suggesting that the graphene sidewall was oxidised by the neutrophils, mediated by myeloperoxidase within these cells.

Here we addressed the hypothesis if the biodegradation of SWCNT by myeloproxidase of neutrophils was the primary and only mode of degradation and investigated whether such biodegradation was visible in other cell lines and whole tissue. As macrophages are involved in the active clearance of tissues from foreign and pathogenic material, we treated both primary macrophages and THP1 macrophage cell line with SWCNT for 24, 48 and 72 hours. Lung tissue sections of wild type and myeloperoxidase knock-out mice, treated with SWCNT by pharyngeal inhalation, were also taken at 1 day, 7 day and 28 day. Unlike our previous studies which used single point spectra, this study uses a technique for performing 32 x 32 point Raman mapping of both the cells and tissue samples. This technique was optimised using a 100x oil immersion lens, 473nm cobalt laser on an Ntegra Spectra Raman system (NT-MDT, Russia). Macrophages were mapped in a 20µm x 20µm scan which constitutes their total area. 10 representative Raman maps throughout each tissue section (20µm x 20µm or 10µm x 10µm) were recorded. Analysis of the Raman maps recorded was carried out using Matlab (The

Mathworks, USA) software which generated maps based on the Raman spectra which were then used to investigate the D to G ratio in all samples. This approach enabled us to identify and quantify degraded and non-degraded CNTs in cells and lung tissue samples in a model that has a close relevance to their potential physiological and technogenic exposure routes.

[1] Kagan, V. E.; Konduru, N. V.; Feng, W.; Allen, B. L.; Conroy, J.; Volkov, Y.; Vlasova, I. I.; Belikova, N. A.; Yanamala, N.; Kapralov, A.; Tyurina, Y. Y.; Shi, J.; Kisin, E. R.; Murray, A. R.; Franks, J.; Stolz, D.; Gou, P.; Klein-Seetharaman, J.; Fadeel, B.; Star, A.; Shvedova, A. A. *Nat Nano*, **5**, (5), 354-359 (2010).

The Methods of Cell Growth on Carbon Nanotubes Substrates with Making Use Of Electrostimulation

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Over the past thirty years the influence of electric stimulation on the accelerated tissue healing and cell growth was investigated. Traditional methods of bringing the external electric field failed to localize a field in the healing area, so whole organism had to be exposed to electric stimulation. Increasing the work area and the distance between electrodes and the healing area implies increasing of electrical field intensity, required for stimulating individual cells. In that case we show efficiency of using implant nanocomposite electrodes, which intend to help localizing electric field in a specific area. Accelerated tissue regeneration can be achieved by using tiny implant electrodes with a lower intensity amplitudes, and low-frequency signal. Nevertheless, similar invasive methods demand use of the biodegradable materials which help to minimize the influence on the tissue micro environment. The way of electric stimulation of cell growth, using system of the planar electrodes is well-known. Such electrodes are creating fields which can be localized mainly in the area of an organism where the electric field and current are
required. The last results in nanotube ferment-based degradation are discussed as a new scaffold material for tissue regeneration [1]. System of in vitro cell growth, involving a substrate, nanocomposite monolayer and gold needle electrodes was developed. 2 mg of single-walled carbon nanotubes were ultrasonicated with 10 mg of bovine serum albumen and 10 ml of distilled water to create nanocomposite solution. Substrate was treated with sputter deposition of gold to form contact area and then covered with 70 nm nanocomposite film to provide current supply to cells. Embryonic fibroblasts were cultured on 24x24 mm coverslips. Cells were incubatedin 6 well plates for 76 h, at 37°C and 5% CO2, fixed with 4% glutaraldehyde, washed twice with PBS, and then dehydrate using 50%, 70% and 96% ethanol for microscopy analysis. Electro-stimulation with 10, 50, 100 and 200mVpulse signal, at 1 kHz frequency, with 1 sec period was applied for 48 h after one day of standard cultivation. We used MTT method to determinate proliferation index, and investigated cells morphology with optical, atomic-force and scanning electron microscopy. The proliferation index increases on 20% after 50 mV pulses. Dense cell monolayer was found on samples exposed to current on a third day of incubation. As a result, we have shown another way of providing electrical stimulation of cells by using biocompatible conductive albumen-nanotube composite.

[1] L.B. Allen, G.P. Kotchey, Y. Chen et al,*J. Am. Chem. Soc.,* **131**(47), 17194–17205, (2009).

Indolizine Modified Fluorescent Single-Walled Carbon Nanotubes For Detection Of Nitroaromatics

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Since nitroaromatics are present in explosive warfare agents including TNT and ammonium picrate, and pollute the environment, detection of trace amount of nitroaromatic compounds is important both in terms of homeland security and environmental monitoring. Herein an indolizine modified SWNT based photochemical sensor has been presented, for the first time, to detect trace amount of nitroaromatic compounds, o-nitrophenol, m-nitrophenol, p-nitrophenol, p-nitrotoluene and 2,4-dinitrotoluene, in solution and solid phase. Indolizines, the simplest hetero-aromatic molecules containing both a π-excessive pyrrole and a π- deficient pyridine ring, have attracted special attention due to their luminescent properties with potential sensing applications.[1,2] Pyridine functionalized single-walled carbon nanotubes (SWNTs),[3] formed following the addition of pyridine diazonium to nanotubes, have been used to prepare pyridinium ylides, generated from simple Kröhnke salts, covalently bound to a nanotube surface which undergo a 1,3-dipolar cycloaddition with dimethyl acetylenedicarboxylate in a ‘click’ chemistry type fashion to yield indolizine modified SWNTs. The indolizine functionalized SWNTs generated emit blue light when excited at 330 nm.[4] The location and distribution of the functional groups was determined by AFM using electrostatic interactions with gold nanoparticles. The indolizine functionalized SWNTs were further characterized using FTIR, UV-vis-NIR, TGA-MS and XPS. Fluorescent quenching experiments demonstrated that the SWNTs having the fluorescent indolizine groups could be used as a potential photochemical sensor for detection of aromatic nitro compounds with a detection limit of 6.66×10^{-8} M.

[1] F.Delattre, F. Cazier, A. Tine, *Current Analytical Chemistry*, **5**, 48-52(2009).
[2] G. G. Surpateanu, M. Becuwe, N. C. Lungu, P. I. Dron, S.Fourmentin, D. Landy, G. Surpateanu, *Journal of Photochemistry and Photobiology a-Chemistry*, **185**, 312-320(2007).
[3] M.K. Bayazit, L.S. Clarke, K.S. Coleman, N. Clarke, *Journal of the American Chemical Society*, **132**, 15814-15819, (2010).
[4] M.K. Bayazit, K.S. Coleman, *Journal of the American Chemical Society*, **131**, 10670-10676, (2009).

What Are The Critical Factors In Multi-walled Carbon Nanotubes For Mesothelial Carcinogenesis?

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Multi-walled carbon nanotubes (MWCNTs) have potential for widespread applications in engineering and materials science. However, due to their needle-like, nanoscale shape and high durability, concerns have been raised that MWCNTs of certain characteristics may induce asbestos-like pathogenicity. Even though recent studies have demonstrated various types of reactivities induced by MWCNTs, the physicochemical features of MWCNTs that determine or trigger the cytotoxicity and carcinogenicity in mesothelial cells remain unclear. In the present study we show that the deleterious effects of non-functionalised MWCNTs on human mesothelial cells are associated with their diameter-dependent piercing of the cell membrane. Thin MWCNTs with high crystallinity showed mesothelial cell piercing and cytotoxicity *in vitro* and subsequent mesotheliomagenicity *in vivo*. In contrast, thick or tangled MWCNTs were much less toxic and carcinogenic, whereas all MWCNTs affected macrophages similarly. Furthermore, we show that the target genes for MWCNT-induced mesothelial carcinogenesis were the same as those by asbestos. Our results suggest that control of the diameter of MWCNTs may contribute to reduce the risks to human health.

[1] Toyokuni S, *IUBMB Life*, **60**: 441-447 (2008).
[2] Toyokuni, S, *Cancer Sci*, **100**: 6-16 (2009).
[3] Toyokuni S, *Nagoya J Med Sci*, **71**: 1-10 (2009).
[4] Nagai H and Toyokuni S, *Arch Biochem Biophys* **502**: 1-7 (2010).

When Macrophages Digest Carbon Nanotubes: Intra-Cellular Dispersion And Decarbonation of Iron-Based Nanoparticles Attached To Carbon Nanotubes

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An increasing amount of literature evaluates health effects of carbon nanotube (CNT), but the respective roles of CNT themselves and of remaining catalyst residues present in CNT samples are still to be elucidated. Here, we focus on the fate of iron-based nanoparticles in raw HiPCO Single-Walled Carbon Nanotubes (SWCNT, from Unidym, Sunnyval, CA) samples, when incorporated inside murin macrophage cells (RAW 264.7 cell line). Such nanoparticles are in the form of cementite Fe_3C in the raw material [1], they are surrounded by carbon shells and attached to the nanotubes [2]. Advanced physical methods like micro-X-ray fluorescence [3], micro-XANES (X-ray Absorption Near Edge Spectra), STEM-HAADF (High Angle Annular Dark Field-Scanning Transmission Electron Microscopy) and EELS (Electron Energy Loss Spectroscopy) have been used here to get chemical and spatial information on iron-based nanoparticles in-situ, inside cells. Our results [1] demonstrate that cementite nanoparticles, although initially protected from biological media thanks to their carbon surrounding shells, are finally accessed and further transformed inside macrophages, through decarbonation and oxidation reactions. Free iron nanoparticles are found in the cytoplasm and in the nucleus of the macrophages. In the presence of exogenous particles, the phagocytic function of macrophages is activated, leading to the formation of phagolysosomes, intracellular organelles presenting an acidic pH [4]. We will discuss the possible role of the acidic environment in phagolysosomes in the detachment and transformation of iron-based nanoparticles. To the best of our knowledge, the present results are the first demonstration of catalyst detachment from CNT backbone along with its chemical modification as a result of an intracellular process. These nanoparticles may play a role in the biological effects associated to CNT exposure.

[1] C. Bussy, J. Cambedouzou, B. Fayard, M. Pinault, N. Brun, C. Mory, E. Belade, M. Huard, V. De Andrade, J. Boczkowski, P. Launoisand S. Lanone, submitted for publication
[2] G. Charron, S. Mazerat, M. Erdogan, A. Gloter, A. Filoramo, J. Cambedouzou, P. Launois, E. Rivière, W. Wernsdorfer, J.-P. Bourgoin and T. Mallah, *New J. Chem.* **33**, 1211(2009).
[3] C. Bussy, J. Cambedouzou, S. Lanone, E. Leccia, V. Heresanu, M. Pinault, M. Mayne-l'Hermite, N. Brun, C. Mory, M. Cotte, J. Doucet, J. Boczkowski, and P. Launois, *Nano Lett.* **8** (9), 2659-2663 (2008)
[4] N. Demaurex, News in *Physiological Science* **17**, 1 (2002)

Biocompatibility And Toxicological Research Of Surfaces Modificated With Different Carbon Nanotubes

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Carbon nanotubes (CNTs) are one of the most promising products of nanotechnology, which can be used in tissue engineering of biological objects as a scaffold material. This property of CNTs is due to the fact that they are geometrically similar structure with collagen, which is the main protein of connective tissue of animals. Unique electronic properties, high mechanical strength, high flexibility and low density of CNTs can create biocompatible composite materials with new properties.

At the moment there are a number of researches describing the creation of composite materials based on nanotubes for bio-engineering, in particular the regeneration of bones and cartilages [1]. But there is the issue of biocompatibility and cytotoxicity of CNTs. In the research to determine the toxicological parameters of CNTs, the engineering characterization of nanotubes was developed. The formation process of the scaffold material based on carbon nanotubes and cell growth on these structures was studied. Characterization of the nanotubes was carried out by scanning (SEM) and transmission electron microscopy (TEM), atomic force microscopy (AFM) for identification the geometric dimensions and structure, secondary ion mass spectroscopy (SIMS) for determination the concentration and composition of impurities.

As the nanotubes material were chosen single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) of the three largest Russian suppliers. SWNTs obtained by arc evaporation of graphite, were provided by the Institute of Problems of Chemical Physics with average diameter, 2,9 ± 1,5 nm, length 570 ± 158 nm. MWNTs sample number 1, obtained by catalytic pyrolysis of hydrocarbons, provided LLC STC "Granat" with the average diameter of 4.9 ± 0.5 nm, length 475 ± 120 nm. MWNTs sample number 2, obtained by catalytic pyrolysis of hydrocarbons, provided LLC "NanoTechCenter" with average diameter of 36.0 ± 6.0 nm, length 1203 ± 400 nm.

Culturing Vero cell line on the surfaces of cover glasses the size of 24x24 mm^2 and a thickness of 0.13-0.17 mm, modified with carbon nanotubes, SWNTs, MWNTs number 1 and MWNTs number 2 was carried out. Coverslips with CNTs was placed in culture dish and sterilized in an autoclave at 120 °C, 1 atmosphere, 20 min., followed by the introduction of Vero cells at a concentration of 100,000 cells / ml. Cultivation was carried out in an incubator for 72 hours, and then coverslips were removed from culture dish, fixed and stained for morphological researches. Investigation of cell morphology demonstrated that during cultivation on modified surfaces morphology of normal cells, also formed a dense cell monolayer. The result of the work is the following: carbon nanotubes are not cytotoxic and can be used as a basis for the cells cultivation, as well as a frame material for cell engineering. When cultured glioblastoma cells(GL6) and human embryo fibroblast cells (HEF) on coverslips modified SWNTs and MWNTs number 1 showed a slight decrease in proliferative activity of cell lines and cell viability. While MWNTs number 1 have the greatest toxic effect on tumor cells human glioblastoma.

[1] Zanello L.P., Zhao B., Hu H. *Nano Letters*, **6**[III], 2006; 562-67.

High Uptake Cytotoxicity of Single-Walled Carbon Nanohorns in Murine Macrophage RAW264.7

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Nanometer-sized carbonaceous materials are attractive new materials in the field of electronics, chemical engineering, medicals, etc. With the advances of these researches, concerns about safety of the nanocarbons have increased, and their toxicological studies have been progressing. Among the nanocarbons, carbon nanotubes (CNTs) are the most popular one and their toxicological studies revealed their toxicity depended on the structures. For example, when carbon nanotubes (CNTs) with long and rigid sturucture enter a body, intratracheal and intraperitoneal administrations of CNTs in rodents show that macrophages cannot completely engulf large CNTs, which is designated as frustrated phagocytosis. The macrophages in this state release inflammatory cytokines and ROS, which cause lesions in vivo. On the other hand, CNTs with small size and appropriately functionalized, if not excreted from a body, are possibly captured by tissue macrophages and stay in the tissues for a long period without causing adverse pathological changes. In this context, however, the toxicity at high doses of small CNTs is not well known. The toxicological studies at high doses are necessary, concerning about the possibility of the long term continuous uptake of CNTs in bodies or accidental high exposure in the occupational area. One major reason why such study at high doses has not been progressed is the difficulties in obtaining small CNTs in a large quantity with high purity. To advance the toxicological study for nanocarbons, we performed the cytotoxicity study using single-walled carbon nanohorns (SWNHs), a type of nano-carbons, in macrophage. SWNHs have many advantages of large available quantity, high purity, uniform size, and high dispersion in solutions which other nanocarbons including CNTs do not have. SWNHs are single graphene nano-tubules with diameters of 2 - 5 nm and lengths of 40 - 50 nm. About 2000 of SWNHs assemble to form a spherical aggregate with diameters of 80 - 100 nm. The aggregate are robust and cannot be separated individually easily. Their potential applications to drug delivery systems are reported, and the low toxicity of SWNHs has been shown in rodents. We also clarified that SWNHs intravenously administered into mice accumulated in macrophages in liver, spleens, lungs without adverse histological changes. In this study, we show the cytotoxicity caused by excess uptake of SWNHs, the mechanism of cell death, and cytokine release in macrophage RAW 264.7. The high accumulation of SWNHs in lysosomes was observed, which induced ROS generation and lysosomal membrane destabilization, causing the cell death. Despite the cell death by high quantity uptake of SWNHs, the released cytokine (TNF-FI, IL-1FI and IL-6) quantity was small, from which we expect that SWNHs will not induce severe inflammatory reaction in vivo.

Biocompatibility And Functionalization Of Isolated, ssDNA Suspended Single- Wall Carbon Nanotubes

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The ability of carbon nanotubes (CNTs) to bind molecules with specific function, such as agents against infectious diseases, provides the opportunity for the use of CNTs as biomedical vectors for drug delivery. Single-wall carbon nanotubes (SWNTs) are known for their capability to transport biologically active cargos into living systems for the purpose of disease diagnosis and therapy [1] . To facilitate biomedical application of CNTs, they need to be solubilized in water, which is typically achieved by non-covalent functionalization with single-stranded DNA (ssDNA). In this study we focus on chirality enriched (6,5) single-wall carbon nanotubes coated with d(GT)16 oligomers as dispersion additive. Studies of nanotube cytotoxicity are often affected by cytotoxic effects of metal contaminants or particle aggregates, which may completely mask the actual cellular response to isolated SWNTs [2]. In this work, samples of well isolated SWNTs with specific diameter and chirality are carefully prepared from CoMoCat starting material by sonication and ultracentrifugation assisted density gradient differentiation. Cytotoxic effects of these nanotube samples are primarily tested on J774.1 murine macrophages. After 24 hours of incubation the number of metabolic active cells is determined by the absorbance of a dye that is sensitive to reduction and therefore an indicator for the effective cell metabolism. The bio-stability of ssDNA-CNT conjugates is also crucial for their potential use as vector. A particular concern is the disintegration of ssDNA-SWNT hybrids under chemical strains inside the cell. Dissociation of ssDNA-SWNT structures is expected to lead to potentially undesirable precipitation and concentration of SWNTs in lipophilic regions of the cell interior. We therefore do not only study the behavior of ssDNA-CNT conjugates in environments with pH varying from 0 to 14 but also their stability with respect to protein mixture and enzyme activity like DNase I. After evaluation of the sample stability and exclusion of cytotoxicity, carbon nanotubes can be functionalized so that they can be used in a drug-delivery system. For this purpose covalent bonds can be formed in specific crosslinking reactions between functional groups in DNA strands and side chains of the agent. In this study we present newly developed successful routes for functionalization of ssDNA-CNT hybrids. A dansyl fluorophore is used as model compound to demonstrate successful functionalization.

[1] N.W.S. Kam, T.C. Jessop, P.A. Wender, H. Dai, *J. Am. Chem. Soc.*, **126**, 6850-6851, (2004).
[2] P. Wick, P. Manser, L.K. Limbach, U. Dettlaff-Weglikowska, F. Krumeich, S. Roth, W.J. Stark, A. Bruinink, *Toxicol. Lett.*, **168**, 121-131, (2007).

Carbon Nanotube Films Preparations for Electronic, Sensors and Bioengineering Application

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Carbon nanotubes films (CNTF) are suggested to be more technological material in production process of devices and systems. It’s now considered as radiation resistive transistors and sensors [1], transparent and conductive layers for optoelectronics devices, scaffold material for biological application in tissue engineering. Nevertheless different technological methods of carbon nanotubes films formation biased on chemical vapor deposition, electrophoresis and ink printing are suggested. In this work we describe the development of different methods carbon nanotubes deposition for electronic, sensors and bioengineering with making use of chemical vapor deposition (CVD), dielectrophoresis (DEF) or deposition from surfactant solvents. It was shown the different methods produce different film that can be used or specific applications. CNTF films produced by low temperature CVD demonstrate rather good conductive and transparent properties for nanotubes with diameters 10 – 100 nm. The carbon nanotubes film deposited with making use of dielectrophoresis techniques allow us to control concentration and geometry of nanotubes film. We used DEF for sensor’s active layer development based on quasi-one-dimensional structures composite of carbon nanotubes and oxide zinc nanorods. The different surfactants was investigated for CNTF production. To produce biocompatible material we suggested to use bovine albumin (BSA) as surfactant for single-wall carbon nanotubes dissolution. Earlier we used nanotubes-albumin composite as scaffold material for cartilage regeneration [2]. This method was used for transparent conductive film formation by rolling up method on cover slips. We investigated the optical and electrical properties of such film and used them for cell growth electro-stimulation. Thus different methods can be used for CNTF formation. We have shown that method based on carbon nanotubes solution with biological surfactant provide transparent conductive biocompatible films.

[1] D.V. Gromov, V.V. Elesin, G.V. Petrov, I.I. Borinetskii, V.K. Nevolin. Radiation Effects in Nanoelectronic Elements, *Semiconductors*, **Vol. 44**(13), 1699–1702, (2010).

[2] S.A. Ageeva, I.I. Bobrinetskii, V.K. Nevolin, V.M. Podgaetskii, S.V. Selishchev, M.M. Simunin, V.I. Konov, V.V. Savranskii. Nanotube-based three-dimensional albumin composite obtained using continuous laser radiation, *Semiconductors*, **Vol. 43**(13), 1714- 1718, (2009).

An Optical SWNT Biosensor for Explosives

Daniel Heller[1*], George Pratt[1], Jingqing Zhang[1], Nitish Nair[1], Adam Hansborough[1], Ardemis Boghossian[1], Nigel Reuel[1], Paul Barone[1], Michael Strano[1]

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A class of peptides from the bombolitin family, not previously identified for nitroaromatic recognition, allows near-infrared fluorescent single walled carbon nanotubes (SWNT) to transduce specific changes in their conformation. In response to the binding of specific nitroaromatic species, such peptide-nanotube complexes form a virtual ‘chaperone sensor’ which reports modulation of the peptide secondary structure via changes in SWNT near-infrared photoluminescence. A novel split-channel microscope constructed to image quantized spectral wavelength shifts in real-time, in response to nitroaromatic adsorption, results in the first single- nanotube imaging of solvatochromic events. The described indirect detection mechanism, as well as an additional exciton quenching-based optical nitroaromatic detection method, illustrate that functionalization of the carbon nanotube surface can result in completely unique sites for recognition, resolvable at the single-molecule level.

The Methods of Cell Growth on Carbon Nanotubes Substrates with Making Use Of Electrostimulation

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Over the past thirty years the influence of electric stimulation on the accelerated tissue healing and cell growth was investigated. Traditional methods of bringing the external electric field failed to localize a field in the healing area, so whole organism had to be exposed to electric stimulation. Increasing the work area and the distance between electrodes and the healing area implies increasing of electrical field intensity, required for stimulating individual cells. In that case we show efficiency of using implant nanocomposite electrodes, which intend to help localizing electric field in a specific area. Accelerated tissue regeneration can be achieved by using tiny implant electrodes with a lower intensity amplitudes, and low-frequency signal. Nevertheless, similar invasive methods demand use of the biodegradable materials which help to minimize the influence on the tissue micro environment. The way of electric stimulation of cell growth, using system of the planar electrodes is well-known. Such electrodes are creating fields which can be localized mainly in the area of an organism where the electric field and current are
required. The last results in nanotube ferment-based degradation are discussed as a new scaffold material for tissue regeneration [1]. System of in vitro cell growth, involving a substrate, nanocomposite monolayer and gold needle electrodes was developed. 2 mg of single-walled carbon nanotubes were ultrasonicated with 10 mg of bovine serum albumen and 10 ml of distilled water to create nanocomposite solution. Substrate was treated with sputter deposition of gold to form contact area and then covered with 70 nm nanocomposite film to provide current supply to cells. Embryonic fibroblasts were cultured on 24x24 mm coverslips. Cells were incubatedin 6 well plates for 76 h, at 37°C and 5% CO2, fixed with 4% glutaraldehyde, washed twice with PBS, and then dehydrate using 50%, 70% and 96% ethanol for microscopy analysis. Electro-stimulation with 10, 50, 100 and 200mVpulse signal, at 1 kHz frequency, with 1 sec period was applied for 48 h after one day of standard cultivation. We used MTT method to determinate proliferation index, and investigated cells morphology with optical, atomic-force and scanning electron microscopy. The proliferation index increases on 20% after 50 mV pulses. Dense cell monolayer was found on samples exposed to current on a third day of incubation. As a result, we have shown another way of providing electrical stimulation of cells by using biocompatible conductive albumen-nanotube composite.

[1] L.B. Allen, G.P. Kotchey, Y. Chen et al,*J. Am. Chem. Soc.*, **131**(47), 17194–17205, (2009).

Adsorption Of Procion Blue MX-R (Reactive Blue 4) Dye From Water Solutions By Single-Walled Carbon Nanotubes And Multi-Walled Carbon Nanotubes

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Carbon nanotubes (CNTs), with nano-sized diameter and tubular microstructure, have been the worldwide hotspot of study since their discovery because of their unique morphologies and various potential applications. Because of their relatively large specific surface areas and easily modified surfaces, much attention has been paid to the adsorption by CNTs of contaminants such as heavy metals [1-7] and biological contaminants [8,9], in aqueous effluents. However, the use of CNTs for dye decontamination of aqueous effluents has not yet been extensively employed [10-15].

In the present work, single-walled carbon nanotubes (SWCNT) prepared by catalytic chemical vapour deposition (CCVD), with mean diameter of 1,37 nm, were compared with commercial multi-walled carbon nanotubes (MWCNT) and these materials were used as adsorbents for the successful removal of Procion Blue MX-R (Reactive Blue 4) textile dye from aqueous solutions The adsorbents were characterised by Raman spectroscopy, N_2 adsorption/desorption isotherms and scanning and transmission electron microscopy.The effect of temperature on the equilibrium adsorption of Procion Blue MX-R (Reactive Blue 4) dye from aqueous solution using both CNTs was investigated. The equilibrium adsorption data were analyzed using three widely applied isotherms: Langmuir, Freundlich and Liu. Kinetic analyses were conducted using pseudo-first, second-order, Avrami fractional-order and the intra-particle diffusion models.

[1] C.S Lu, H.S. Chiu, *Chem Eng Sci*, **61**, 1138-1145, (2006).
[2] C. Lu, C. Liu, J *Chem Technol Biotechnol*, **81**, 1932-1940, (2006).
[3] Y.H.Li, S. Wang, Z. Luan, J. Ding, C. Xu, D. Wu, *Carbon*, **41**,1057-1062, (2003).
[4] Y.H.Li, Z. Di, J. Ding, D. Wu, Z. Luan, Y. Zhu,*Water Res*, **39**, 605-609, (2005).
[5] J. Hu, C. Chen, X. Zhu, X. Wanga, *J Hazard Mater*,**162**, 1542-1550, (2009).
[6] K. Pillaya, E.M. Cukrowska, N.J. Coville, *J Hazard Mater*, **166**, 1067-1075, (2009).
[7] C.Y. Kuo, *Desalination* **249**, 781-785, (2009).
[8] V.K.K.Upadhyayula, S. Deng, M.C. Mitchell, G.B. Smith, *Sci Total Environ*, **408**, 1-13, (2009).
[9] V.K.K. Upadhyayula, S. Deng, G.B. Smith, M.C. Mitchell, *Water Res*, **43**, 1-9, (2009).
[10] C. Wu, *J. Hazard. Mater*., **144**, 93-100, (2007).
[11] C.Y. Kuo, C.H. Wu, J.Y. Wu, *J. Colloid Interface Sci*., **327**, 308-315, (2008).
[12] J.L. Gong, B. Wang, G.M. Zeng, C.P. Yang, C.G. Niu, Q.Y. Niu, et al., *J. Hazard. Mater*. **164**, 1517-1522 (2009).
[13] A.K. Mishra, T. Arockiadoss, S. Ramaprabhu, *Chem. Eng. J*., **162**, 1026-1034, (2010).
[14] G.P. Hao, W.C. Li, S. Wang, S. Zhang, A.H. Lu, *Carbon*, **48**, 3330-3339, (2010).
[15] Y. Yao, F. Xu, M. Chen, Z. Xu, Z. Zhu, *Bioresou. Technol*., **101**, 3040-3046, (2010).

Development of Glucose Sensor Using CNT Compound Materials

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A bio-nanosensor consisting of a silicon-based chip contains a poly[ethylene glycol]- grafted (PEG)-grafted carbon nanotubes (PEG-CNTs) modified with living body materials (ex. enzyme, antibody, and DNA etc.) using plasma ion irradiation (plasma activation) method, developed.[1,2] We developed a method for measuring changes in the electrical conductivity of a CNT surfacereaction, which is a time-based detection method impedance type). Specifically, we immobilized the glucose oxidase (GOD) on a sensor chip with a CNT base and we then measured changes in impedance caused by the catalyst reaction at the point where the glucose was dripped onto the chip. After evaluating various characteristics, we used PEG to enhance the dispersion of the multiwalled CNTs (MWCNTs) used when the sensor was fabricated. According to evaluation of the glucose sensor manufactured by using glucose oxidase (GOD), impedance revealed an increase due to a catalyst reaction of PEG-CNTs surface. Furthermore, the impedance change which originated in the blood glucose of small animal (rat) was confirmed. The results suggested that a bio-nanosensor made sure concentration dependency of blood glucose.

[1] T. Hirata, S. Amiya, M. Akiya, O. Takei, T. Sakai, and R. Hatakeyama, *Appl. Phys. Lett.*, **90**, 233106-1-233106-3, (2007).
[2] T. Hirata, S. Amiya, M. Akiya, O. Takei, T. Sakai, T. Nakamura, J. K. Tsuzuku, T. Yamamoto, and R. Hatakeyama, Jpn J. Appl. Phys., Vol.47, 2067-2071, (2008).

When Macrophages Digest Carbon Nanotubes: Intra-Cellular Dispersion And Decarbonation of Iron-Based Nanoparticles Attached To Carbon Nanotubes

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An increasing amount of literature evaluates health effects of carbon nanotube (CNT), but the respective roles of CNT themselves and of remaining catalyst residues present in CNT samples are still to be elucidated. Here, we focus on the fate of iron-based nanoparticles in raw HiPCO Single-Walled Carbon Nanotubes (SWCNT, from Unidym, Sunnyval, CA) samples, when incorporated inside murin macrophage cells (RAW 264.7 cell line). Such nanoparticles are in the form of cementite Fe_3C in the raw material [1], they are surrounded by carbon shells and attached to the nanotubes [2]. Advanced physical methods like micro-X-ray fluorescence [3], micro-XANES (X-ray Absorption Near Edge Spectra), STEM-HAADF (High Angle Annular Dark Field-Scanning Transmission Electron Microscopy) and EELS (Electron Energy Loss Spectroscopy) have been used here to get chemical and spatial information on iron-based nanoparticles in-situ, inside cells. Our results [1] demonstrate that cementite nanoparticles, although initially protected from biological media thanks to their carbon surrounding shells, are finally accessed and further transformed inside macrophages, through decarbonation and oxidation reactions. Free iron nanoparticles are found in the cytoplasm and in the nucleus of the macrophages. In the presence of exogenous particles, the phagocytic function of macrophages is activated, leading to the formation of phagolysosomes, intracellular organelles presenting an acidic pH [4]. We will discuss the possible role of the acidic environment in phagolysosomes in the detachment and transformation of iron-based nanoparticles. To the best of our knowledge, the present results are the first demonstration of catalyst detachment from CNT backbone along with its chemical modification as a result of an intracellular process. These nanoparticles may play a role in the biological effects associated to CNT exposure.

[1] C. Bussy, J. Cambedouzou, B. Fayard, M. Pinault, N. Brun, C. Mory, E. Belade, M. Huard, V. De Andrade, J. Boczkowski, P. Launoisand S. Lanone, submitted for publication
[2] G. Charron, S. Mazerat, M. Erdogan, A. Gloter, A. Filoramo, J. Cambedouzou, P. Launois, E. Rivière, W. Wernsdorfer, J.-P. Bourgoin and T. Mallah, *New J. Chem.* **33**, 1211(2009).
[3] C. Bussy, J. Cambedouzou, S. Lanone, E. Leccia, V. Heresanu, M. Pinault, M. Mayne-l'Hermite, N. Brun, C. Mory, M. Cotte, J. Doucet, J. Boczkowski, and P. Launois, *Nano Lett.* **8** (9), 2659-2663 (2008)
[4] N. Demaurex, News in *Physiological Science* **17**, 1 (2002)

Indolizine Modified Fluorescent Single-Walled Carbon Nanotubes For Detection Of Nitroaromatics

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Since nitroaromatics are present in explosive warfare agents including TNT and ammonium picrate, and pollute the environment, detection of trace amount of nitroaromatic compounds is important both in terms of homeland security and environmental monitoring. Herein an indolizine modified SWNT based photochemical sensor has been presented, for the first time, to detect trace amount of nitroaromatic compounds, o-nitrophenol, m-nitrophenol, p-nitrophenol, p-nitrotoluene and 2,4-dinitrotoluene, in solution and solid phase. Indolizines, the simplest hetero-aromatic molecules containing both a π-excessive pyrrole and a π-deficient pyridine ring, have attracted special attention due to their luminescent properties with potential sensing applications.[1,2] Pyridine functionalized single-walled carbon nanotubes (SWNTs),[3] formed following the addition of pyridine diazonium to nanotubes, have been used to prepare pyridinium ylides, generated from simple Kröhnke salts, covalently bound to a nanotube surface which undergo a 1,3-dipolar cycloaddition with dimethyl acetylenedicarboxylate in a 'click' chemistry type fashion to yield indolizine modified SWNTs. The indolizine functionalized SWNTs generated emit blue light when excited at 330 nm.[4] The location and distribution of the functional groups was determined by AFM using electrostatic interactions with gold nanoparticles. The indolizine functionalized SWNTs were further characterized using FTIR, UV-vis-NIR, TGA-MS and XPS. Fluorescent quenching experiments demonstrated that the SWNTs having the fluorescent indolizine groups could be used as a potential photochemical sensor for detection of aromatic nitro compounds with a detection limit of 6.66 x 10^{-8}M.

[1] F.Delattre, F. Cazier, A. Tine, *Current Analytical Chemistry*, **5**, 48-52(2009).
[2] G. G. Surpateanu, M. Becuwe, N. C. Lungu, P. I. Dron, S.Fourmentin, D. Landy, G. Surpateanu, *Journal of Photochemistry and Photobiology a-Chemistry*, **185**, 312-320(2007).
[3] M.K. Bayazit, L.S. Clarke, K.S. Coleman, N. Clarke, *Journal of the American Chemical Society*, **132**, 15814-15819, (2010).
[4] M.K. Bayazit, K.S. Coleman, *Journal of the American Chemical Society*, **131**, 10670-10676, (2009).

Small-Sized Aggregates of Carbon Nanohorns Enabling Cellular Uptake Control

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The size of nanocarbons such as nanotubes, nanohorns, and graphene ribbons is a critical parameter for medical applications. The small-sized nanoparticles, especially 30-50 nm, are believed to be helpful to avoid the uptake by reticuloendothelial system (RES) including various macrophage cells and therefore to enhance the targeting ability in drug delivery system (DDS). However, the size control of nanocarbons is not easy especially below 100 nm. Here, we first present our new method to obtain small-sized aggregates (20-50 nm) of carbon nanohorns (S-SWNHs) by an oxidation exfoliation method from normal-sized aggregates (80-100 nm) of single-walled carbon nanohorns (L-SWNHs). The obtained S-SWNHs were large in quantity and high in purity. They had a high ability of material storage. S-SWNHs were hydrophilic and highly dispersed in water. These advantages suggest that S-SWNHs could be more suitable to the medical application than the other nanocarbons examined so far.

We next show superior property of S-SWNH than L-SWNH toward the drug delivery, namely, low uptake by macrophages and high uptake by cancer cells. The cellular uptake was observed with confocal microscopy and quantified by optical absorption measurements, where SWNHs were identified by their black color or strong optical absorption in visible range. No fluorescent label was needed. The results showed that the uptake-quantities of S-SWNHs by macrophage (Raw 267.4) cells were much lower than those of L-SWNHs even without functionalization. By the functionalization with DSPE-PEG (noncovalently), S-SWNHs completely avoided the engulfment by the macrophage cells while the L-SWNHs did not. Folic acid modified S-SWNHs showed a higher uptake by KB cells (folate acide receptor over expressed) than the folic acid modified L-SWNHs. This controllable cellular uptake of S-SWNHs by the functionalization suggests their potential in the realization of ideal drug delivery system, selective delivery of drugs to the specific tissues or cells.

Coronenes Encapsulated Single-walled Carbon Nanotubes for Imaging Probes Targeted to Cancer Cells

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Single-walled carbon nanotubes (SWCNTs) have great potentials for drug delivery and diagnostic imaging agents. One of the advantages of SWCNTs is that the outer surface of SWCNTs can be functionalized covalently or non-covalently, independent of the encapsulated molecules. Proper functionalization of the tube wall leads to a high selective targeting ability to the particular cells or tumours. Furthermore, the encapsulated agents and drugs are isolated from active molecules by the tube wall, which leads to the superior durability of the materials. Here, we demonstrates that fluorescent molecules, coronene ($C_{12}H_{24}$), encapsulated SWCNTs can be used for such nano-carrier type imaging probes targeted to cancer cells. Coronene encapsulated SWCNTs (Coronenes-SWCNTs) were synthesized by sublimation in a vacuum. According to the TEM images, coronene molecules are packed into the SWCNTs and take a one-dimensional stacking structure in high yield [1]. We observed a fluorescence spectrum of Coronenes-SWCNTs micelle solution by 350 nm wavelength excitation. The obtained spectral shape was sharply different from those of the coronene molecules dissolved in an organic solvent and the three-dimensional coronene solid. The difference in the spectral shape suggests that the encapsulated coronenes have unique electronic and optical properties due to the one-dimensional arrangements inside SWCNTs. In order to confirm the uptake of Coronenes-SWCNTs by cells, phospholipid poly(ethyleneglycol)(PL-PEG),which has no cytotoxicity, wrapped Coronenes-SWCNTs(PEG-Coronenes-SWCNTs) was added to macrophage cells (RAW264.7). Confocal microscope images showed that PEG-Coronenes-SWCNTs were successfully internalized inside macrophage cells by phagocytosis. We then carried out similar experiment by using cancer cells. To investigate the targeting efficiency to cancer cells, Coronenes-SWCNTs were wrapped by PL-PEG functionalized with folic acid (FA-PEG-Coronenes-SWCNTs). FA receptor positive cancer cells (KB cell) were incubated with FA-PEG-Coronenes-SWCNTs and the control sample, PEG-Coronenes-SWCNTs, respectively. Confocal microscope images showed that much higher fluorescence signals of coronenes were observed in FA-PEG Coronenes-SWCNTs treated cells. The results suggest that the functionalized SWCNTs encapsulating fluorescent agents are attractive imaging probes targeted to cancer cells.

[1] T. Okazaki, Y. Iizumi, S. Okubo, H. Kataura, Z. Liu, K. Suenaga, Y. Tahara, M. Yudasaka, S. Okada and S. Iijima, *Angew. Chem. Int. Ed.*, in press.

Cationic Carbon Nanotubes for Nucleic Acid Delivery

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Recently, functionalized carbon nanotubes (CNTs) have attracted great interest due to their potential biomedical applications, their improved water dispersibility and their ability to penetrate into the cells. In particular their capacity to complex genetic material has indicated them as promising candidate carriers for plasmid DNA or siRNA both in vitro[1] and in vivo[2]. In this work CNTs have been functionalized with positively charged moieties in order to interact with nucleic acids and permit their delivery inside the cells. For the purpose of directing the delivery specifically inside mitochondria, CNTs have been coupled to a characteristic peptide called mitochondria target sequence peptide (MTS). The final goal of this work is to create a complex between functionalized CNTs and nucleic acids and to selectively target them into mitochondria in order to have the possibility to cure diseases originated from mitochondrial DNA mutation. In this communication, we will present the synthetic strategy to generate the cationic CNTs, bearing ammonium or guanidinium groups and their further modification with MTS peptide. The presence of guanidinium groups will enhance the affinity of CNTs for nucleic acids and will improve the bio-distribution of the final complex. In addition, the cell uptake and sub- cellular distribution of the different conjugates will be discussed.

[1] D. Pantarotto et al., Angew. *Chem. Int. Ed.*, **43**, 5242-5246, (2004)
K. T. Al-Jamal et al., *FASEB J,* **24**, 4354-4365, (2010)
M. A.Herrero et al. *J. Am. Chem. Soc.*, **131**, 9843-9848, (2009)
[2] J. E. Podesta et al., *Small*, **5**, 1176-1185, (2009)

High Uptake Cytotoxicity of Single-Walled Carbon Nanohorns in Murine Macrophage RAW264.7

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Nanometer-sized carbonaceous materials are attractive new materials in the field of electronics, chemical engineering, medicals, etc. With the advances of these researches, concerns about safety of the nanocarbons have increased, and their toxicological studies have been progressing. Among the nanocarbons, carbon nanotubes (CNTs) are the most popular one and their toxicological studies revealed their toxicity depended on the structures. For example, when carbon nanotubes (CNTs) with long and rigid structure enter a body, intratracheal and intraperitoneal administrations of CNTs in rodents show that macrophages cannot completely engulf large CNTs, which is designated as frustrated phagocytosis. The macrophages in this state release inflammatory cytokines and ROS, which cause lesions in vivo. On the other hand, CNTs with small size and appropriately functionalized, if not excreted from a body, are possibly captured by tissue macrophages and stay in the tissues for a long period without causing adverse pathological changes. In this context, however, the toxicity at high doses of small CNTs is not well known. The toxicological studies at high doses are necessary, concerning about the possibility of the long term continuous uptake of CNTs in bodies or accidental high exposure in the occupational area. One major reason why such study at high doses has not been progressed is the difficulties in obtaining small CNTs in a large quantity with high purity. To advance the toxicological study for nanocarbons, we performed the cytotoxicity study using single-walled carbon nanohorns (SWNHs), a type of nano-carbons, in macrophage. SWNHs have many advantages of large available quantity, high purity, uniform size, and high dispersion in solutions which other nanocarbons including CNTs do not have. SWNHs are single graphene nano-tubules with diameters of 2 - 5 nm and lengths of 40 - 50 nm. About 2000 of SWNHs assemble to form a spherical aggregate with diameters of 80 - 100 nm. The aggregate are robust and cannot be separated individually easily. Their potential applications to drug delivery systems are reported, and the low toxicity of SWNHs has been shown in rodents. We also clarified that SWNHs intravenously administered into mice accumulated in macrophages in liver, spleens, lungs without adverse histological changes. In this study, we show the cytotoxicity caused by excess uptake of SWNHs, the mechanism of cell death, and cytokine release in macrophage RAW 264.7. The high accumulation of SWNHs in lysosomes was observed, which induced ROS generation and lysosomal membrane destabilization, causing the cell death. Despite the cell death by high quantity uptake of SWNHs, the released cytokine (TNF-FI, IL-1FI and IL-6) quantity was small, from which we expect that SWNHs will not induce severe inflammatory reaction in vivo.

Functionalization of Single-Walled Carbon Nanotubes with Ribonucleic Acids

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Optical properties of single-walled carbon nanotubes (SWCNTs) dispersed in ribonucleic acids (RNA), purified from Escherichia coli, were studied using photoluminescence (PL), Raman, and absorption spectroscopy. Isolated SWCNT-RNA hybrids were successfully synthesized. Two distinct PL peaks at 1.248eV and 1.392eV were observed originating from (6,5) and (6,4) SWCNT, respectively. Atomic force microscopy (AFM) images and height profile also showed the evidence of isolated SWCNT-RNA hybrids.

Carbon Nanotubes: Effects of Plasma Protein Binding

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In biomedical applications of carbon nanotubes (CNTs) the CNTs will come into contact with blood and its various components. It has been shown that among the many proteins present in human plasma, only a few bind to various pristine and chemically modified CNTs. We show the binding is highly selective and dependent on the type of nanotubes (single-walled, multi-walled) and the chemical modification, such as dispersant or oxidation. The proteins which bind in largest quantity are human serum albumin and fibrinogen, and also the lipoprotein complex high density lipoprotein (HDL), which contains phospholipids, cholesterol and the apolipoproteins AIV, AI, CIII. Binding most likely occurs at irregularities in the carbon network. In a competition experiment at least two non-overlapping types of binding sites for proteins on carbon nanotubes were identified. Binding of proteins to CNTs was shown to be unstable. Proteins pre-coated onto CNTs can be displaced fairly easily in blood plasma: for example precoated BSA (bovine serum albumin) is replaced by HSA (human serum albumin) when CNTs are incubated in human plasma. Another important group of proteins found to interact with CNTs are innate immune system proteins. The innate immune response plays a key role in protection against pathogens and synthetic particles. By haemolytic assays and western blots we showed CNTs bind C1q, C3 and C4, which are important proteins of the complement classical and alternative pathways. This indicates that the complement system is activated by CNTs and this activation may promote inflammation, granuloma formation and interaction with cells that have receptors for complement proteins. When complement is activated, C3b (the large fragment of activated C3) binds covalently to most targets, via OH or NH_2 groups on the target. The same occurs for C4b. CNTs do not have many available reactive groups of this type, therefore C3b and C4b may bind covalently to other proteins adsorbed to the CNTs; or they may bind by hydrophobic interaction. No evidence was found for covalent binding of C3b to other plasma proteins bound to the CNTs and therefore hydrophobic binding is assumed. We are currently studying interactions of CNTs with red blood cells which may occur by binding of the C3b coated on the CNTs to the receptor CR1 on red blood cells. Furthermore as C3b is a strong opsoniser, a signal for phagocytes to take up C3b-coated particles, we are examining the role of C3 in uptake of CNTs.

Biocompatibility And Toxicological Research Of Surfaces Modificated With Different Carbon Nanotubes

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Carbon nanotubes (CNTs) are one of the most promising products of nanotechnology, which can be used in tissue engineering of biological objects as a scaffold material. This property of CNTs is due to the fact that they are geometrically similar structure with collagen, which is the main protein of connective tissue of animals. Unique electronic properties, high mechanical strength, high flexibility and low density of CNTs can create biocompatible composite materials with new properties.

At the moment there are a number of researches describing the creation of composite materials based on nanotubes for bio-engineering, in particular the regeneration of bones and cartilages [1]. But there is the issue of biocompatibility and cytotoxicity of CNTs. In the research to determine the toxicological parameters of CNTs, the engineering characterization of nanotubes was developed. The formation process of the scaffold material based on carbon nanotubes and cell growth on these structures was studied. Characterization of the nanotubes was carried out by scanning (SEM) and transmission electron microscopy (TEM), atomic force microscopy (AFM) for identification the geometric dimensions and structure, secondary ion mass spectroscopy (SIMS) for determination the concentration and composition of impurities.

As the nanotubes material were chosen single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) of the three largest Russian suppliers. SWNTs obtained by arc evaporation of graphite, were provided by the Institute of Problems of Chemical Physics with average diameter, 2,9 ± 1,5 nm, length 570 ± 158 nm. MWNTs sample number 1, obtained by catalytic pyrolysis of hydrocarbons, provided LLC STC "Granat" with the average diameter of 4.9 ± 0.5 nm, length 475 ± 120 nm. MWNTs sample number 2, obtained by catalytic pyrolysis of hydrocarbons, provided LLC "NanoTechCenter" with average diameter of 36.0 ± 6.0 nm, length 1203 ± 400 nm.

Culturing Vero cell line on the surfaces of cover glasses the size of 24x24 mm^2 and a thickness of 0.13-0.17 mm, modified with carbon nanotubes, SWNTs, MWNTs number 1 and MWNTs number 2 was carried out. Coverslips with CNTs was placed in culture dish and sterilized in an autoclave at 120 °C, 1 atmosphere, 20 min., followed by the introduction of Vero cells at a concentration of 100,000 cells / ml. Cultivation was carried out in an incubator for 72 hours, and then coverslips were removed from culture dish, fixed and stained for morphological researches. Investigation of cell morphology demonstrated that during cultivation on modified surfaces morphology of normal cells, also formed a dense cell monolayer. The result of the work is the following: carbon nanotubes are not cytotoxic and can be used as a basis for the cells cultivation, as well as a frame material for cell engineering. When cultured glioblastoma cells(GL6) and human embryo fibroblast cells (HEF) on coverslips modified SWNTs and MWNTs number 1 showed a slight decrease in proliferative activity of cell lines and cell viability. While MWNTs number 1 have the greatest toxic effect on tumor cells human glioblastoma.

[1] Zanello L.P., Zhao B., Hu H. *Nano Letters*, **6**[III], 2006; 562-67.

Synthesis Bombesin-Naphthalenediimide Conjugate Functinalized Single Walled Carbon Nanotubes as a Novel Receptor Imaging Probe

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We hereby report a new cancer probe including carbon nanotube, of advanced purity and with well understood physico-chemical properties and which are wrapped with a cancer cells receptor-binding bombesin-naphthalene diimide conjugate (NDI- bombesin)[1]. Our probes are totally biocompatible and soluble in cell medium which makes them particularly attractive for cancer cells receptor imaging. The specific peptide tag helps carbon nanotubes to target Gastrin-Releasing Peptide Receptor (GRPR) which is highly expressed on prostate cancer cells (PC3) membrane and also helps to ferry carbon nanotube into prostate cancer cells. Therefore, our new bombesin- NDI conjugate functionalized carbon nanotubes(BN-NDI-SWNTs) targeting the GRPR can be viewed as promising tools for the non-invasive diagnosis, monitoring and potential treatment of prostate cancer in future.

[1] Pantos, G. D.; Pengo, P.; Sanders, J. K.,*Angew. Chem., Int. Ed.,* **46**（1-2）, 194-197, (2007).

Self Assembly of Lipid Nanostructures in Aligned Carbon Nanotubes

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Lipids, like other amphiphilic molecules, show a tendency to self-assemble into more or less complex aggregates when their concentration exceeds the critical micelle concentration. They are the main structures forming the cell membranes and their self assembly is crucial for the appropriate function of living organisms. At the attempt of stabilizing carbon nanotube (CNT) suspensions, the adsorption of amphiphiles on the CNT surface has been studied before, particularly with the anionic surfactant SDS.1 It was shown that their self-assembly on the CNT surface can follow the carbon pattern.1 This suggests that – apart from stabilizing suspensions - CNTs could be used as orientation inducing substrates or templates for amphiphilic molecules. In this work we have investigated the self assemblies of biological lipid molecules in the presence of aligned arrays of carbon nanotubes, which include the surface adsorption as well as the assembly in the narrow channels between the nanotubes. We have observed various lyotropic nanostructures that are found for corresponding lipids in the bulk under dry and hydrated conditions. The structural studies were performed using small and wide angle X-ray scattering techniques. This work is most desirable for designing the nano-micro-fluidic architectures, novel composites, nanoscale devices, platforms for ultra-sensitive recognition of antibodies and supported model membranes.

[1] a) C. Richard et al., *Science*,**300**, 775-778 (2003);
b) K. Yurekli et al., *JACS,* **126**, 9902-9903(2004).

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Electrochemically Functionalized Carbon Nanotubes and Graphene : From Device Applications to On-chip Nanobiosensors

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Carbon in both its one-dimensional (carbon nanotubes - CNTs) and two-dimensional (graphene) allotropic forms is emerging to be a major candidate for a number of on-chip device applications. Chemical functionalization routes designed to expand the spectrum of realizable applications bring in specialized properties that are unattainable in these systems in their pristine form. Our focus is on the use of electrochemistry both as a preparative and as an analytical tool for the design and operation of devices based on single-wall CNTs (SWCNTs) and graphene. The devices comprise of individual or few SWCNTs or reduced graphene oxide flakes contacted by electrodes working in a field-effect transistor configuration. The first part will focus on the use of electrochemistry as a preparative tool, to functionalize the surface of contacted SWCNTs and graphene flakes. We have designed a generic route to attach a wide spectrum of receptors on to the surface of carbon nanostructures either in a covalent or non-covalent manner [1]. The receptors range from simple organic moieties through nanoparticles to biomolecules. In comparison to other approaches electrochemical modification (ECM) offers the specific advantage that the energy level of the chosen carbon nanostructure can be selectively tuned, allowing one to chemically or biologically tailor their surface properties in a very controlled manner [2]. The extent of functionalization can be controlled in situ by monitoring its conductance while performing ECM. In addition, only the addressed nanotubes are functionalized giving a very high site-specificity. Deploying this principle we demonstrate controlled modification of carbon nanotube networks resulting in purely semiconducting device characteristics. The advantages of using electrochemistry to modify electronic structure will be highlighted here in the context of other chemical functionalization methods.

The second part will deal with the use of functionalized carbon nanostructure devices as highly sensitive analytical tools for the detection of gaseous, chemical and biological species. Representative sensing paradigms will be presented:
(a) hydrogen sensors based on Pd- nanoparticle decorated SWCNTs or graphene [3]
(b) pH sensors with aniline moieties and
(c) enzyme-free sugar sensors based on boronic acid receptors on the CNT surface [4]. The focus here is on the ability to tune the chemical nature of the receptor coupling to the carbon nanostructure and thereby have a good control over the functional interface. Electrochemistry allows us to switch this coupling between covalent and non-covalent without altering the binding characteristics of the receptor. For example, with covalently and non-covalently attached boronic acid receptors we corroborate in detail the transduction mechanism of our CNT sensors. The talk concludes with implications for future on-chip SWCNT chemical and

bio sensors.

[1] K. Balasubramanian and M. Burghard, *J. Mater. Chem*, **18**, 3071, (2008).
[2] K. Balasubramanian, M. Burghard and K. Kern, *Phys. Chem. Chem. Phys.***10**, 2256 (2008).
[3] R.S. Sundaram, C. Gomez-Navarro, K. Balasubramanian, M. Burghard and K. Kern, Adv. Mater.20, 3050 (2008).
[4] A. Vlandas, T. Kurkina, A. Ahmad, K. Kern and K. Balasubramanian, *Anal. Chem.***82**, 6090 (2010).

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CNBMT11

Antibacterial Activity of Graphite, Graphite Oxide, Graphene Oxide and Reduced Graphene Oxide: Membrane and Oxidative Stress

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Health and environmental impacts of graphene-based nanomaterials need to be thoroughly evaluated before their potential applications. Graphene has strong cytotoxicity towards bacteria. To better understand its antimicrobial mechanism, we compared antibacterial activity of four types of graphene-based nanomaterials (Graphite (Gr), Graphite oxide (GtO), graphene oxide (GO) and reduced graphene oxide (rGO)) towards a bacterial model – Escherichia coli. Under similar concentration and incubation conditions, GO dispersion shows the highest antibacterial activity, sequentially followed by rGO, Gt, and GtO. Dynamic light scattering analysis shows that GO has the smallest average size among the four types of materials. Scanning electron microscope images demonstrate direct contact with graphene nanosheets disrupts cell membrane. No reactive oxygen species (ROS) (e.g. superoxide anion, $O^{2\bullet-}$) production is detected. However, the four types of materials can oxidize glutathione, which serves as redox state mediator in bacteria. Conductive rGO and Gt have higher oxidation capacities than insulating GO and GtO. Results suggest that antimicrobial actions are contributed by both membrane and oxidation stress. We propose that a three-step antimicrobial mechanism, previously used for carbon nanotubes, is applicable to graphene- based materials. It includes initial cell deposition on graphene-based materials, membrane stress caused by direct contact with sharp nanosheets, and the followed ROS-independent oxidation. We envision that physicochemical properties of graphene-based materials, such as density of functional groups, size and conductivity, can be precisely tailored to either lessening their health and environmental risks or increasing their application potentials.

Sensitivity of Boron Nitride Nanotubes toward Biomolecules

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Interfacing biomolecules with nanomaterials and understanding the applicability of bio-conjugated nanostructured materials in technologically important areas are forefront research activities. There exist numerous studies that have focused on carbon-based nanostructures, addressing the challenges to interface biomolecules with nanomaterials, e.g., non-uniformity and instability of carbon nanotubes in solutions. Semiconducting boron nitride nanotubes (BNNTs) which possess morphology similar to that of carbon nanotubes (CNTs), but with distinct properties on their own, appear to be more appropriate candidates for bio-medical applications. Recent experiments report that functionalized BNNTs with biological epitopes can mediate protein and cell binding, and also deliver DNA-oligomers to the interior of cells with no apparent toxicity.

We investigated the electronic response of BNNT in the presence of the DNA and RNA nucleobases adenine (A), guanine (G), cytosine (C), thymine (T) and uracil (U)- and the amino acids – arginine (Arg), tryptophan (Trp) and aspartic acid (Asp). Trp is a non-polar aromatic amino acid whereas Asp and Arg are polar amino acids. The results obtained from density functional theory calculations show that molecular interactions between BNNT and nucleobases are mainly governed by van der Waals (vdW) forces [1]. The calculated order of the binding energy is predicted to be $G > A \approx C \approx T \approx U$, implying that the interaction strength of the high curvature BNNT with the nucleobases is very similar, G being an exceptional case. The higher binding energy for the G-BNNT conjugate appears to result from hybridization of the molecular orbitals of G and the BNNT. For the case of amino acid molecules, the calculated results find Asp and Arg to be closer to the tubular surface relative to Trp. Negligible charge transfer is found for the Trp-BNNT complex suggesting the dominance of non-covalent interactions. An occurrence of a relatively large charge transfer from the polar amino acids to the tubular surface of BNNT suggests stabilization of the io-conjugated complex due to electrostatic interactions. The results find modulation of the band gap of pristine BNNT by Trp, though no change in band gap is seen for polar conjugates. A relatively large binding energy of the Arg-BNNT complex may suggest the possibility of Arg to be the amino acid that can facilitate a direct link to BNNT. Thus, the results suggest BNNTs to be candidate nanomaterials for design and development of a new class of biological probes at the nanoscale.

[1] S. Mukhopadhyay, S. Gowtham, R. H Scheicher, R. Pandey, and S. P. Karna; *Nanotechnology* **21**, 165703, (2010)

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Biodegradation Of Carbon Nanotubes Investigated Using Raman Spectroscopy

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One of the key expectations of the nascent field of nanomedicine is that in the near future it will be possible to produce new drugs incorporating nanocarriers for use in the human body. It is therefore essential to both understand the ultimate biological fate of these nanocarriers and to develop reliable methods for evaluating their uptake and degradation as many candidate nanocarriers undergo little or no biodegradation. Carbon nanotubes (CNTs) are under extensive research due to their unique mechanical, electrical and magnetic properties. The large surface area to volume ratio of CNTs is attractive for biological applications such as drug delivery and their rich electronic properties have been explored for nanoscale biosensors. However, these attractive characteristics make the biological consequences of CNT largely unpredictable and numerous studies have reported their cytotoxicity. For this reason CNTs were the primary candidate nanocarriers used in this study, which is ultimately concerned with quantifying the degradation of CNTs in cells and tissues using an innovative in vitro approach. Previously we have shown the biodegradation of single- walled carbon naotubes (SWCNT) by human neutrophils using Raman spectroscopy.[1] It was found that there was an increase in the disorder D band relative to the G band with increasing incubation time, suggesting that the graphene sidewall was oxidised by the neutrophils, mediated by myeloperoxidase within these cells.

Here we addressed the hypothesis if the biodegradation of SWCNT by myeloproxidase of neutrophils was the primary and only mode of degradation and investigated whether such biodegradation was visible in other cell lines and whole tissue. As macrophages are involved in the active clearance of tissues from foreign and pathogenic material, we treated both primary macrophages and THP1 macrophage cell line with SWCNT for 24, 48 and 72 hours. Lung tissue sections of wild type and myeloperoxidase knock-out mice, treated with SWCNT by pharyngeal inhalation, were also taken at 1 day, 7 day and 28 day. Unlike our previous studies which used single point spectra, this study uses a technique for performing 32 x 32 point Raman mapping of both the cells and tissue samples. This technique was optimised using a 100x oil immersion lens, 473nm cobalt laser on an Ntegra Spectra Raman system (NT-MDT, Russia). Macrophages were mapped in a 20µm x 20µm scan which constitutes their total area. 10 representative Raman maps throughout each tissue section (20µm x 20µm or 10µm x 10µm) were recorded. Analysis of the Raman maps recorded was carried out using Matlab (The

Mathworks, USA) software which generated maps based on the Raman spectra which were then used to investigate the D to G ratio in all samples. This approach enabled us to identify and quantify degraded and non-degraded CNTs in cells and lung tissue samples in a model that has a close relevance to their potential physiological and technogenic exposure routes.

[1] Kagan, V. E.; Konduru, N. V.; Feng, W.; Allen, B. L.; Conroy, J.; Volkov, Y.; Vlasova, I. I.; Belikova, N. A.; Yanamala, N.; Kapralov, A.; Tyurina, Y. Y.; Shi, J.; Kisin, E. R.; Murray, A. R.; Franks, J.; Stolz, D.; Gou, P.; Klein-Seetharaman, J.; Fadeel, B.; Star, A.; Shvedova, A. A. *Nat Nano*, **5**, (5), 354-359 (2010).

The Growth Pattern and Thickness Evaluation of Mesenchymal Stem Cells Cultured on a Variety of Single-Walled Carbon Nanotube

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Since their discovery in 1991, carbon nanotubes (CNTs) have attracted much attention because of their electrically conductive properties and potential for a wide variety of biological applications such as tissue engineering scaffolds, the delivery of drugs, cell tracing and growth platform for neuronal circuits. [1] Mesenchymal stem cells (MSCs) are of special interest because they are self-renewable and multipotent, and can also trans-differentiate into specific tissue cells such as osteoblasts, chondroblasts, adipocytes, and even neuronal cells both in vitro and in vivo.[2] Unlike embryonic stem cells, MSCs are isolated from a variety of tissues, such as bone marrow and adipose tissues. Since MSCs have large differentiation potential, its ex vivo culture expansion and the preservation of stem cell properties have been attracted researcher's attentions. The aim of this study is to evaluate the growth and shape of MSCs cultured on various single-walled carbon nanotube (SWNT) films that have different degrees of thickness and roughness. The thickness, roughness and directional alignment of SWNT films are found to affect the growth pattern of MSCs including their thickness. Our results provided fundamental information on carbon nanotubes for the biocompatibility, and demonstrated that SWNT films can be utilized as substrates for controlling the growth and differentiation of MSCs through the surface modification and the thickness control of the films. Furthermore, to investigate the effect of SWNT films on differentiation property of MSCs, we induced adipogenesis using adipogenic medium, and stained it with oil red O solution. Our results demonstrated that the SWNT Langmuir-Blodgett film and SWNT network film based scaffolds did not show any cytotoxicity, and on the other hand it promoted differentiation property of MSCs comparing to normal culture controls. In addition, lipid vesicles in adipocytes were also differentiated. Our study may suggest for the differentiation to other specific cells by utilizing various SWNT films.

[1] G. Cellot, E. Cilia, S. Cipollone, V. Rancic, A. Sucapane, S. Giordani, L. Gambazzi, H. Markram, M. Grandolfo, D. Scaini, F. Gelain, L. Casalis, M. Prato, M. Giuglizno and L. Ballerini, *Nat. Nanotechnol.*, **4**, 126 (2009)
[2] L. Ferreira, J. M. Karp, L. Nobre and R. Langer, *Cell*, **3**, 136 (2008)

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CNBMT11

PAMAM Dendrimers Decorating Carbon Nanohorns Surface as Efficient Gene Delivery Materials for Prostate Cancer Cells

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Carbon nanohorns (CNHS) represent a new type of carbon-based nanostructures with interesting properties for applications in materials science, biology and medicine. CNH primary particle consists of a sheet of graphene rolled into a tube (with a structure similar to single-walled carbon nanotubes) of 2-5 nm in diameter with a length of 40-50 nm and with a conically-closed tip. CNHs usually aggregate in assemblies that are reminiscent of dahlia flowers with a diameter that goes from 80 to 100 nm, although they can also constitute buds and seeds. The high purity achieved in the synthesis of CNHs is one of its greatest advantages over carbon nanotubes. CNHs are synthesized in the absence of metal catalyst and thus obtained metal-free. These nanomaterials have a high surface absorption and inherent interstitial holes. The size of CNHs aggregates allow their inclusion through endocytosis into the inner cell decreasing the citotoxicity and the globular shape might avoid the asbestos-like toxicity associated to the use of carbon nanotubes. Chemical modification of these materials will allow its manipulation and therefore it allows the synthesis of hybrid nanocomposites with different applications. Thus, anchoring PAMAM dendrimers of different generations renders CNHs with almost unaltered features but significantly enhances its solubility. The presence of a large number of positive charges due to the amino groups located on the PAMAM periphery makes these hybrids ideal for coupling genetic material by means of electrostactic interactions and these materials are therefore suitable for their use as gene carriers into cells. Similarly, the decoration of the CNHs with dendrimer encapsulated nanoparticles (DENs) could allow us monitoring the gene carrier trafficking without the need to use other vehicle markers.

In this work we show the development of a new non-viral vector family for gene therapy that is based on CNHs decorated with PAMAM dendrimers. These hybrid nanomaterials have been applied successfully as small interfering ribonucleic acid (siRNA) transfection agent for gene delivery in prostate cancer cells. Here we report the full characterization of these materials as well as the biological results that clearly demonstrate the potential usefulness of these carriers to deliver siRNA.

Molecular-Scale Tailoring of Graphene Surface Chemistry via Organic Functionalization

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Graphene has emerged as one of the leading materials in condensed matter physics due to its superlative electrical and mechanical properties. With an eye towards expanding its functionality and applications, this talk will highlight our latest efforts to tailor the surface chemistry of graphene via organic functionalization. At the molecular scale, we employ ultra-high vacuum (UHV) scanning tunneling microscopy (STM) to characterize organically modified graphene. For example, a suite of perylene-based molecules form highly ordered self-assembled monolayers (SAMs) on graphene via gas-phase deposition in UHV [1]. Due to their noncovalent bonding, these SAMs preserve the superlative electronic properties of the underlying graphene while providing uniform and tailorable chemical functionality. In this manner, disparate materials (e.g., high-k gate dielectrics) can be seamlessly integrated with graphene, thus enabling the fabrication of capacitors, transistors, and related electronic/excitonic devices. Alternatively, via aryl diazaonium chemistry, functional polymers can be covalently grafted to graphene [2]. In addition to presenting opportunities for graphene-based chemical and biological sensing, covalent grafting allows local tuning of the electronic properties of the underlying graphene. Beyond UHV STM characterization, this talk will also delineate our efforts to nanopattern self- assembled monolayers on graphene at the sub-10 nm scale [3]. Nanopatterning chemically functionalized graphene presents opportunities for tailoring the electronic and chemical properties of graphene nanoribbons in addition to providing a molecular-scale resolution template for subsequent materials growth on graphene surfaces.

[1] Q. H. Wang and M. C. Hersam, *Nature Chemistry*,**1**, 206 (2009).
[2] Md. Z. Hossain, et al., *Journal of the American Chemical Society*, **132**, 15399 (2010).
[3] Q. H. Wang and M. C. Hersam, *Nano Letters*, **11**, 589 (2011).

Selective Edge Functionalization of Graphene by Room Temperature Mild Plasma Treatment

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Room-temperature controllable edge functionalization and doping of graphene by a NH_3 plasma has been developed [1]. Based on a detailed Raman mapping analysis and an electrical measurement, a direct correlation between carrier doping and selective edge functionalization has been revealed for the first time. The Raman mapping analysis shows that the D-peak near the edge of the graphene sheet is selectively increased after NH_3 mild (m)-plasma treatment. The electrical measurement reveals that the Dirac point position of the graphene nano ribbon (GNR) device clearly shifts toward a negative gate-bias voltage after NH3 m-plasma treatment. This selective edge functionalization and doping by controlled plasma treatment could yield outstanding benefits in realizing graphene-based high- performance nanoelectronic device applications.

[1] T. Kato, L. Jiao, X. Wang, H. Wang, X. Li, L. Zhang, R. Hatakeyama, and H. Dai, *Small* **7**, 574 (2011).

Fabrication of Graphene-based Electronic Devices by Selective Electrochemical Reduction in Air

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While graphene application in digital electronics does require very high performance, there are other promising sectors (packaging, plastic electronics etc.) where, more than high charge mobility, cost reduction will be fundamental. This can be achieved by bulk production and chemical processing of graphene in liquids or air, at room temperature.

Here we describe a simple approach to fabricate graphene-based field-effect-transistors (FETs), starting from aqueous solutions of graphene-oxide (GO), processed entirely under ambient conditions. The process relies on the site-selective reduction of GO sheets deposited in between micro- or nano-electrodes. The same electrodes are first used for voltage-induced electrochemical GO reduction, and then as the source and drain contacts of FETs, allowing for the straightforward production and characterization of ambipolar devices. The nano-scale morphology and electric properties of the devices are then studied by conductive and Kelvin Probe scanning microscopy.

An overview of potential applications of graphene deposited on or embedded into different organic materials will also be given.

Highly Efficient Exfoliation and Sorting of Graphite flakes

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We demonstrate high yield production of graphene in liquid phase [1] via low power sonication of graphite in sodium deoxycholate (SDC) followed by a separation in preparative ultracentrifugation. There are two main approaches to ultracentrifugation: sedimentation-based separation (SBS) and isopycnic separation. The former discriminates particles by their difference in mass. The latter exploits subtle density differences between particles in a density gradient medium [2,3]. A fracture mechanics model is presented to explain the exfoliation process. During sonication, the bubbles implosion imposes an inward radial fluid flow, which induces viscous forces on the graphite flakes [4]. Such forces must be sufficiently high for exfoliation, but low enough to avoid in-plane fracture, in order to produce large graphene flakes. Our results suggest that graphite exfoliation via sonication produces on average flakes with lateral sizes that increase with the number of layers. Thus the exploitation of SBS permits to obtain a separation based on the number of layers other than on their mass [5]. TEM and Raman spectroscopy indicate that ~65% of the flakes produced by SBS are monolayer with average size~600nm^2 [6,7]. Isopycnic separation, besides number of layers sorting, allows us to obtain larger flakes than SBS. The sorting strategy relies on the creation of density differences between graphite flakes with different number of layers. Surfactants provide this density variation [8]. We show that sorting by number of layers is strongly affected by the flakes surface/volume ratio and the coverage and clustering of the surfactant molecules. SDC is the most effective surfactant for exfoliation and sorting of graphite flakes, with ~60% of the flakes in the topmost fraction being monolayers, with average size 1μm^2.

[1] Y. Hernandez et al. *Nature Nano*, **3**, 563, (2008).
[2] M. S. Arnold et al., *Nature Nano*, **1**, 60, (2006).
[3] F. Bonaccorso et al., *Journal of Physical Chemistry C*, **114**, 17267, (2010).
[4] R. W. Fox, A. T. McDonald, P. J. Pritchard, *Introduction to Fluid Mechanic*, Wiley, 6 Edition ISBN 0471202312, (2003)
[5] F. Bonaccorso et al., submitted (2011).
[6] O.M. Marago' et al., *ACS Nano*, **4**, 7515, (2010).
[7] F. Bonaccorso et al., *Nature Photonics*, **4**, 611, (2010).
[8] A. A. Green et al, *Nano Lett*. **9**, 4031, (2009).

Atomic Layer Growth of Graphene Films

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Graphene has been shown to have unique electronic, chemical and physical properties over the past few years and this is opening many opportunities for its use.[1] However, to date most of the experiments have been performed on graphene exfoliated from natural graphite and the graphene films have been rather small, hundreds of microns squared. Transport properties equivalent to those achieved on exfoliated graphene have also been achieved on layers of graphene on SiC; [2] but this graphene is not easily transferred to other substrates. There is now a need to develop high quality, large area single crystal graphene. A few years ago Li et al. discovered the growth of graphene on copper metal foils by chemical vapor deposition (CVD) using methane gas [3] which led for the first time to the growth of meter square graphene [4]. The current CVD process can indeed grow very large graphene films but the films are polycrystalline. [5] The domain size for the baseline process is a few tens of microns in diameter [5] and in principle there is pathway to achieving much larger domain size films. Large single crystals, 0.5 mm size, have recently been reported [6] and perhaps we can learn from these results how to extend them to grow even large graphene films with higher quality. The growth mechanisms of graphene and single crystal growth of graphene will be presented and discussed together with a discussion of what the semiconductor industry would need to make graphene a reality.

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science* **306**, 666-669 (2004).
[2] C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, *The Journal of Physical Chemistry B* **108**, 19912-19916 (2004).
[3] X. Li, W. Cai, J. H. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, and R. S. Ruoff, *Science* **324**, 1312-1314 (2009).
[4] S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y.-J. Kim, K. S. Kim, B. O. Zyilmaz, J.-H. Ahn, B. H. Hong, and S. Iijima, *Nature Nanotechnology* **5**, 574 (2010).
[5] X. Li, C. W. Magnuson, A. Venugopal, J. An, J. W. Suk, B. Han, M. Borysiak, W. Cai, A. Velamakanni, Y. Zhu, L. Fu, E. M. Vogel, E. Voelkl, L. Colombo, and R. S. Ruoff, *Nano Letters* **10**, 4328-34 (2010).
[6] X. Li, C. W. Magnuson, A. Venugopal, R. M. Tromp, J. B. Hannon, E. M. Vogel, L.Colombo, and R. S. Ruoff, *Journal of the American Chemical Society* **133**, 2816-2819 (2011).

Epitaxial CVD Growth of Single-Layer Graphene over Metal Films Crystallized on Sapphire and MgO

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Graphene is emerging as a new building block of future nanoelectronics and microelectro-mechanical systems. Recently, catalytic CVD growth has attracted considerable interest as an effective means to produce large-area graphene films. However, because most of the CVD growth has been done over polycrystalline metal foils/films, as-grown graphene has relatively small grain size and its orientation is not controlled. We studied the growth of graphene films over crystalline metal films deposited on single crystalline substrates and reported the formation of square and triangular-shaped graphene films on such crystalline metal catalyst [1]. Here, we performed atmospheric CVD growth over crystalline Co and Cu films deposited on c-plane sapphire or MgO(111)substrates. Large-area, uniform single-layer graphene was obtained on the Co film in spite that Co metal has high carbon solubility at high CVD temperature [2]. The low-energy electron diffraction (LEED) measurements revealed that the orientation of single-layer grapheme matches with underneath Co(111) (or Cu(111)) lattices indicating epitaxial CVD growth of graphene [2,3]. This enables us to determine the graphene orientation from the sapphire's crystallographic orientation. Furthermore, the as-grown graphene was found to have very large domain sizefrom the low-energy electron microscope (LEEM) analysis. We also demonstrate that amorphous carbon can be converted to uniform single-layer graphene by simply annealing it on crystalline Co or Ni films deposited on sapphire [4]. Our study offers a new route to grow high-quality single-layer graphene even on different metal films and gives new insights into the growth mechanism of graphene.

[1] H. Ago, I. Tanaka, C. M. Orofeo, M. Tsuji, *Small*, **6**, 126 (2010).
[2] H. Ago, Y. Ito, N. Mizuta, K. Yoshida, B. Hu, C. M. Orofeo, M. Tsuji, K. Ikeda, S. Mizuno, *ACS Nano*, **4**, 7407 (2010).
[3] B. Hu, H. Ago, Y. Ito, M. Tsuji, E. Magome, K. Sumitani, N. Mizuta, K. Ikeda, S. Mizuno, submitted.
[4] C. M. Orofeo, H. Ago, B. Hu, M. Tsuji, *Nano Res.*, in press.

Direct Growth of Nanographene on Glass

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Nanograpehene was directly deposited on glass at 750 °C by thermal chemical deposition, without using any additional metallic catalyst. Annealing of nanographene film at 300 °C to 500 °C leads to an increase of the in-plane crystal size from ~ 15 nm up to ~ 23 nm, when the annealing is done in the presence of an adlayer of nickel, subsequently deposited on the graphene after the initial deposition. This study clearly demonstrates that nanographene can be directly deposited on glass and the crystallite size is controllable.

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Graphene Technology: Production, Assembly & Applications

Growth Dynamics of Graphene Nanoislands, Nanoripples and Nanobubbles

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Majority of the solution-phase methods produce irregularly-sized and shaped graphene sheets due to the intrinsic randomness in the defect-mediated exfoliation or cutting process of the precursor graphitic flakes. To produce highly regular graphene nanostructures, a fabrication process that is driven by thermodynamics, as in crystal growth, should be more suitable than defect-mediated fragmentation processes. To this end, we demonstrate a metal-template catalyzed route to fabricate regular-sized graphene quantum dots from fullerene. Using Scanning Tunneling Microscopy, the growth dynamics of carbon nanostructures derived from the decomposition of fullerene on metal surfaces is studied. We discover that fullerene is a unique precursor because of its density-dependent decomposition and polymerization reaction on metal, yielding a very rich surface chemistry. Decomposed fullerene molecules produce carbon clusters that undergo diffusion-aggregation on metal surfaces to form well defined carbon nanostructures. Polymerised fullerene molecules can act as special template for the growth of bilayer graphene or unique intercalated graphene layers. Molecular dynamics simulation was carried out to obtain an insight into the dynamics of graphene growth from carbon clusters and decomposed fragments. From the templated synthesis of graphene nanoislands in UHV environment (recorded by dynamic STM), we will move on to discuss the evolution of special strain relief features on the surface of graphene during its growth on metal surfaces, ranging from nano-bubbles to periodic ripples. In addition, we will also show how the graphene moiré structure can be used as a special template for the assembly of nanostructures.

[1]Jiong Lu and Kian Ping Loh et. al. *Nature Nanotechnology*, **6**, 247–252, (2011)

Transport in Graphene Constrictions and Quantum Dots

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Nanostructures made from graphene on thermal SiO_2 have become an experimental reality in recent years. In quantum transport experiments for example, the Coulomb blockade effect and coherent Aharonov–Bohm oscillations have been observed in quantum dots and quantum rings. However, the observation of the predicted quantized conductance in simple constrictions turns out to be hard. In addition, a large number of transport experiments on nanostructures have shown evidence for strong localization effects in narrow constrictions [1- 5], in contrast to the robust superior transport properties of large-area graphene. Transport studies of individual graphene constrictions confirm the presence of strongly localized states and investigate the geometry-dependence of the conductance [6-10]. Two recent publications report data on the temperature dependent conductance of graphene nanoribbons and interpret the data in terms of Efros-Shklovskii variable-range hopping [11,12]. We have studied the temperature-dependent conductance of a number of ribbons with different geometries. Our data can be characterized by a temperature-independent low-temperature conductance, which turns into an Arrhenius-type of activated transport at elevated temperatures. We are able to extract the activation energies as a function of back-gate voltage and find a striking similarity between this quantity and finite-bias spectroscopy data taken at the lowest temperature. We discuss the implications of this finding for the microscopic picture of transport in the constrictions.

[1] C. Stampfer, E. Schurtenberger, F. Molitor, J. Güttinger, T. Ihn, and K. Ensslin, *Nano Lett.* **8**, 2378 (2008).
[2] X. Liu, J. B. Oostinga, A. F. Morpurgo, and L. M. K. Vandersypen, *Phys. Rev. B* **80**, 121407 (2009).
[3] F. Molitor, S. Dröscher, J. Güttinger, A. Jacobsen, C. Stampfer, T. Ihn, and K. Ensslin, *Appl. Phys. Lett*. **94**, 222107 (2009).
[4] S. Schnez, J. Güttinger, M. Huefner, C. Stampfer, K. Ensslin, and T. Ihn, *Phys. Rev. B* **82**, 165445 (2010).
[5] J. Güttinger, J. Seif, C. Stampfer, A. Capelli, K. Ensslin, and T. Ihn, *Phys. Rev. B* **83**, 165445 (2011).
[6] M. Han, B. Özyilmaz, Y. Zhang, and P. Kim, *Phys. Rev. Lett*. **98**, (2007)
[7] F. Molitor, A. Jacobsen, C. Stampfer, J. Güttinger, T. Ihn, and K. Ensslin, *Phys. Rev. B* **79**, (2009).
[8] C. Stampfer, J. Güttinger, S. Hellmüller, F. Molitor, K. Ensslin, and T. Ihn, *Phys. Rev. Lett.* **102**, (2009).
[9] K. Todd, H.-T. Chou, S. Amasha, and D. Goldhaber-Gordon, *Nano Letters* **9**, 416-421 (2009).
[10] P. Gallagher, K. Todd, and D. Goldhaber-Gordon, *Phys. Rev. B* **81**, 115409 (2010).
[11] J. B. Oostinga, B. Sacépé, M. F. Craciun, and A. F. Morpurgo, *Phys. Rev. B* **81**, (2010).
[12] M. Y. Han, J. C. Brant, and P. Kim, *Phys. Rev. Lett.* **104**, 056801 (2010).

Graphene Charge Detectors Meet Nanotube Quantum Dots

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Carbon nanomaterials, such as carbon nanotubes (CNTs) and graphene, both exhibiting unique electronic and mechanical properties are very promising materials for future nanoelectronic applications. The absence of the hyperfine field in ^{12}C enriched carbon materials makes CNTs and graphene particularly interesting for hosting quantum dots which potentially allow the realization of spin-qubits with long coherence times. Here we present the fabrication and electrical characterization of an all carbon device based on a nanotube quantum dot with a nearby few-layer graphene nanoribbon charge detector. We show that the few-layer graphene nanoribbon can be used to detect single charging events in the nearby CNT quantum dot (QD). The CNTs are grown on a 300 nm SiO_2 on highly doped Si substrate by a ferritin-based catalytic chemical vapor deposition (CVD) process. Subsequently, graphene has been deposited by mechanical exfoliation on the SiO_2 with the pre-grown nanotubes. Electron beam (e-beam) lithography and dry etching techniques are used to pattern the graphene nanoribbons. An additional, e-beam step and lift-off techniques are used to place metal contacts on the individual graphene-nanotube devices. We present low-temperature transport measurements on a CNT quantum dot with an integrated graphene charge detector. The device consists of a 100 nm narrow few-layer graphene nanoribbon which is located around 150 nm next to a contacted single-walled carbon nanotube (SWNT). From Coulomb diamond measurements in the SWNT QD charging energies of about 8 meV are extracted. We show that resonances in the nanoribbon can be used to detect single charging events in the SWNT QD. The charging induced potential change on the quantum dot causes a steplike change of the current in the charge detector. The relative change of the current measures up to 20% for detecting individual charging events and thus demonstrates the quality of the detector.

Spin-orbit coupling and weak localisation in graphene

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We model the influence of spin-orbit coupling on electronic transport in graphene, particularly on the weak localisation correction to conductivity. As is often the case in semiconductors, the presence of spin-orbit coupling in graphene will tend to produce an anti-localization effect. As temperature is lowered, this would be manifest as a change in the sign of the magnetoconductivity $\delta\sigma(B) < 0$ as the dephasing length increases beyond the relevant spin-orbit length scale. An alternative scenario is that the spin-orbit coupling conserves the out-of-plane (z) component of electronic spin. This type of spin-orbit coupling leads to a random precession of the electron spin around the z axis, causing the relaxation of the in-plane polarization of electrons. It also distinguishes between up and down spin electrons, generating, for each, an effect equivalent to time-reversal symmetry breaking for Dirac electrons, and, therefore, it suppresses weak localization. We discuss the possible origin of such spin-orbit coupling in graphene, including intrinsic effects and the role of disorder, and we explain how measurements of magnetoconductivity in mesoscopic devices may shed light on sources of spin decoherence in graphene.

Energy Dissipation and Transport in Graphene Devices

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Energy dissipation, conversion and flow are of great importance for the design of energy-efficient electronics and energy-conversion systems. This is also a rich domain for both fundamental discoveries as well as technological advances.
This invited talk will describe several recent lessons learned from examining dissipation in graphene devices, as model materials for 2-dimensional electronics. Graphene could benefit from lower power dissipation compared to silicon electronics due to its higher mobility and saturation velocity [1]. Infrared (IR) imaging carried out on functioning graphene transistors has recently revealed the effect of electrostatics on thermal dissipation and ambipolar transport [2]. Moreover, thermoelectric effects recently observed at graphene device contacts could be used to partially remove the heat generated during operation [3]. The results suggest much room for the optimization of graphene-based electronics through the design of substrates, geometry and interfaces.

[1] V.E. Dorgan, M.-H. Bae, E. Pop, *Appl. Phys. Lett*.**97**, 082112 (2010)
[2] M.-H. Bae, Z.-Y. Ong, D. Estrada, E. Pop, *Nano Letters* **10**, 4787, (2010)
[3] K. Grosse, M.-H. Bae, F. Lian, E. Pop, W.P. King, *Nature Nanotechnology*, DOI: 10.1038/NNANO.2011.39 (2011)

High-Frequency Graphene Devices and Circuits

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Graphene has generated enormous research interest because of its unique physical and electronic properties. In particular, a large part of the research interests and activities arise from the high intrinsic carrier mobility and saturation velocity in graphene that may lead to higher-performance and higher-frequency electronic devices/circuits than can be achieved by conventional semiconductor materials. Here we present recent progress on high-frequency graphene devices and integrated circuits.

For technological applications it is important to work with large (wafer) scale, well-characterized graphene. Two types of graphene synthesized by different approaches are studied and explored for high-frequency devices and circuits. In one approach, the graphene wafer was epitaxially grown on the Si face of a SiC substrate by thermal decomposition, yielding a film of 1-2 layers of graphene over the entire wafer. In another approach, large-area, single-layer graphene was grown on a Cu film and transferred to an insulating substrate. Wafer-scale synthesis and device fabrication were demonstrated on both types of graphene. Top-gated graphene field-effect transistors were fabricated with a high-k and metal gate stack. By optimizing the device fabrication and structure, a cut-off frequency of above 100 GHz is achieved for both epitaxial graphene and CVD graphene [1,2]. In addition, wafer-scale graphene integrated circuits where all circuit elements are monolithically fabricated on a single SiC substrate is demonstrated, where the graphene circuit operates as a broadband mixer at 10 GHz.

[1] Y.-M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, and P. Avouris, *Science* **327**, 662 (2010).
[2] Y. Wu, Y.-M. Lin, A. Bol, K. A. Jenkins, F. Xia, D. Farmer, Y. Zhu and P. Avouris, *Nature* **472**, 47 (2011)

High Frequency Coplanar Graphene Waveguides on Low-loss Dielectric Substrates

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Graphene is of great interest for high-frequency circuit applications, including high-f_T transistors [1,2]. High-frequency passive element applications based on gyrotropy have also been recently identified [3]. We present here our work on integration of graphene into low-loss coplanar waveguides (CPWs) using large area graphene fabrication methods. Chemical vapor deposition with a methane/hydrogen gas mixture at 900 °C was used to grow graphene on copper foils [4]. Raman spectroscopy was used to verify high-quality monolayer growth. A standard photoresist was used as the polymer handle for CVD graphene transfer to quartz substrates, where the functional diazo groups of the resist also served to heavily hole-dope the graphene [5]. A low- frequency sheet resistance of 1.1-1.3 kΩ /square was measured in the transferred graphene. Standard lithography and metal deposition techniques were used to form CPWs, after which graphene was patterned into signal-signal and signal-ground CPW test structures by oxygen plasma etching. The microwave scattering parameters, and thus impedance, of CVD graphene have been measured from 40 MHz to 40 GHz, with measurements up to 110 GHz underway. Great care was exercised in obtaining good calibrations and minimizing contact errors. Measurements are compared with full-wave electromagnetic field simulations. We find that the graphene aspect ratio can be easily used to control the transmitted and reflected microwave power. Our work sets the basis for high-frequency CPW circuits incorporating passive and active graphene circuit elements.

1. F. Schwiertz, “Graphene Transistors”, *Nature Nanotech.*, **5**, 487-496 (2010).
2. Y. Wu, Y. Lin, A .Bol, K. Jenkins, F. Xia, D. Farmer, Y. Zhu, P. Avouris *Nature*, 472, 74-78, (2011).
3. D. Sounas, C. Caloz. *App. Phys. Lett.*, **98**, 021911:1-3, (2011).
4. A. Guermoune, T. Chari, F. Popescu, S. Sabri, J. Guillemette, H. Skulason, T. Szkopek, M. Siaj. under review.
5. D. Farmer, R. Golizadeh-Mojarad, V. Perebeinos, Y. Lin, G. Tulevski, J. Tsang, P. Avouris. *Nano Letters*, **9**, 1, 388-392 (2009).

Graphene RF Devices: New Opportunities for Ubiquitous Electronics

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Since the first isolation of graphene in 2004, graphene research has generated great excitement among device engineers due to the outstanding material properties of this single layer of sp^2-bonded carbon atoms. Mobilities in excess of 100,000 cm^2/Vs, perfect carrier confinement within one monolayer, and ballistic transport over unprecedented distances make graphene an almost ideal candidate for the next generation of electronic circuits and systems. In addition to being quantitatively better than conventional semiconductors, graphene is qualitatively different. Its one monolayer thickness confers to this material unique structural and optical properties. These properties allow its use in flexible electronics, and ease its integration with arbitrary substrates and materials, including kapton, plastic and fabrics. In this talk, we will discuss some of the opportunities that graphene technology offers for a new class of electronic systems, flexible, transparent and, potentially, cheap enough to become ubiquitous.

In this work, we will focus on graphene films grown by chemical vapor deposition (CVD) on nickel or copper layers. This technology allows the growth of very large-area samples, the size only being limited by the size of the growth reactor. After the synthesis of the graphene layer, this is transferred to a carrier substrate, where the device fabrication takes place. Field effect transistors fabricated on this material with a gate length of 2 µm show a current-gain cut-off frequency in excess of 12 GHz. These results represent some of the highest performance measured in CVD graphene until now. Once that transistors with high enough extrinsic performance are obtained, it is possible to use them in a wide variety of circuit-level applications. Graphene frequency multipliers, for example, allow us to generate high frequency harmonics of an input signal with unprecedented efficiency. As a second example, the strong non-linear behavior of graphene devices induced by their ambipolar transport enables the fabrication of very-low-noise mixers that have been recently used in the first graphene radio demodulator. The performance of these and other circuits is quickly improving and very soon these circuits will start impacting system level performance.

In addition to being an excellent material for new RF electronic devices, the high transconductance of graphene transistors makes it ideal for chemical sensing applications. In this paper, we will review how the graphene transistors used for communication applications can be modified to get chemical sensors with record sensitivity and noise level. These sensors can easily being integrated in a variety of substrates to enable cost effective sensing of numerous analytes of interest to environmental health, biology and industry.

Graphene Bionanoscience & Engineering: Toward Single-molecule DNA Sequencing

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Graphene is an outstanding new carbon material, which presents surprising electrical, optical, and mechanical properties, due to its two-dimensional structure. Potential biological applications of graphene are manifold (genomic DNA sequencing, epigenetics, pharmaceuticals, bio-sensors, to name a few) and can benefit from chemistry and chemical engineering. Particularly promising for the next generation of sequencing are devices where a single DNA molecule could be read – base per base – while sliding through a recorder that has a smaller size than each individual base. We discovered that graphene (less than 0.5 nm thick; i.e., thinner than the distance between two bases in single-stranded DNA) is an ideal material to that respect.

We first developed a simple and fast water-based method for transferring graphene onto arbitrary surfaces, with micrometer alignment precision. Using this method, we fabricated ranges of graphene membranes in which nanometer sized pores were sculpted. Under an electron beam, we discovered that graphene undergoes a temperature sensitive self-repair mechanism that allows damage-free atomic scale sculpting of perfectly crystalline graphene nanostructures, such as nanopores with crystalline edges. When mounted between two flow chambers containing buffered DNA, these extremely thin nanopores were used to detect DNA molecules. As individual DNA molecules translocate through the pore, characteristic temporary conductance changes were observed in the ionic current through the nanopore, setting the stage for future single-molecule genomic screening devices. In the future, we plan to use the conductive properties of graphene to measure the tunneling current through individual bases of DNA as they translocate through a graphene nano-gap.

Graphene for Next-Generation Electronics: Limits and Perspectives

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Graphene has appealing physical properties for electronic applications like large carrier mobility, which has triggered an important collective effort aimed at a good understanding of its electrical behaviour. Still, from an engineering point of view, the main question to be answered is: “Will graphene be capable in the mid term to meet Semiconductor Industry requirements to keep the pace of Moore’s law?”.

The investigation of graphene-based devices is an open issue due to the many fabrications problems which remain unsolved. In this respect, numerical simulations can represent a powerful tool in order to assess the potential performance of graphene devices.

In this work, we present a simulation study to investigate the limits and the perspectives of graphene devices, considering a wide span of devices, ranging from graphene nanoribbons (GNR) to monolayer and bilayer graphene Field Effect Transistors.

The main issue regarding graphene is the lack of an energy gap, which prevents its use for digital electronic applications. Such issue can be overcome by defining lateral confinement through electron beam lithography or chemical procedures, which in turn introduce edge roughness drastically reducing electron mobility [1]. Through a full-band investigation of electron-phonon interaction, we will show that, even in the case of perfect edges, the intrinsic mobility of GNRs is strongly limited by remote phonon scattering, which leads to scattering lengths of the order of tens of nanometers for GNR widths of 1-2 nm, and mobilities of the order of few hundreds cm^2/Vs, three orders of magnitude smaller than mobility experimentally obtained in graphene [2]. Graphene hydrogenation can represent a viable way in order to induce a gap in graphene: the larger the degree of hydrogenation, the larger the energy band-gap. However, its electrical properties have not yet been thoroughly investigated. To this purpose, we have performed multi-scale simulations based on ab-initio calculations in order to compute deformation potential and mobility in graphene with different degrees of hydrogenation: even in the best case, we will show that expected mobility is smaller than that measured in bulk silicon.

An energy gap can also be electrically induced by means of an electric field in bilayer graphene: simulations results show that such material has potential for ultra-low voltage applications, when exploited in tunnel FET devices (the so-called green transistors). Analog electronics does not need an energy gap. Graphene, both monolayer and bilayer, shows huge potential when exploited in Esaki-like diodes, where a negative differential resistance can be observed. We will also show that bilayer graphene can be exploited in a current amplifier, since, even for short-channel devices, current saturation may occur to some extent, leading to quite large current gain.

[1] A. Betti et al. IEDM 2009, 5-7 December, Baltimore, USA.
[2] K.I. Bollotin et al., *PRL*, **101**, 096802, 2008.

Graphene Logic Gates and Memories with Improved Current On/Off Ratio

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Over the past few years there has been a surge of interest in graphene, a recently isolated single sheet of graphite. From the application point of view this interest has mainly been driven by the high carrier mobility of graphene which enables fabrication of field-effect transistors(FETs) with much smaller channel resistance compared to their Si counterparts. In this manner, the ultimate limits of Si technology, which are expected at the sub-10 nm scale, may be overcome, paving the way for digital nanoelectronics. Here we demonstrate the operation of graphene logic gates and memories with a current on/off ratio much higher than this in conventional back-gated graphene devices. The same resistance of a graphene FET can be obtained for two different gate voltages, one on either side of the Dirac point. This was exploited to fabricate four basic logic gates (XOR, NAND, OR, and NOT) with a single graphene FET. However, these logic gates require off chip resistors to operate, i.e., they are not integrated on the same graphene flake. An integrated graphene digital logic gate was obtained by integrating one p- and one n-type graphene FET on the same sheet of monolayer graphene. Both FETs initially exhibited p-type behaviour at low gate voltages, since air contamination shifted their Dirac points from zero to a positive gate voltage. Contaminants in one FET were removed by electrical annealing, which shifted its Dirac point back and therefore restored n-type behaviour. Boolean inversion is obtained by operating the FETs between their Dirac points.

In order to improve the on/off ratio of graphene FETs an alternative gate stack was fabricated. Incorporation of such graphene FETs in logic gates resulted in an increase in small-signal voltage gain of around two orders of magnitude in comparison to conventional back-gated devices. Use of these FETs in a complementary inverter eliminated need for current annealing and ensured a gain larger than unity under ambient conditions. Such a high gain is a main prerequisite for direct cascading of logic gates. An alternative promising strategy to increase the on/off ratio relies upon patterning of graphene nanoribbons (GNRs), wherein quantum confinement and edge effects open a bandgap inversely proportional to the ribbon width. Here we demonstrate a high performance GNR memory cell based on a nondestructive storage mechanism, i.e., gate voltage pulses of opposite polarity are used to switch between the distinct on and off states of the device. The devices were fabricated by patterning graphene into nanoribbons using V_2O_5 nanofibres as etching masks. A pronounced memory effect is observed under ambient conditions, which is attributed to charge traps in the vicinity of the GNRs. Reliable switching between two conductivity states is demonstrated for clock frequencies of up to 1 kHz and pulse durations as short as 500 ns (tested limits) for $>10^7$ cycles. The durable and stable memory cell can be rendered nonvolatile upon exclusion of oxygen and humidity. GNRs thus emerge as promising components of highly integrated memory arrays.

Selective-area-grown Graphene Transistor by Thermal Chemical Vapor Deposition Method

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Graphene is a single atomic layer of carbon atoms that form a honeycomb structure, and thus, it is the ultimate thin layer. Thanks to its high carrier mobility, graphene is one of the materials with most promise to open a new era of electrical and optical integrated circuits. A method needs to be developed to grow graphene directly on sub-nm-order flat insulating layers in order to fabricate electrical and optical devices that utilize graphene. In addition, using a Si wafer as a substrate is strongly desirable. The current big Si-electronics industry has accumulated enormous amounts of knowledge and know-how concerning Si. Thus, starting graphene-electronics on a Si substrate seems practical.

We recently reported on a growth method for graphene on a sapphire substrate [1] and on an Al_2O_3 layer sputter-deposited on a SiO_2/Si substrate [2]. This paper presents a new selective-area growth method for graphene on a fine-patterned Al_2O_3 layer fabricated on a SiO_2/Si substrate. We fabricated graphene transistors successfully utilizing this selective-area growth method and obtained their excellent electrical characteristics.

Our fabrication process for graphene transistors is follows: A sputter-deposited Al_2O_3 layer (15 nm thick) on SiO_2 (100 nm thick)/Si substrate is patterned to channel, source, and drain regions. The source and drain regions are connected by the channel region. Graphene layers are grown on the patterned Al_2O_3 regions selectively with no growth on SiO_2 surface by thermal chemical vapor deposition method. The growth temperature is 800 ˚C and using propylene flows (4 ml/min) as the source gas and argon (400 ml/min) as the carrier gas. The graphene layers have piled structure of small platelets with a domain size of 30 nm. The averaged number of layers is 2.6 for 2-minute growth. The source and drain regions are covered with Au (100 nm thick)/Ti (10 nm thick) electrodes by using electron beam evaporation method and lift-off process.

The fabricated graphene transistors gives electrical conductance of more than 10,000 S/m which corresponds to effective electron mobility of a few tens cm^2/Vs. The drain current is modulated by gate voltage and $(I_{max}-I_{min})/I_{min}$ is more than 70% when the gate voltage changes from -40 V to + 40 V. The drain current is minimum when the gate voltage is around +30 V.

[1] M. Okai, et al., *Tenth International Conference on the Science and Application of Nanotubes* 2009 (Beijing, China), paper D13, 2009.
[2] M. Okai, et al., *Carbon* 2010 (Clemson, USA), paper Th-2A-5, 2010.

Straining Graphene By CVD On Cu And Magnetotransport On Large Scale Graphene.

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Strain can be used as an alternate way to tune the electronic properties of graphene. Here we demonstrate that it is possible to tune the uniform strain of graphene simply by changing the chemical vapour deposition growth temperature of graphene on copper. Due to the cooling of the graphene on copper system, we can induce a uniform biaxial compressive strain on graphene. The strain is monitored by Raman spectroscopy, where a shift in the 2D peak is observed and compared to our *ab initio* calculations of the graphene on copper system as a function of strain. The most striking features are a change in Fermi velocity and more notably a shift in the Fermi energy with respect to the Dirac point as a function of strain [1]. With subsequent transfer of graphene onto SiO_2/Si via PMMA and thermal release tape magneto-transport measurements were performed. The resulting centimeter-sized graphene samples were measured at temperatures down to 30 mK in a magnetic field, where we observe a very sharp peak in resistance at zero field, which is well fitted by weak localization theory. The samples also exhibit conductance fluctuations symmetric in field, which are attributed to large scale inhomogeneities consistent with the grain boundaries of copper during the CVD growth [2].

[1] V. Yu, E. Whiteway, J. Masseen, and M. Hilke, arXiv: 1101.1884
[2] E. Whiteway, V. Yu, J. Lefebvre, R. Gagnon, and M. Hilke, arXiv: 1011.5712

Graphene Film for Flexible and Stretchable Electronics

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Flexible and stretchable electronics have attracted a great deal of attention in the last decade because of their potential applications in various areas, such as paperlike roll-up displays and conformable X-ray imagers. However, it is very difficult to accomplish such devices with conventional electronic materials or even with more recent systems. Graphene, the thinnest elastic material, has superb electronic properties that make it a promising host for device applications. In particular, graphene has an extremely good mechanical property, offering a great opportunity to flexible and stretchable electronics that should maintain a stable operation under a high strain. The recent advances in large-scale synthesis of graphene films by chemical vapor deposition are expected to enable various macroscopic applications such as semiconducting and transparent conducting films useful for flexible and stretchable electronics.[1] In this talk, we present a large area growth of high-quality, large area graphene films and transfer printing method onto arbitrary substrates which can provide improved scalability and processibility of graphene films ready for use in flexible and stretchable electronics.[2,3]In addition, we report some of examples for device applications including flexible OLED lighting and FETs.

[1] S. Bae et al, *Nat. Nanotech.*, **5**, 574 (2010).
[2] Lee Y. et al, *Nano Lett*. **10**, 490 (2010).
[3]Kim B. et al, *Nano Lett*. **10**, 3464 (2010).

Graphene xylophone

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We studied a mechanical resonance properties of graphene sheets and their applications. Rectangular shape of graphene sheet was prepared using O_2 plasma and suspended structure was made on the pre-patterned trench by the micro contact transfer printing method. Xylophone like structure was prepared for studying length and thickness dependence of mechanical properties of graphene resonator. Single layer graphene sheet shows nonlinear and bistable behaviors the actuation voltage was increased. The resonance frequency of graphene sheet can be tuned by applied DC bias voltage. Based on our results, we will suggest the potential application of the graphene resonator to the broadband tunable RF components.

Electrically Switchable, Flexible Smart Windows Using Graphene-based Transparent Conductors

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Scarcity, brittleness, processing limitations and fabrication costs of Indium Tin Oxide (ITO) are crucial limiting factors towards the development of flexible displays and electronics requiring flexible, transparent conducting electrodes (TCEs). Carbon nanotubes (CNTs) and graphene offer ideal TCE alternatives[1,2,3,4]. Both CNT and graphene liquid dispersions can be used in roll to roll (R2R) processing. The performance of CNT networks is limited by inter-tube junction resistance. This can be reduced by interspersed graphene flakes. A solution processable hybrid CNT-graphene conducting film is therefore an attractive proposition for R2R manufacturability of electronic devices requiring flexible TCEs.

Electrically switchable smart windows (ESSWs) employ liquid crystal (LC) droplets embedded in a polymer, sandwiched between two TC electrodes. An electric field controls the overall alignment direction of LC molecules, allowing light modulation through the device[5]. The TCE requirements for ESSWs is high transmittance (>80%) and low sheet resistance, typically in the range of ~1kΩ/□ or smaller [6].Here, we demonstrate an up- scalable CNT-graphene hybrids TCE for a smart window. We employ wire-wound rod coating for the liquid dispersions of CNTs and graphene on a polyethylene terephthalate (PET) substrate. The CNT-graphene hybrid coating has 1kΩ/□ sheet resistance, 94-97% transparency in the visible spectrum with <2% standard deviation in optical uniformity across ~200cm^2. The TCEs exhibit ~15% change in resistance when bent to a radius of 3.5mm in 10 cycles, far surpassing the ~25000% increase in a 60 Ω/□ ITO sample. A 120cm^2 flexible smart window is then fabricated. The device exhibits excellent electric field induced light transmittance (~60%) even under flexion. When OFF, the device transmits <0.25%, giving a >230 contrast ratio.

[1] F. Bonaccorso, et al., *Nat Photon* **4**, 611 (2010).
[2] S. Bae, et al., *Nat Nano* **5**, 574 (2010).
[3] G. Gruner, *J. Mater. Chem.* **16**, 3533 (2006).
[4] S. De, et al., *Small* **6**, 458 (2010).
[5] J.L. Fergason US Patent 4435047, (1984).
[6] C.M. Lampert, *Sol. Energy Mater. Sol. Cells* **52**, 207 (1998)

Graphene NEMS: Direct Readout and Magnetometry

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I will describe our recently developed technique [1] of direct electrical readout of graphene mechanical resonators, as a faster alternative to the commonly used mixing technique. More recently, we have achieved purely capacitive readout (i.e. readout with zero applied bias, and in the absence of transconductance) which is useful at low temperatures and in the quantum Hall (QH) regime. Using these advances, we show that high quality graphene resonators can be used as torque magnetometers in an applied magnetic field. We obtain for the first time de-Haas van-Alphen oscillations of magnetization in graphene, which are qualitatively different in single- and bi- layers, due to their intrinsically different low energy electronic structure. At incompressible QH states, the interplay between mechanical motion and charge equilibration leads to interesting consequences for the frequency and amplitude of the resonator.

[1] *Appl. Phys. Lett*. **97**, 243111 (2010)

Characterizing Devices and Twisted Layers of Graphene by Resonance Raman Scattering

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Raman spectroscopy is a very useful tool to study graphene, since it furnishes information about the atomic structure, presence of disorder, defects, charges and strain. However, important information about electrons can be also obtained in a resonance Raman investigation, where the energy of the laser excitation can be tuned. We will present experimental results on graphene devices, where an applied electric field and changes in the Fermi level can be controlled by an external gate voltage, showing that Raman spectroscopy is useful to quantify the interaction of graphene with its surrounding environment. We will also show that Raman spectroscopy can be useful to characterize twisted graphene layers in samples grown by CVD on copper foils. Finally, we will present resonance Raman results of the electronic dispersion in uniaxial strained bilayer graphene.

Spectroscopic Characterization of Atomically Precise Graphene Nanoribbons

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Commonly reported top-down nano-fabrication methods have so far proved unsuccessful to produce atomically precise graphene nanoribbon s[1]. Our group has recently developed a method to synthesize chemically defined graphene nanoribbons on metallic substrates [2] and in solution, from different polymer precursors [3]. Taking advantage on developed exfoliation methods [4, 5] stable dispersions of as-synthesized graphene nanoribbons in organic solvents for spectroscopic characterization can be readily obtained. Here we report for the first time the spectroscopic characterization of two types of chemically precise graphene nanoribbons dispersions. The dispersed nanoribbons characterized by absorption spectroscopy display van Hove singularities that can be correlated to transitions between energy levels in the density of states. Preliminary fluorescence measurements feature emission peaks that suggest band gap photoluminescence. In addition, the chemically synthesized graphene nanoribbons display peaks in the Raman spectra that corroborate their dimensionality and crystal quality.

[1] Wang X, Dai H. *Nat Chem.***2** (8):661-5 (2010).
[2] Cai J, Ruffieux P, Jaafar R, Bieri M, Braun T, Blankenburg S, et al. *Nature*. **466**(7305):470-3 (2010).
[3] Dössel L, Gherghel L, Feng X, Müllen K. *Angewandte Chemie International Edition.* **50**(11):2540-3 (2011).
[4] Hernandez Y, Nicolosi V, Lotya M, Blighe FM, Sun Z, De S, et al. *Nature Nanotech*. **3**(9):563-8 (2008).
[5] Bergin SD, Nicolosi V, Streich PV, Giordani S, Sun Z, Windle AH, et al. *Adv Mater*. **20**(10):1876-81 (2008).

Wideband Tunable, High-power Ultrafast Lasers Mode-locked By Graphene

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Ultrafast passively mode-locked lasers with spectral tuning capability and high output power have widespread applications in biomedical research, spectroscopy and telecommunications [1,2]. Currently, the dominant technology is based on semiconductor saturable absorber mirrors (SESAMs) [2,3]. However, these typically have a narrow tuning range, and require complex fabrication and packaging [2,3]. A simple, cost-effective alternative is to use single wall carbon nanotubes (SWNTs) [4-9] and graphene [9-14]. Wide- band operation is possible using SWNTs with a wide diameter distribution [5,9]. However, SWNTs not in resonance are not used and may contribute to unwanted insertion losses [9]. The linear dispersion of the Dirac electrons in graphene offers an ideal solution for wideband ultrafast pulse generation [9-13,15].

Here, we report graphene saturable absorbers (GSA) for wideband tunable and high power ultrafast laser sources. Tunable ultrafast pulses are generated with an Erbium-doped fiber laser mode-locked by GSA [11]. The output wavelength is tunable from 1525nm to 1559nm.Even wider range tunability is feasible with broader filters [11]. The full width at half maximum (FWHM) spectral bandwidth is ~3 nm. The output pulse duration is ~1 ps. High power ultrafast pulses are generated using a solid-state laser. A Nd:YVO_4 crystal is employed as gain medium. The peak output wavelength is ~1064 nm. The FWHM of the output spectrum is ~0.17nm. The average output power of the laser increases almost linearly with the pump power. The maximum average output power is ~1W at 2.6W pump power. The corresponding pulse energy is ~14nJ.

[1]Martin E. Fermann et.al., Ultrafast Lasers Technology and Applications, (2003) .
[2]U. Keller, Ultrafast solid-state lasers. (Elsevier, Amsterdam, 2004).
[3]U. Keller,*Nature* **424**, 831 (2003).
[4] S. Y. Set et al., in *Optical Fiber Communication Conference* (OFC), 2003.
[5] F. Wang et al.*Nat. Nanotechnol*. **3**, 738 (2008).
[6] Z. Sun et.al., *Appl. Phys. Lett*. **95**, 253102 (2009)
[7] V. Scardaci et al.,*Adv. Mater*. **20**, 4040 (2008).
[8] E. J. R. Kelleher et al., *Appl. Phys. Lett.* **95**, 111108 (2009).
[9] T. Hasan et.al., *Adv. Mater*. **21**, 3874 (2009).
[10] Z. Sun et.al., *ACS Nano* **4**, 803(2010).
[11] Z. Sun et.al., *Nano Res*. **3**, 653(2010).
[12] F. Bonaccorso et.al., *Nat. Photonics* **4**, 611(2010).
[13] D. Popa et.al.,*Appl. Phys. Lett*. **97**, 203106 (2010).
[14] D. Popa et al., *Appl. Phys. Lett*. **98**, 073106 (2011).
[15] A. K. Geim et al.,*Nat. Mater*. **6**,183(2007).

Graphene Bubble As Adaptive Focus Lens

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Conventional zoom and focus optical systems require the precise mechanical movement of their components. Thus, these systems are complex, expensive, bulky and high power- consuming. Graphene is a two-dimensional material with unique properties. Most of the research has been concentrated on its electronic properties [1]. However, this material shows further remarkable properties: graphene is impermeable to every gas, it is very elastic, robust and optically transparent [2].

Here we investigate graphene bubbles as adaptive focus lenses. The bubbles are typically formed after graphene deposition and they have been characterized by Atomic Force Microscopy and Raman Spectroscopy. The bubbles have been also used as a prototype to study the Raman spectrum of graphene under biaxial strain: the G peak does not show any splitting, no large variation in the FWHM of the 2D peak is observed, or dependence in the Raman intensity on the light polarization [3], in contrast to uniaxial strain [4].

We show that it is possible to control the curvature of the bubble by applying a gate voltage. This makes graphene bubbles perfect candidates as lenses in mobile phone cameras, space-based camera systems and cheap devices.

[1] A. K. Geim, K. S. Novoselov,*Nature Mat*. **6**, 183 (2007)
[2] A. K. Geim, *Science* **324**, 1530 (2009)
[3] J. Zabel, R. R. Nair, T. Georgiou, P. Klar, K. S. Novoselov, C. Casiraghi, submitted
[4] T. M. G. Mohiuddin, A. Lombardo, R. R. Nair, A. Bonetti, G. Savini, R. Jalil, N. Bonini, D. M. Basko, C. Galiotis, N. Marzari, K. S. Novoselov, A. K. Geim and A. C. Ferrari, *Phys. Rev. B* **79**, 205433 (2009)

Electron Emission from Free-Standing Graphene Edge

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We demonstrated a practical process to produce free-standing graphene attached on a tungsten tip. The single and few-layer graphene were prepared from a stable suspension graphene solution prepared by rapid quenching of highly oriented pyrolytic graphite (HOPG) in an aqueous solution of NH_4HCO_3 [1]. The exfoliation phenomenon was attributed to the formation of cracks on the HOPG surface during the rapid quenching followed by infiltration of NH_4HCO_3 into the material. Subsequent decomposition of NH_4HCO_3 leads to the formation of steam and carbon dioxide which help the exfoliation process. The suspension graphene in an aqueous solution of NH_4HCO_3 was then transferring to a TEM copper grids. Those graphene on the edge of copper grids will be easyliy found under optical microscope. Then we use a cleaned tungsten microtip to pick up the graphene and assembly into the electron field emission source. The electron-field-emission characteristics of the graphene was then measured in a vacuum chamber with a vacuum of 10^{-7} Torr shows good F-N performance [2]. The anode was a phosphors screen which can identify the image of the electron beam emitting from the edge of graphene. We show that repeatable stable field emission current can be obtained after a careful conditioning process. The turn-on field is relate to the layers of graphene what single layer present the lowest turn-on field of 3.02 V/μm. And the electron beam patterns can be correlated to the layers of the graphene which identified by the Raman spectrum.

[1]. Y. B. Tang, C. S. Lee, Z. H. Chen, G. D. Yuan, Z. H. Kang, L. B. Luo, H. S. Song, Y. Liu, Z. B. He, W. J. Zhang, I. Bello, S. T. Lee; *Nano Lett.***9**, 1374–1377 (2009).
[2]. Z. S. Wu, S. F. Pei, W. C. Ren, D. M. Tang, L. B. Gao, B. L. Liu, F. Li, C. Liu, H. M. Cheng; *Adv. Mater.* **21**, 1756–1760 (2009).

Microwave Impedance Measurements of Graphene and Graphene Oxide

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Non-invasive measurement methods for assessing the quality of graphene films are important for future applications of this remarkable material. We are developing a microwave impedance measurement method for this purpose. Large scale graphene layers have been deposited at Imperial College, by a number of routes, including graphene oxide liquid phase preparation as well as CVD deposition on a range of substrates. Transport properties of these samples are being investigated at NPL, without the need for electrical contacts, by making microwave surface impedance measurements. A graphene or graphene oxide sample deposited on a low microwave loss dielectric such as quartz perturbs both the microwave resonant frequency and quality factor Q of a high Q dielectric resonator. Modelling of the combined dielectric resonator, graphene layer and substrate properties enable these measurements to estimate the real and imaginary dielectric constants of the graphene layer. The variation of microwave resonant frequency and loss with heat treatment can then reveal the removal of adsorbed or intercalated water from the graphene samples. Further modifications, including operation of this system at cryogenic temperatures should reveal more details of temperature dependent mobility. In addition we have begun investigating the mechanical properties of suspended graphene oxide films using substrates with pre-patterned wells over which a graphene sheet can be deposited. We may then use a modification of the high Q dielectric resonator system as a microwave near-field scanning microscope to measure both the electromagnetic and the mechanical responses of suspended graphene films.

Threshold Behavior of Stimulated Terahertz Emission from Optically Pumped Graphene

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Graphene has attracted much attention for device applications due to its exceptional electronic and optical properties. Recently, we have proposed terahertz lasers using optically pumped graphene [1-3]. Population inversion can occur at terahertz frequency owning to the gapless dispersion and fast energy relaxation of photoexcited carriers by optical phonon emission, and stimulated emission can be realized by interband radiative recombination. In previous works, we measured the carrier relaxation dynamics in optically pumped epitaxial graphene on silicon [4] and exfoliated graphene [5] at room temperature using terahertz time domain spectroscopy based on an optical pump/terahertz & optical probe technique, and we observed the amplification of terahertz waves. In this paper, we measured the dependence of terahertz amplification on the pumping intensity. An exfoliated monolayer-graphene/SiO2/Si sample was examined and a CdTe crystal was placed on top of it, acting as a terahertz probe emitter as well as an electrooptic sensor. An 80 fs, 1550 nm fiber laser with 4 mW average power and 20 MHz repetition was used for optical pump and probe. The pumping pulse was impinged from the back surface of the sample, exciting the graphene and the CdTe. The latter emits the terahertz pulse by optical rectification. A terahertz echo pulse reflected in the CdTe interfaces and passing through the graphene can then be detected. Comparing amplitudes of the echo pulse for sample spots with/without graphene, we calculated the gain of the optically pumped graphene for the terahertz wave. By changing the pumping intensity, we observed clear threshold behavior of the terahertz gain. The threshold pumping intensity was 7×10^6 W/cm^2 and the gain increases monotonically with intensity. We also conducted numerical calculation based on the Boltzmann equation [3]. We took into account the energy relaxation and recombination of carriers by intra and interband optical phonon scattering and the quasi equilibration by the carrier-carrier scattering. We calculated the time evolution of the quasi-Fermi level and carrier temperature, which characterize the carrier distribution, after the pulse excitation. We then calculated the time evolution of the dynamic conductivity at THz frequencies. When the dynamic conductivity becomes negative, graphene exhibits the gain. The theoretical result agrees qualitatively well with the experimental result for the threshold behavior. This agreement indicates that the terahertz amplification is due to the achievement of population inversion in graphene by optical pumping and demonstrates the possibility of the terahertz lasers based on graphene.

[1] V. Ryzhii, M. Ryzhii, and T. Otsuji, *J. Appl. Phys.*, **101**, 083114, (2007).
[2] V. Ryzhii, M. Ryzhii, A. Satou, T. Otsuji, A. A. Dubinov, and V. Ya Aleshkin, *J. Appl. Phys.*, **106**, 084507, (2009).
[3] A. Satou, T. Otsuji, and V. Ryzhii, *Technical Digest of 2nd International Symposium on Graphene Devices: Technology, Physics, and Modeling, Sendai*, Japan, 27-29 Oct. 2010.
[4] H. Karasawa, T. Komori, T. Watanabe, H. Fukidome, M. Suemitsu, V. Ryzhii, and T. Otsuji, *J. Infrared Milli. Thrz. Waves* online 2010. doi: 10.1007/s10762-010-9677-1.

[5] S. Boubanga-Tombet, S. Chan, A. Satou, T. Watanabe, V. Ryzhii, and T. Otsuji, *European Optical Society Annual Meeting* 2010, Paris, France, 26-29 Oct. 2010.

Plasmonic Enhanced Graphene Photodetector

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The electrical and optical properties of graphene make it an ideal material for photonics and optoelectronics [1]. Graphene based photodetectors with a bandwidth up to 16 GHz have been demonstrated [2]. In these detectors, the separation of the photo-generated electron-hole pairs relies on the formation of a pn-junction in the vicinity of the metal contacts. The metal contacts lead to a Fermi level shift underneath the contacts, due to the difference in work function of metal and graphene [3]. However, the electrical signal produced when shining light on the graphene-based photodetector is small compared to traditional semiconductor based detectors [2,4], due to the small 2.3% absorption of graphene [5]. In order to increase the effective light absorption, we integrate plasmonic nanostructures into the devices, so to collect light over a larger area and concentrate the light energy into the near-field region right where the pn-junction is located. Metal nanogratings and nanodots are fabricated on graphene by e-beam lithography. Photovoltage mapping is then carried out at different gate voltages, laser powers, polarizations and wavelengths. Raman spectroscopy [6] is used to confirm monolayer thickness, probe doping levels [7,8] and confirm absorption enhancement [9]. We detect up to 20 times photovoltage enhancement in the device with metal nanostructures. Also, we find a wavelength dependent response, tuneable by the geometry of the applied metal nanostructures. Further, the polarization dependence of the incident light with respect to the nanostructures orientation strongly influences the magnitude of the generated photovoltage, being maximum for polarization parallel to the axis of our nanogratings.

[1] F. Bonaccorso, Z. Sun, T. Hasan, A.C. Ferrari, *Nat. Photonics* **4**, 611 (2010).
[2] T. Mueller, F. Xia, P. Avouris, *Nat. Photonics* **4**, 297 (2010).
[3] G, Giovanetti et. al., *Phys. Rev. Lett.* **101**, 026802 (2008).
[4] F. Xia et. al., *Nano Lett.* **9**, 1039 (2009).
[5] R.R. Nair et. al., *Science* **320**, 5881 (2008).
[6] A.C. Ferrari et. al., *Phys. Rev. Lett.* **97**, 187401 (2006).
[7] A. Das et. al., *Nat. Nanotech.* **3**, 210 (2008).
[8] S. Pisana et. al., *Nat. Mater.* **6**, 198 (2007).
[9] F. Schedin et. al., *ACS Nano* **4**, 5617 (2010).

Selective-area-grown Graphene Transistor by Thermal Chemical Vapor Deposition Method

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Graphene is a single atomic layer of carbon atoms that form a honeycomb structure, and thus, it is the ultimate thin layer. Thanks to its high carrier mobility, graphene is one of the materials with most promise to open a new era of electrical and optical integrated circuits. A method needs to be developed to grow graphene directly on sub-nm-order flat insulating layers in order to fabricate electrical and optical devices that utilize graphene. In addition, using a Si wafer as a substrate is strongly desirable. The current big Si-electronics industry has accumulated enormous amounts of knowledge and know-how concerning Si. Thus, starting graphene-electronics on a Si substrate seems practical.

We recently reported on a growth method for graphene on a sapphire substrate [1] and on an Al_2O_3 layer sputter-deposited on a SiO_2/Si substrate [2]. This paper presents a new selective-area growth method for graphene on a fine-patterned Al_2O_3 layer fabricated on a SiO_2/Si substrate. We fabricated graphene transistors successfully utilizing this selective-area growth method and obtained their excellent electrical characteristics.

Our fabrication process for graphene transistors is follows: A sputter-deposited Al_2O_3 layer (15 nm thick) on SiO_2 (100 nm thick)/Si substrate is patterned to channel, source, and drain regions. The source and drain regions are connected by the channel region. Graphene layers are grown on the patterned Al_2O_3 regions selectively with no growth on SiO_2 surface by thermal chemical vapor deposition method. The growth temperature is 800 ˚C and using propylene flows (4 ml/min) as the source gas and argon (400 ml/min) as the carrier gas. The graphene layers have piled structure of small platelets with a domain size of 30 nm. The averaged number of layers is 2.6 for 2-minute growth. The source and drain regions are covered with Au (100 nm thick)/Ti (10 nm thick) electrodes by using electron beam evaporation method and lift-off process.

The fabricated graphene transistors gives electrical conductance of more than 10,000 S/m which corresponds to effective electron mobility of a few tens cm^2/Vs. The drain current is modulated by gate voltage and $(I_{max}-I_{min})/I_{min}$ is more than 70% when the gate voltage changes from -40 V to + 40 V. The drain current is minimum when the gate voltage is around +30 V.

[1] M. Okai, et al., *Tenth International Conference on the Science and Application of Nanotubes* 2009 (Beijing, China), paper D13, 2009.
[2] M. Okai, et al., *Carbon* 2010 (Clemson, USA), paper Th-2A-5, 2010.

A Chemists Method For Making Pure Clean Graphene

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Graphene is a two dimensional highly crystalline material and can be described as a single layer of all-sp^2 carbon atoms packed into a benzenoid ring structure [1]. It is widely used to describe the structural and electronic properties of many carbon-based materials, including graphite, fullerenes and nanotubes. For example, carbon nanotubes are usually thought of as graphene sheets rolled up into nanometre-sized cylinders. In 1859, Brodie discovered that pure graphite, when treated with potassium chlorate and nitric acid, formed crystalline graphitic acid (also known as graphitic oxide or graphene oxide). It is likely that he also made small amounts of graphene and in any case he speculated a new form of carbon was present and proposed the name Graphon (Gr)[2]. However, graphene was not shown to be stable until 2004 when Geim and Novoselov [3] described the "Scotch tape" method to peel graphene from samples of crystalline graphite. This mechanical exfoliation method is slow and labour-intensive as an optical microscope is required to hunt for single and few-layer graphene (FLG) amongst the material peeled-off.

Currently, the interest of physicists in graphene is enormous, but the interest of chemists has so far not been as great, probably resulting from the absence of well-established large scale methods to produce graphene. Therefore, the most important role chemists can play is the establishment of an inexpensive and simple wet-chemical method for making graphene. For example, intercalation compounds of graphite have been of interest for many years [4]. More than 100 reagents can be intercalated into graphite [5]. In this talk, we describe an intercalation method to make clean graphene that has good electrical properties [6]. The graphene material was characterized by HRTEM, Raman, AFM and FET measurements.

[1] J. Wu, W. Pisula and K. Müllen, *Chem Rev*, **107**(3), 718-747, (2007).
[2] B. C. Brodie, *Philos Trans R Soc Lond A*, **14**., 249-259, (1859).
[3] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos and I. V. Grigorieva ‚*Science*, **306**, 666-669, (2004).
[4] L. B. Ebert, *Annu Rev Mater Sci*, **6**,181-211, (1976).
[5] M. S. Dresselhaus and G. Dresselhaus, *Adv Phys,* **51**, 1 (2002).
[6] S. Malik, A. Vijayaraghavan, R. Erni, K. Ariga, I. Khalakhan and J. P. Hill, *Nanoscale*, **2**, 2139-2143, (2010)

Brownian Dynamics Simulations Of Dilute Graphene Solutions

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Many graphene-based materials (such as thin conductive films and nanocomposites) are processed in the liquid phase and require the conformation and alignment of graphene in solution to be precisely controlled. However, prior studies of conformation dynamics of sheetlike macromolecules such as graphene have been limited to equilibrium behavior, and there have been no studies of the dynamics of sheetlike macromolecules on flow processing timescales. Here we develop Brownian Dynamics (BD) algorithms in order to quantify the effects of flow processing on graphene conformation. The method is conceptually similar to those used for linear polymers; we coarse-grain the sheet using a bead-rod lattice of arbitrary 2-D connectivity and develop a novel theoretical framework for bending and metric forces. Using this technique, we simulate the conformation dynamics of dilute sheetlike macromolecule solutions both at equilibrium and in shear flow. We compute the corresponding radius of gyration as a function of time, flowrate, sheet size, and solvent quality.

Determination of the Quantum Capacitance of Gated Bilayer Graphene Using a Five-Nearest Neighbor Tight-Binding Model

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Graphene-based systems have recently attracted much attention from both the experimental and the theoretical points of view. Bilayer graphene is particularly interesting because it becomes a tunable band-gap semiconductor under the application of an external electric field perpendicular to the system due to a voltage difference (ΔV) between the top and bottom gates of the bilayer device. The system thus forms a capacitor with the usual electrostatic capacitance (C_G) depending on its geometry. However since it is an atomic layer system, quantum effects come into play giving rise to the so-called quantum capacitance (C_Q) which is directly related to the change of the density of states $D(E)$ at the Fermi energy EF. In this work, an analytical expression of C_Q for monolayer graphene will first be derived followed by the evaluation of C_Q for our bilayer device system allowing us to compare the different responses of mono- and bi-layer graphene subject to ΔV. Our Hamiltonian is of the tight-binding (TB) type with five nearest intra-layer (within the same layer) neighbours and three inter-layer (between the two layers) hopping parameters contrary to what most authors use to evaluate quantum capacitances which is a total of two intra-layer and one interlayer parameters at most. We expect our model to give a rather clearer and more exact form of the dependence of C_Q on ΔV, liberate new information about gated bi layer graphene systems and possibly explain some discrepancies- found in the literature- between experimental and theoretical Raman shift curves for some particular values of ΔV.

Mechanism of CVD Graphene Growth

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The graphene chemical vapor deposition (CVD) growth on transition metal (TM) surface is the most promising method for high quality and large area graphene synthesis. While its mechanism remains a mystery in spite of the great experimental success. Here we are going to present our recent theoretical study on the mechanism of graphene CVD growth:
(1) C cluster' structural transition from one dimensional (1D) C chain to two dimensional (2D) graphene island and its impact on graphene growth.
(2) The great advantage of graphene nucleation near a metal step edge than that on a terrace.
(3) The magic sized C cluster formation on metal surface.
Based on our theoretical studies, we propose the use of seeded graphene to synthesize high-quality graphene in large area.

Graphene Charge Detectors Meet Nanotube Quantum Dots

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Carbon nanomaterials, such as carbon nanotubes (CNTs) and graphene, both exhibiting unique electronic and mechanical properties are very promising materials for future nanoelectronic applications. The absence of the hyperfine field in ^{12}C enriched carbon materials makes CNTs and graphene particularly interesting for hosting quantum dots which potentially allow the realization of spin-qubits with long coherence times. Here we present the fabrication and electrical characterization of an all carbon device based on a nanotube quantum dot with a nearby few-layer graphene nanoribbon charge detector. We show that the few-layer graphene nanoribbon can be used to detect single charging events in the nearby CNT quantum dot (QD). The CNTs are grown on a 300 nm SiO_2 on highly doped Si substrate by a ferritin-based catalytic chemical vapor deposition (CVD) process. Subsequently, graphene has been deposited by mechanical exfoliation on the SiO_2 with the pre-grown nanotubes. Electron beam (e-beam) lithography and dry etching techniques are used to pattern the graphene nanoribbons. An additional, e-beam step and lift-off techniques are used to place metal contacts on the individual graphene-nanotube devices. We present low-temperature transport measurements on a CNT quantum dot with an integrated graphene charge detector. The device consists of a 100 nm narrow few-layer graphene nanoribbon which is located around 150 nm next to a contacted single-walled carbon nanotube (SWNT). From Coulomb diamond measurements in the SWNT QD charging energies of about 8 meV are extracted. We show that resonances in the nanoribbon can be used to detect single charging events in the SWNT QD. The charging induced potential change on the quantum dot causes a steplike change of the current in the charge detector. The relative change of the current measures up to 20% for detecting individual charging events and thus demonstrates the quality of the detector.

Mechanism Of Near-Field Enhancement In Two-Dimensional Systems.

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A theory for the mechanism of near-field Raman enhancement in two dimensional systems is presented. The enhancement is established by a laser-irradiated nanoplasmonic structure acting as an optical antenna. Our results show that the near-field Raman intensity is inversely proportional to the 10th and 8th power of the antenna-sample distance for incoherent and coherent scattering regimes, respectively.The model is applied to the Raman spectrum of graphene, giving the enhancement mechanism expected for the bond stretching G band (~1580 cm^{-1}), the disorder-induced D band(~1350cm^{-1}), and the two-phonon G'(2D) band(~2700 cm^{-1}).The model is general and can be applied as a guide for obtaining the best experimental conditions (antenna geometry, sample geometry, radiation source, etc.).

CVD Synthesis Of Graphene Using Ethanol And Dimethyl Ether On Ni Foil

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Graphene, a monolayer of sp^2-bonded carbon atoms arranged into a hexagonal lattice, has been attracting a great interest because of its unique structure and promising properties. [1]According to the request of application research of graphene, large-scale and comparable controllable synthesis of graphene is the challenge to realize the potential application. Chemical vapor deposition (CVD) is a powerful tool for large-scale and low-cost synthesis of nano-carbon materials. [2,3] However, comparable simple and controllable CVD growth of graphene remains a challenge.

We demonstrate a facile and stable CVD method to synthesize graphene on Ni foil and compare the results between different carbon source ethanol and dimethyl ether (DME). Monolayer graphene was synthesized on Ni foil by ethanol and DME without annealing gas and special cooling steps during CVD. To investigate the carbon source decomposition conditions in CVD synthesis of graphene, gas-phase thermal decomposition of ethanol and DME with various temperatures at low pressure was simulated using the chemical kinetic model. Temperature of CVD synthesis of monolayer graphene from DME is lower than that from ethanol, which is agree with predicted simulation results. Raman and scanning electron microscopy were used to characterize the synthesized and transferred monolayer graphene by CVD of ethanol and DME.

[1] A.K. Geim, K.S. Novoselov,*Nat. Mater*.**6**.,183-191 (2007).
[2] S. Maruyama, E. Einarsson, Y. Murakami, T. Edamura, *Chem. Phys. Lett*. **403**, 320-323 (2005).
[3] X. S. Li, W. W. Cai, J. H. An, S. Kim, J. Nah, D. X. Yang, R. D. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L, Colombo, R. S. Ruoff,*Science* **324**, 1312-1314 (2009).

Electrically Conductive Oxygen Barrier Film Formed by Graphene Layers

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This study deals with the application of multiply layered-graphene or graphene oxide materials on gas barrier film areas. The lateral structure of the layered graphenes or graphene oxides effectively decreased oxygen gas permeability, and provided the remarkable improvement of gas barrier property by being deposited on film surface.

The graphene oxide was produced by chemical oxidation of graphite by using sulfuric acid and $KMnO_4$. And it was purified by being washed with distilled water, and was re-dispersed in distilled water by ultrasonication method. The resulting graphene or graphene oxide were co-deposited on PET film surface with aid of various kinds of polymers, such as polyvinyl alcohol, poly acrylic acid, and poly(ethylenimine). We examined the characteristics of the coated film, such as light oxygen transmission rate, light transmittance, and sheet resistance depending on the kinds of graphene and polymeric binders.

The coated film showed lower oxygen transmission rate than that of the uncoated bare PET of 8.119 cc/m^2day. The oxygen transmission rate was also dependent on the kinds of polymer binders. In case of polyvinyl alcohol showed very low oxygen transmission rate of 0.267 cc/m^2day, and poly acrylic acid and poly(ethylenimine) provided the transmission of 3.124 cc/m^2day and 6.604 cc/m^2day, respectively.

The light transmittance was determined by the amount of graphene species in coated film and the degree of reduction of graphene oxide. According to our results, the amine functional groups of poly(ethylenimine) accelerated the conversion of graphene oxide to graphene, and resulted the barrier film with lower sheet resistance and lower light transmittance. The films showed the sheet resistance about 0.1~10 MΩ/sq.

Threshold Behavior of Stimulated Terahertz Emission from Optically Pumped Graphene

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Graphene has attracted much attention for device applications due to its exceptional electronic and optical properties. Recently, we have proposed terahertz lasers using optically pumped graphene [1-3]. Population inversion can occur at terahertz frequency owning to the gapless dispersion and fast energy relaxation of photoexcited carriers by optical phonon emission, and stimulated emission can be realized by interband radiative recombination. In previous works, we measured the carrier relaxation dynamics in optically pumped epitaxial graphene on silicon [4] and exfoliated graphene [5] at room temperature using terahertz time domain spectroscopy based on an optical pump/terahertz & optical probe technique, and we observed the amplification of terahertz waves. In this paper, we measured the dependence of terahertz amplification on the pumping intensity. An exfoliated monolayer-graphene/SiO_2/Si sample was examined and a CdTe crystal was placed on top of it, acting as a terahertz probe emitter as well as an electrooptic sensor. An 80 fs, 1550 nm fiber laser with 4 mW average power and 20 MHz repetition was used for optical pump and probe. The pumping pulse was impinged from the back surface of the sample, exciting the graphene and the CdTe. The latter emits the terahertz pulse by optical rectification. A terahertz echo pulse reflected in the CdTe interfaces and passing through the graphene can then be detected. Comparing amplitudes of the echo pulse for sample spots with/without graphene, we calculated the gain of the optically pumped graphene for the terahertz wave. By changing the pumping intensity, we observed clear threshold behavior of the terahertz gain. The threshold pumping intensity was 7×10^6 W/cm^2 and the gain increases monotonically with intensity. We also conducted numerical calculation based on the Boltzmann equation [3]. We took into account the energy relaxation and recombination of carriers by intra and interband optical phonon scattering and the quasi equilibration by the carrier-carrier scattering. We calculated the time evolution of the quasi-Fermi level and carrier temperature, which characterize the carrier distribution, after the pulse excitation. We then calculated the time evolution of the dynamic conductivity at THz frequencies. When the dynamic conductivity becomes negative, graphene exhibits the gain. The theoretical result agrees qualitatively well with the experimental result for the threshold behavior. This agreement indicates that the terahertz amplification is due to the achievement of population inversion in graphene by optical pumping and demonstrates the possibility of the terahertz lasers based on graphene.

[1] V. Ryzhii, M. Ryzhii, and T. Otsuji, *J. Appl. Phys.*, **101**, 083114, (2007).
[2] V. Ryzhii, M. Ryzhii, A. Satou, T. Otsuji, A. A. Dubinov, and V. Ya Aleshkin, *J. Appl. Phys.*, **106**, 084507, (2009).
[3] A. Satou, T. Otsuji, and V. Ryzhii, *Technical Digest of 2nd International Symposium on Graphene Devices: Technology, Physics, and Modeling, Sendai*, Japan, 27-29 Oct. 2010.
[4] H. Karasawa, T. Komori, T. Watanabe, H. Fukidome, M. Suemitsu, V. Ryzhii, and T. Otsuji, *J. Infrared Milli. Thrz. Waves* online 2010. doi: 10.1007/s10762-010-9677-1.

[5] S. Boubanga-Tombet, S. Chan, A. Satou, T. Watanabe, V. Ryzhii, and T. Otsuji, *European Optical Society Annual Meeting* 2010, Paris, France, 26-29 Oct. 2010.

Electronic Structure of Graphene Adsorbed on (0001) Surfaces of SiO_2 Substrate

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Following the first isolation of graphene in 2004, graphene has been keeping a premier position not only in the low-dimensional sciences but also in electronic device engineering due to its unique electronic properties. Recent experiments unravelled that the insulating substrates occasionally modulate the electronic properties of graphene, such as band gap opening and decrease of carrier mobility. Although much effort devoted to elucidate the physical properties of graphene adsorbed on SiO_2 surfaces, the fundamental and unified comprehension on this hybrid system is still unclear yet. Here, we investigate energetics and electronic structures of graphene adsorbed on SiO_2 (0001) surfaces using first-principles total-energy calculations [1]. We find that graphene is bound to SiO_2 surfaces via weak interaction. Despite the weak interaction between them, graphene adsorbed SiO_2 (0001) surfaces exhibits the semiconducting electronic properties. The semiconducting property is ascribed to the spatial undulation of onsite energy on C atomic site induced by the substrate atoms.

[1] N.T. Cuong, M. Otani, and S. Okada, *Phys. Rev. Lett.*, **106**, 106801, (2011).

Functionalization of Graphene Using Nitrogen ion

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We introduce nitrogen ion to modify the electronic properties of the graphene. We could clarify the three nitrogen induced species on the few-layer epitaxial graphene(EG) on SiC(0001), such as N_2, the graphite-like nitrogen and pyridine-like nitrogen in our previous paper.[1] In this paper, we prepared the monolayer and the multilayer EG and irradiated the energy of 100 eV nitrogen ion on the EGs. We gradually annealed the sample to the temperature of 1000 ^{o}C and measured the surface property changes using photoemission spectroscopy (PES), and atomic force microscopy(AFM). After 1000 ^{o}C annealing on the multilayer EG, N 1s core level spectra show that the graphite-like nitrogen remains as a major species and the work function change ($\Delta\varphi$) shows the n-type doping property by decreasing 0.75 eV. The measured shift contains both the band bending at the graphene surface 0.4 eV and an additional contribution from the interface dipole generated by the charge transfer (i.e., 0.35 eV) from nitrogen ion to graphene.

[1] Ki-Jeong Kim, Hangil Lee, Junghun Choi, Hankoo Lee, Min Cherl Jung, H J Shin, T-H Kang, B Kim and Sehun Kim, *J. Phys.: Condens. Matter* **22** 045005 (2010).

Interaction Between Two Graphene Sheets With A Turbostratic Orientational Relationship

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The interaction energy of two rigid defect-free graphene sheets with various turbostratic orientational relationships is examined systematically using a Lennard-Jones potential. When one layer is rotated from the AB stacking order, maxima and minima in the intersheet potential energy surface occur periodically at angles corresponding to the AA and AB stacking orders, respectively. The energy gap between the AA and AB stacking orders is estimated to be much smaller than the average thermal energy at room temperature. Furthermore, the turbostratic structure with a just few degrees of rotational displacement from the AB stacking order diminishes the energy gap during translational displacement effectively to zero. We conclude that the presence of defects or cross-links is required to explain even the low shear strengths inferred from experimental studies of fibres made from pure carbon nanotubes in which there is no commensurate orientation of graphene sheets. In addition, the interaction between flexible graphene sheets with defects will be discussed.

Magnetic Ordering Of Adatoms on Graphene

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We investigate magnetic properties of a dilute ensemble of magnetic adatoms on graphene. The present study is focused on the adatoms residing at the centers of the graphene lattice hexagons. The electron-mediated (RKKY) interaction in an undoped graphene depends on the adatoms positions on the three sublattices of the $\sqrt{3} \times \sqrt{3}$ superlattice formed by intervalley scattering induced Friedel oscillations and it has $1/R^3$ dependence. This leads to an ordering transition of adatoms into an antiferrimagnetic state. We also demonstrate that the long-ranged RKKY coupling between localized magnetic moments of a dilute ensemble of adatoms on grapheme leads to a deviation from Curie-Weiss law for static susceptibility at high temperatures.

Graphene-Based Nanomaterials and Nanostructures: Synthesis, Fabrication, Characterization and Applications

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In this talk, I will summarize the research on synthesis, characterization and applications of graphene-based nanomaterials and nanostructures, which my group has done recently. I will introduce the synthesis and characterization of novel grapheme-based materials [1],especially the first-time synthesized hexagonal close packed Au nanostructures on graphene oxide [1a], and patterned graphene structures [2, 3a-c]. Then I will demonstrate the applications of graphene-based materials in chemical and bio-sensors [3], solar cells [4], electric devices [5], memory devices [6], conductive electrodes [4-7], cell cultures [8], matrix of MALDI-TOF- MS [9], etc.

[1] (a) X. Huang, et al.,*Nat. Commun*. DOI: 10.1038/ncomms1291 (2011). (b) X. Y. Qi, et al., Angew. *Chem. Int*. Ed., 49, 9426-9429(2010). (c) X. Y. Qi, et al.*, Small*, **6**, 663-669 (2010). (d) X. Huang, et al.*, Small*, **6**, 513-516 (2010). (e) X. Z. Zhou, et al., *J. Phys. Chem. C*, **113**, 10842-10846 (2010). (e) X. Huang, et al.*, Small*, DOI: 10.1002/smll.201002009 (2011).
[2] (a) B. Li, et al.*, Langmuir*, **25**, 10455-10458(2009). (b) H. Li, et al., *Langmuir*, **26**, 5603–5609(2010). (c) X. Z. Zhou, et al.*, J. Phys. Chem. C*, **113**, 19119-19122 (2009).
[3](a) Q. Y. He, et al., *ACS Nano*, **4**, 3201-3208 (2010). (b) X. H. Cao, et al.*, Small*, DOI: 10.1002/smll.201100071 (2011). (c) H. G. Sudibya, et al., *ACS Nano*, **5**, 1990-1994 (2011). (d) Z. J. Wang, et al., *J. Phys. Chem. C*, **113**, 14071-14075 (2009). (e) Z. J. Wang, et al., *Biosens. Bioelectron*., DOI: 10.1016/j.bios.2011.03.002 (2011).
[4] (a) Z. Y. Yin, et al., *ACS Nano*, **4**, 5263-5268 (2010). (b) Z. Y. Yin, et al.*, Small*, **6**, 307-312 (2010).
[5]B. Li, et al., *Adv. Mater.,* **22**, 3058-3061 (2010).
[6] (a) J. Q. Liu, et al.*, ACS Nano*, **4**, 3987-3992 (2010). (b) J. Q. Liu, et al., *Small*, **6**, 1536-1542 (2010).
[7] (a) S. X. Wu, et al.*, J. Phys. Che*m. C, **114**, 11816-11821(2010). (b) S. X. Wu, et al., *J. Mater. Chem*., **21**, 3467-3470(2011).
[8] S. Agarwal, et al.*, Langmuir*, **26**, 2244-2247 (2010).
[9] X. Z. Zhou, et al.*, Chem. Commun.,* 46, 6974-6976 (2010).

Valence Band of Graphite Oxide

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We investigated the valence band structure of graphite oxide by photoelectron spectroscopy at the Pohang Accelerator Laboratory, Korea.The typical sp^2 hybridization states found in graphite were also seen in graphite oxide. However, the π state disappeared near the Fermi level because of bonding between the π and oxygen-related states originating from graphite oxide, indicating electron transfer from graphite to oxygen and resulting ina downward shift of the highest occupied molecular orbital (HOMO) state to higher binding energies. The band gap opening increasedto about 1.8 eV, and additional oxygen-related peaks were observed at 8.5 and 27 eV.The electronic states of graphite were also found in graphite oxide. Thus, graphite oxide has an electronic structure similar to that of pristine graphite except for the states near the Fermi level and oxygen-related states.

Stacking Dependent Electronic Structure and Transport in Bilayer Graphene Nanoribbons

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The stacking-dependent electronic structure and transport properties of bilayer graphene nanoribbons suspended between gold electrodes are investigated using density functional theory coupled with non-equilibrium Green's functional method. Two different stacking arrangements, namely the AA and Bernal (AB) of monolayer graphene nanoribbons are considered. In the AA stacking, all carbon atoms of the hexagonal rings sit atop each other, whereas only half of the atoms sit atop each other in the AB-stacked bilayer configuration. For monolayer and bilayer nanoribbon configurations, the current (I)-voltage (V) characteristics show a linear behaviour in the bias range from 0 to 1 V. Our calculations show substantially enhanced electron transmission as well as tunnelling currents inthe AA stacking of bilayer nanoribbons compared to the single-layer graphene nanoribbon. Interlayer separation between the nanoribbons appears to have a profound impact on the conducting featuresof the bilayer nanoribbons, which is found to be closely related to the topology and overlap between the edge-localized π orbitals. This feature of the bilayer graphene nanoribbons can be used to develop practical nanoscale electronic devices.

Melamine for Stabilization Of Graphene Sheets by Ball Milling Processes

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Graphene is a two-dimensional material, composed of layers of carbon atoms forming six-membered rings. It has recently attracted great attention as a new material with many advantageous properties. However, one of the main challenges in the production of graphene is the scalable processing and handling of individual graphene sheets. Although single- and bi-layers graphene were first obtained by the micromechanical cleavage of graphite,[1] several strategies have been developed for the synthesis of graphene since them.[2] By these techniques, very large entities of single-layer graphene can be produced, but the scalability and handling problems remain. The most promising route is the direct exfoliation into various solvents of either chemically modified or unfunctionalized graphite. For example, graphene oxide can be exfoliated from graphite via acidic treatments.[3] However, the oxidation process results in the formation of structural defects, which may lower the conductivity of graphene dramatically.

We present a scalable and easy technique for exfoliation of graphene sheets in the presence of melamine by ball milling processes in solvent free conditions. After treatment, the materials were suspended in a variety of aqueous solutions and organic solvents by means of soft sonication, in order to obtain solutions of graphene. This procedure presents a powerful approach in order to form stable dispersions of single- and few-layer graphene sheets for several days. Layers of graphene were characterized by various techniques, such as transmission electron microscopy, UV-vis spectroscopy, Raman spectroscopy and thermogravimetric analysis.

This new approach opens the way to carry out different organic reaction on stable graphene sheets, in order to produce specific structures for several applications.

[1] K. S. Novoselow, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science,* **306**, 666-669, (2004).
[2] S. Park, R. S. Ruoff, Nat. *Nanotechnol.*, **4**, 217-224, (2009).
[3] W. S.Hummers, R. E. Offeman, *J. Am. Chem. Soc.*, **80**, 1339-1340, (1958).

Graphene-Based Multifunctional Iron Oxide Nanosheets with Tunable Properties

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We report the synthesis of graphenes with tunable properties due to the growth of needle-like iron oxide (IO) nanoparticles on their surfaces. The electrical conductivity, flexibility, and magnetic properties of graphene nanosheets (GNSs) could be tuned on demand by fine controlling both the surface coverage and the length of the IO nanoneedles. The degree of coverage of the IO nanoparticles on the surface of the GNSs made it possible to control the resulting properties of the IO/GNSs on demand. As examples of the utility of such materials, paperlike materials were generated by simple filtration, and the resulting IO/GNS nanocomposites showed extraordinary removal capacity and fast adsorption rates for As^{V} and Cr^{VI} ions in water, and possibility for preparation of multifunctional films equipped with conductivity, flexibility and magnetic properties. The fabrication process is easy to scale up at a low cost. In addition, both the colloidal solution and film forms of the resulting IO/GNSs were effective for removal of heavy metal ions, meaning this material could be utilized for actual industrial applications.

Graphene Nanocomposite-Trigered Enhancing Growth of Metal Oxide: An Ideal Nanocatalyst for Removing Poison

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Recently, iron oxide nanoparticles have been extensively studied as drug carriers, contrast agents, heating mediators, and catalysts in many industrial processes. The particle size of iron oxide is a critical factor for almost all of the aforementioned applications. By such reasons, controlled growth of iron oxide NPs is a priority for advanced applications. Au NPs were homogeneously synthesized on graphene via adsorption and reduction of corresponding precursors, and used as catalytic template for growth of iron oxide. We found that iron oxide NPs remarkably grow into needlelike structures on Au NP-coated graphene due to catalytic synergetic effect of Au NPs and functionalized carbons, compared to graphene. Growth of iron oxide NPs on templates could be easily tuned by controlling the size and quantity of Au NPs on graphene. Such graphene-derivatives showed excellent performance for chemo- selective reduction of nitrobenzenes to their respective anilines under room temperature.

Direct Growth of Nanographene on Glass

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Nanograpehene was directly deposited on glass at 750 ^{o}C by thermal chemical deposition, without using any additional metallic catalyst. Annealing of nanographene film at 300 ^{o}C to 500 ^{o}C leads to an increase of the in-plane crystal size from ~ 15 nm up to ~ 23 nm, when the annealing is done in the presence of an adlayer of nickel, subsequently deposited on the graphene after the initial deposition. This study clearly demonstrates that nanographene can be directly deposited on glass and the crystallite size is controllable.

Interaction And Self-assembly Of Pyrene Molecules On Graphene Studied By Raman Spectroscopy

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Different techniques have been proposed to allow large-scale production and processing in solution of graphene, mostly by chemical exfoliation of graphite. However, most of them are based on covalent modification, which permanently changes the graphene structure. A milder chemical treatment, which does not affect graphene conjugation, is based on the exfoliation of graphite using supramolecular, non-covalent, reversible interactions with tailored organic molecules such as aromatic molecules.

Here we use pyrene molecules (1-pyrenecarboxylic acid dispersed in water)in order to exfoliate graphite. We use Raman spectroscopy to characterize the quality of the suspension and to investigate the supramolecular interaction of the molecules with graphene.

Raman Spectroscopy was performed directly on solution and on some flakes deposited on a silicon substrate. Several bilayers and few-single layers graphene of few µm size were isolated. The Raman spectrum of the new hybrid material composed by pyrene molecules grafted on graphene layers shows: i) no residual fluorescence from the pyrene; ii) strong D and D’ peak; iii) new sharp peaks, with very low intensity, lying between 1200 and 1500 cm^{-1}.

In order to further investigate the interaction between the molecules and graphene, we deposited the molecules directly on graphene, produced by micro-mechanical exfoliation. A similar Raman spectrum has been observed. Thus, the D and D’ peaks can be attributed to the presence of the molecules on graphene, while the low intensity peaks are attributed to pyrene vibrations, now visible, since the fluorescence is quenched by the interaction of the molecules with graphene.

Graphene Bubble As Adaptive Focus Lens

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Conventional zoom and focus optical systems require the precise mechanical movement of their components. Thus, these systems are complex, expensive, bulky and high power- consuming. Graphene is a two-dimensional material with unique properties. Most of the research has been concentrated on its electronic properties [1]. However, this material shows further remarkable properties: graphene is impermeable to every gas, it is very elastic, robust and optically transparent [2].

Here we investigate graphene bubbles as adaptive focus lenses. The bubbles are typically formed after graphene deposition and they have been characterized by Atomic Force Microscopy and Raman Spectroscopy. The bubbles have been also used as a prototype to study the Raman spectrum of graphene under biaxial strain: the G peak does not show any splitting, no large variation in the FWHM of the 2D peak is observed, or dependence in the Raman intensity on the light polarization [3], in contrast to uniaxial strain [4].

We show that it is possible to control the curvature of the bubble by applying a gate voltage. This makes graphene bubbles perfect candidates as lenses in mobile phone cameras, space-based camera systems and cheap devices.

[1] A. K. Geim, K. S. Novoselov, *Nature Mat*. **6**, 183 (2007)
[2] A. K. Geim, *Science* **324**, 1530 (2009)
[3] J. Zabel, R. R. Nair, T. Georgiou, P. Klar, K. S. Novoselov, C. Casiraghi, submitted
[4] T. M. G. Mohiuddin, A. Lombardo, R. R. Nair, A. Bonetti, G. Savini, R. Jalil, N. Bonini, D. M. Basko, C. Galiotis, N. Marzari, K. S. Novoselov, A. K. Geim and A. C. Ferrari, *Phys. Rev. B*, **79**, 205433 (2009)

CO_2 Detection by Polyethyleneimine Functionalized Graphene Field Effect Transistors

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Graphene field effect transistors (gFETs) are promising as gas sensors owing to the sensitivity of conduction in a gFET channel to charge transfer doping. Small molecule gases have been sensed with gFETs at levels approaching single molecule adsorption [1]. Carrier density modulation of graphene by oxygen exposure has recently been explained in terms of charge transfer between graphene and oxide substrate, mediated by redox reactions within an adsorbed water layer [2]. This redox mechanism can be invoked to explain gFET response to other small molecules such as H_2 and NH_3. Nonetheless, the response of gFETs to some molecules, such as CO_2, is insufficient for sensing purposes. We demonstrate non-covalent functionalization of gFETs with a polyethyleneimine (PEI) coating to induce CO_2 sensitivity, in a manner similar to that employed for CO_2 sensing with carbon nanotube field effect transistors (NTFETs) [3]. CVD grown graphene was transferred to insulating substrates using a poly(methyl methacrylate)handle. Raman spectroscopy was used to verify high quality monolayer growth[4,5]. Si/SiO_2 was chosen as the substrate for back-gated electrical measurements. Bulk In electrical contacts were mechanically applied to the graphene. A solution of PEI in Tetrahydrofuran (0.0044mg/mL) was drop cast on the graphene and dried for 12 hours, resulting in a PEI film of ~40nm mean thickness.

Electrical measurements were performed in a vacuum chamber (base pressure of 10^{-5}Torr) at 300K with a variable gas environment. Devices were not thermally annealed, leaving H_2O vapour within the hygroscopic PEI film. A leak valve and pressure gauge were used to controllably dose the graphene FET with CO_2 (99.99% pure). PEI coating of the gFET leads to an n-type doping as compared to the uncoated gFET, interpreted in previous NTFET measurements with direct electron transfer from amine groups [6]. Exposure to CO_2 leads to p-type doping. PEI responds to CO2 through the formation of carbamates [7],

$CO_2 + 2R_2NH \rightarrow RNH_2^+ + RNCOO^-$

and subsequent reaction with CO_2 and H_2O leads to the formation of bicarbonate anions [7],

$CO_2 + 2H_2O + RNCOO^- \rightarrow RNH_2^+ + 2HCO_3^-$

We believe that the p-type doping of PEI-gFETs in response to CO_2 arises from direct electron transfer from graphene to protonated amine groups in proximity with the graphene surface. Cycled CO_2 exposure and evacuation of the measurement chamber were performed at 500s intervals, with the gFET biased at V_{DS} =1.5V and a gate voltage V_{GS}=0V. Change in source-drain conductance due to exposures was measured. Evacuation restores the original conductance, albeit with a long time scale. Multiple exposure experiments reveal an accumulated dosing affect, as well as an increased response to higher CO_2 pressure. It is not clear what mechanism limits the kinetics of the charge transfer doping of the gFET. Work to address drift in the baseline current, shorter response time in thinner PEI films, and quantitative CO_2 dosimetry based on shift in graphene neutrality point are underway.

[1] F. Schedin et al., *Nature Materials*, **6**, 652-655 (2007).

[2] P.L. Levesque et al., *Nano Lett*. **11**, 132-137 (2011).
[3] A. Star et al,. *Adv. Mater*. **16**, 222049-2052 (2004).
[4] A. Guermoune et al., under review.
[5] X. Li et al., *Scienc*e **324**, 1312-1314 (2009).
[6] M. Shim et al., *J Am. Chem. Soc*. **23**, 11512-11513 (2010).
[7] S. Satyapal et al., *Energy & Fuels*, **15** 250-255 (2001).

Spectroscopic Characterization of Atomically Precise Graphene Nanoribbons

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Commonly reported top-down nano-fabrication methods have so far proved unsuccessful to produce atomically precise graphene nanoribbons[1]. Our group has recently developed a method to synthesize chemically defined graphene nanoribbons on metallic substrates [2] and in solution, from different polymer precursors [3]. Taking advantage on developed exfoliation methods [4, 5] stable dispersions of as-synthesized graphene nanoribbons in organic solvents for spectroscopic characterization can be readily obtained. Here we report for the first time the spectroscopic characterization of two types of chemically precise graphene nanoribbons dispersions. The dispersed nanoribbons characterized by absorption spectroscopy display van Hove singularities that can be correlated to transitions between energy levels in the density of states. Preliminary fluorescence measurements feature emission peaks that suggest band gap photoluminescence. In addition, the chemically synthesized graphene nanoribbons display peaks in the Raman spectra that corroborate their dimensionality and crystal quality.

[1] Wang X, Dai H.. *Nat Chem.* **2**(8):661-5 (2010).
[2] Cai J, Ruffieux P, Jaafar R, Bieri M, Braun T, Blankenburg S, et al. *Nature*. **466** (7305):470-3 (2010).
[3] Dössel L, Gherghel L, Feng X, Müllen K. *Angewandte Chemie International Edition.* **50**(11):2540-3 (2011)
[4] Hernandez Y, Nicolosi V, Lotya M, Blighe FM, Sun Z, De S, et al. *Nature Nanotech.* **3**(9):563-8 (2008).
[5] Bergin SD, Nicolosi V, Streich PV, Giordani S, Sun Z, Windle AH, et al. *Adv Mater.* **20**(10):1876-81 (2008).

Raman Spectroscopy of Graphane, Fluoro-graphene and Oxidized Graphene

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Graphene has been recently proposed as one of the basic building block for future nano-electronics. The ultimate 2D character of the material confers exceptional electronic properties such as outstanding carrier mobility [1]. However, graphene shows metallic behavior making it hard to create graphene based transistors. In order to overcome this problem, various approaches to tune and control the electronic properties of graphene have been adopted, such as cutting graphene into nanoribbons and defect engineering with electron beams or chemical modification. Here we aim at studying by Raman spectroscopy and transport measurements how the optical and electronic properties of graphene change after introducing different types of defects in the crystal lattice by plasma treatment. Graphane [2] and Fluoro-graphene [3] have been used as prototype materials to study defects in graphene: here the D peak is activated by the conversion of a sp^2 site into a sp^3 and the defects concentration can be easily controlled by changing the plasma conditions [2-3]. Single layers and double layer graphene have been exposed to H_2 and CF_4 plasma. Further samples under O_2 plasma have been made too. Changes in G, D and 2D Raman peaks shapes and intensity as a function of the amount of disorder and excitation wavelength are monitored. We use the D/G peak intensity ratio to probe the amount of defects induced by the plasma treatment [4]. In particular we show that the 2D peak intensity is strongly sensitive to electron-defects interactions [5]. Transport measurements are performed before and after plasma treatment correlating amount of induced defects with electronic properties.

[1] Geim and Novoselov, *Nature Materials*, **6**, p183 (2007)
[2] Elias et al., *Science,* **323**, 610 (2009)
[3] Nair et al., *Small*, **6**, 2877 (2010)
[4] Ferreira et al, *Physical Review B*, **82**, 125429 (2010)
[5] Venezuela et al., arXiv:1103.4582v1

Electron Emission from Free-Standing Graphene Edge

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We demonstrated a practical process to produce free-standing graphene attached on a tungsten tip. The single and few-layer graphene were prepared from a stable suspension graphene solution prepared by rapid quenching of highly oriented pyrolytic graphite (HOPG) in an aqueous solution of NH_4HCO_3 [1]. The exfoliation phenomenon was attributed to the formation of cracks on the HOPG surface during the rapid quenching followed by infiltration of NH_4HCO_3 into the material. Subsequent decomposition of NH_4HCO_3 leads to the formation of steam and carbon dioxide which help the exfoliation process. The suspension graphene in an aqueous solution of NH_4HCO_3 was then transferring to a TEM copper grids. Those graphene on the edge of copper grids will be easily found under optical microscope. Then we use a cleaned tungsten microtip to pick up the graphene and assemble into the electron field emission source. The electron-field-emission characteristics of the graphene was then measured in a vacuum chamber with a vacuum of 10^{-7} Torr shows good F-N performance [2]. The anode was a phosphors screen which can identify the image of the electron beam emitting from the edge of graphene. We show that repeatable stable field e mission current can be obtained after a careful conditioning process. The turn-on field is relate to the layers of graphene what single layer present the lowest turn-on field of 3.02 V/μm. And the electron beam patterns can be correlated to the layers of the graphene which identified by the Raman spectrum.

1. Y. B. Tang, C. S. Lee, Z. H. Chen, G. D. Yuan, Z. H. Kang, L. B. Luo, H. S. Song, Y. Liu, Z. B. He, W. J. Zhang, I. Bello, S. T. Lee*; Nano Lett.* **9**, 1374–1377 (2009).
2. Z. S. Wu, S. F. Pei, W. C. Ren, D. M. Tang, L. B. Gao, B. L. Liu, F. Li, C. Liu, H. M. Cheng; *Adv. Mater.* **21**, 1756–1760 (2009).

Stretching A Bilayer Graphene

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In the present work, bilayer graphene flakes have been subjected to a uniaxial tension using the polymer cantilever beam technique. In all cases the mechanical response was monitored by simultaneous Raman measurements using different excitation wavelengths, mainly 514 nm (2.41 eV), 633 nm (1.96 eV) and 785 nm (1.58 eV). The flakes were either laid bare on a polymer substrate or covered by another polymer layer to minimize a possible slippage during loading. For comparison, monolayer graphene flakes close to the studied bilayers were monitored during the same experiment. In all cases, when both the mono- and bilayer are a part of the same flake, they show the same behavior under tension, with shift rates of approx. 31 and 10 cm^{-1}/% for G^- and G^+, resp. The G^-/G^+ relative intensities of such samplesremain the same too, confirming the integrity of the respective layers.The behavior of the G band is the same when studied with different wavelengths.
On the contrary, the 2D bandevolution under tension differs upon the used laser line. The most pronounced changes can be observed with 1.58 eV excitation, mainly in the evolution of the highest-frequency component ($2D_{11}$), which originates from the double resonance process involving the "original" π_1 and π_1* bands belonging to the single layer. For the fitting procedure with Lorentzian line shapes the FWHMs were set as equal for all components and otherwise left unconstrained. The shift rates of the three lower frequency components involving the π_2 and π_2* electronic bands are all similar - close to 50 cm^{-1}/%. However, the $2D_{11}$ shifts at a rate of only 30 cm^{-1}/%. The relative intensities of the components evolve differently. The $2D_{12}$ experiences a twofold intensity increase in the observed strain range, mainly at the cost of the $2D_{11}$. The evolution of $2D_{11}$ and $2D_{12}$ closely resembles the splitting behavior of the 2D band in a monolayer when excited with the same wavelength [1].

[1] O. Frank, M. Mohr, J. Maultzsch, C. Thomsen, I. Riaz, R. Jalil, K.S. Novoselov, G. Tsoukleri, J. Parthenios, K. Papagelis, L. Kavan, C. Galiotis, *ACS Nano* **5**, 2231–2239 (2011).

Characterizing Devices and Twisted Layers of Graphene by Resonance Raman Scattering

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Raman spectroscopy is a very useful tool to study graphene, since it furnishes information about the atomic structure, presence of disorder, defects, charges and strain. However, important information about electrons can be also obtained in a resonance Raman investigation, where the energy of the laser excitation can be tuned. We will present experimental results on graphene devices, where an applied electric field and changes in the Fermi level can be controlled by an external gate voltage, showing that Raman spectroscopy is useful to quantify the interaction of graphene with its surrounding environment. We will also show that Raman spectroscopy can be useful to characterize twisted graphene layers in samples grown by CVD on copper foils. Finally, we will present resonance Raman results of the electronic dispersion in uniaxial strained bilayer graphene.

Straining Graphene By CVD On Cu And Magnetotransport On Large Scale Graphene.

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Strain can be used as an alternate way to tune the electronic properties of graphene. Here we demonstrate that it is possible to tune the uniform strain of graphene simply by changing the chemical vapour deposition growth temperature of graphene on copper. Due to the cooling of the graphene on copper system, we can induce a uniform biaxial compressive strain on graphene. The strain is monitored by Raman spectroscopy, where a shift in the 2D peak is observed and compared to our *ab initio* calculations of the graphene on copper system as a function of strain. The most striking features are a change in Fermi velocity and more notably a shift in the Fermi energy with respect to the Dirac point as a function of strain [1]. With subsequent transfer of graphene onto SiO_2/Si via PMMA and thermal release tape magneto-transport measurements were performed. The resulting centimeter-sized graphene samples were measured at temperatures down to 30mK in a magnetic field, where we observe a very sharp peak in resistance at zero field, which is well fitted by weak localization theory. The samples also exhibit conductance fluctuations symmetric in field, which are attributed to large scale inhomogeneities consistent with the grain boundaries of copper during the CVD growth [2].

[1] V. Yu, E. Whiteway, J. Masseen, and M. Hilke, arXiv: 1101.1884
[2] E. Whiteway, V. Yu, J. Lefebvre, R. Gagnon, and M. Hilke, arXiv: 1011.5712

Ab initio study of optical properties of rippled graphene

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Isolation of graphene layer has opened new frontiers for the researches. Recent observations showed that suspended graphene sheets are not perfectly flat showing corrugations that has been detected from electron microscopy and diffraction. Besides the intrinsic corrugation structure of graphene supported on substrate was found to be dedicated by its roughness. Establishment of relation between properties and geometrical configuration of graphene may add to the design of electronic and optical devices.

We have performed ab initio calculations using plane-wave self-consistent field formalism to investigate electronic and optical properties of ripples graphene. Armchair-edged graphene models were constructed using a cylindrical arrangement of carbon atoms. The response is calculated using DFT with the random phase approximation.

Structure anisotropy causes the anisotropy in electronic properties. It was found that the density of states depends sensitively on the position of carbon atom on the curved surface of graphene. However all structures remain metallic with a low DOS value at the Fermi level. We found that corrugation of graphene results in appearance of additional peaks in the imaginary components of the dielectric function and in shift of main resonances typical for flat graphene for certain light polarization. Analysis of interband transitions demonstrated a contribution of electron transitions being forbidden for the flat graphene ($\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi^*$ transitions for $E \perp c$ and $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions for c II E) in the in-plane and out-of-plane components of dielectric function of rippled graphene. Thereby, we conclude that positions and shape of peaks in optical absorption spectra are very sensitive to the geometry of rippled models. Stressing the graphene mechanically or placing the layer on an artificial substrate one could control the graphene rippling constructing a material with optical properties adjusted for a certain application. Particularly, bending of graphene can tune optical transparency window of the material.

Graphene For Next-Generation Electronics: Limits And Perspectives

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Graphene has appealing physical properties for electronic applications like large carrier mobility, which has triggered an important collective effort aimed at a good understanding of its electrical behaviour. Still, from an engineering point of view, the main question to be answered is: “Will graphene be capable in the mid term to meet Semiconductor Industry requirements to keep the pace of Moore’s law?”.

The investigation of graphene-based devices is an open issue due to the many fabrications problems which remain unsolved. In this respect, numerical simulations can represent a powerful tool in order to assess the potential performance of graphene devices.

In this work, we present a simulation study to investigate the limits and the perspectives of graphene devices, considering a wide span of devices, ranging from graphene nanoribbons (GNR) to monolayer and bilayer graphene Field Effect Transistors.

The main issue regarding graphene is the lack of an energy gap, which prevents its use for digital electronic applications. Such issue can be overcome by defining lateral confinement through electron beam lithography or chemical procedures, which in turn introduce edge roughness drastically reducing electron mobility [1]. Through a full-band investigation of electron-phonon interaction, we will show that, even in the case of perfect edges, the intrinsic mobility of GNRs is strongly limited by remote phonon scattering, which leads to scattering lengths of the order of tens of nanometers for GNR widths of 1-2 nm, and mobilities of the order of few hundreds cm^2/Vs, three orders of magnitude smaller than mobility experimentally obtained in graphene [2]. Graphene hydrogenation can represent a viable way in order to induce a gap in graphene: the larger the degree of hydrogenation, the larger the energy band-gap. However, its electrical properties have not yet been thoroughly investigated. To this purpose, we have performed multi-scale simulations based on ab-initio calculations in order to compute deformation potential and mobility in graphene with different degrees of hydrogenation: even in the best case, we will show that expected mobility is smaller than that measured in bulk silicon.

An energy gap can also be electrically induced by means of an electric field in bilayer graphene: simulations results show that such material has potential for ultra-low voltage applications, when exploited in tunnel FET devices (the so-called green transistors). Analog electronics does not need an energy gap. Graphene, both monolayer and bilayer, shows huge potential when exploited in Esaki-like diodes, where a negative differential resistance can be observed. We will also show that bilayer graphene can be exploited in a current amplifier, since, even for short-channel devices, current saturation may occur to some extent, leading to quite large current gain.

[1] A. Betti et al. IEDM 2009, 5-7 December, Baltimore, USA.
[2] K.I. Bollotin et al., *PRL*, **101**, 096802, 2008.

Highly Efficient Exfoliation and Sorting of Graphite flakes

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We demonstrate high yield production of graphene in liquid phase [1] via low power sonication of graphite in sodium deoxycholate (SDC) followed by a separation in preparative ultracentrifugation. There are two main approaches to ultracentrifugation: sedimentation-based separation (SBS) and isopycnic separation. The former discriminates particles by their difference in mass. The latter exploits subtle density differences between particles in a density gradient medium [2,3]. A fracture mechanics model is presented to explain the exfoliation process. During sonication, the bubbles implosion imposes an inward radial fluid flow, which induces viscous forces on the graphite flakes [4]. Such forces must be sufficiently high for exfoliation, but low enough to avoid in-plane fracture, in order to produce large graphene flakes. Our results suggest that graphite exfoliation via sonication produces on average flakes with lateral sizes that increase with the number of layers. Thus the exploitation of SBS permits to obtain a separation based on the number of layers other than on their mass [5]. TEM and Raman spectroscopy indicate that ~65% of the flakes produced by SBS are monolayer with average size~600nm^2 [6,7]. Isopycnic separation, besides number of layers sorting, allows us to obtain larger flakes than SBS. The sorting strategy relies on the creation of density differences between graphite flakes with different number of layers. Surfactants provide this density variation [8]. We show that sorting by number of layers is strongly affected by the flakes surface/volume ratio and the coverage and clustering of the surfactant molecules. SDC is the most effective surfactant for exfoliation and sorting of graphite flakes, with ~60% of the flakes in the topmost fraction being monolayers, with average size 1μm^2.

[1] Y. Hernandez et al. *Nature Nano*, **3**, 563, (2008).
[2] M. S. Arnold et al., *Nature Nano*, **1**, 60, (2006).
[3] F. Bonaccorso et al., *Journal of Physical Chemistry C*, **114**, 17267, (2010).
[4] R. W. Fox, A. T. McDonald, P. J. Pritchard, *Introduction to Fluid Mechanic*, Wiley, 6 Edition ISBN 0471202312, (2003)
[5] F. Bonaccorso et al., submitted (2011).
[6] O.M. Marago' et al., *ACS Nano*, **4**, 7515, (2010).
[7] F. Bonaccorso et al., *Nature Photonics*, **4**, 611, (2010).
[8] A. A. Green et al, *Nano Lett*. **9**, 4031, (2009).

Facile Functionalization of Graphene Sheets with Photoactive Groups via "Click" Chemistry

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Graphene sheets (GS)decorated with various functional groups have attracted broad attention, for their potential application in various fields, such as photovoltaic, optoelectronics and nanosensor[1, 2, 3]. Herein we report a new way for the surface modification of GS under mild conditions, which is based on copper(I)-catalyzed 1,3-dipolar cycloaddition of azides and alkynes reaction, also known as "click" chemistry[4]. We employed GS modified by phenylacetylene moieties as a general platform for attaching various photoactive functional molecules via "click" chemistry. The produced functionalized GS exhibited good solubility in common organic solvents, making the manipulation very simple. Thin films of photoactive GS films on various substrates (SiO_2, ITO, etc.) were fabricated by spin-coating and Langmuir-Blodgett technique. The photo-induced electron transfer properties of the thin films of the photoactive GSs were characterized in a photoelectrochemical cell, which showed significantly improved photocurrent responses compared with the unmodified GS. Considering the advantages of "click" chemistry, such as high yield, easy reaction conditions, good reliability and the obtained triazole ring retains the conjugation required for electronic transport, this method is particularly well-suited for studying the charge transport properties between the attached functional groups and the GS. It is anticipated that the good chemical and opto-physical properties of the photoactive GS nanomaterials may find wide applications in photoenergy conversion or photosensing devices.

[1] Y.H. Zhang, Y.B. Chen, K.G. Zhou, C.H. Liu, J. Zeng., H.L. Zhang* and Y. Peng, *Nanotechnology*, **20**, 185504, (2009).
[2] Y.H. Zhang, K.G. Zhou, K.F. Xie, J. Zeng, H.L. Zhang* and Y. Peng, *Nanotechnology,* **21**, 065201, (2010).
[3] L. Tan, K.G. Zhou, Y.H. Zhang, H.X. Wang, X.D. Wang, Y.F. Guo and H.L. Zhang*, *Elechem. Comm.*, **12**, 557-560, (2010).
[4] H.X. Wang, K.G. Zhou, Y.L. Xie, J. Zeng, N.N. Chai, J. Li and H.L. Zhang*, *Chem.Comm.*, DOI:10.1039/C1CC11121C, (2011).

Electrically Switchable, Flexible Smart Windows Using Graphene-based Transparent Conductors

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Scarcity, brittleness, processing limitations and fabrication costs of Indium Tin Oxide (ITO) are crucial limiting factors towards the development of flexible displays and electronics requiring flexible, transparent conducting electrodes (TCEs). Carbon nanotubes (CNTs) and graphene offer ideal TCE alternatives[1,2,3,4]. Both CNT and graphene liquid dispersions can be used in roll to roll (R2R) processing. The performance of CNT networks is limited by inter-tube junction resistance. This can be reduced by interspersed graphene flakes. A solution processable hybrid CNT-graphene conducting film is therefore an attractive proposition for R2R manufacturability of electronic devices requiring flexible TCEs.

Electrically switchable smart windows (ESSWs) employ liquid crystal (LC) droplets embedded in a polymer, sandwiched between two TC electrodes. An electric field controls the overall alignment direction of LC molecules, allowing light modulation through the device[5]. The TCE requirements for ESSWs is high transmittance (>80%) and low sheet resistance, typically in the range of ~1kΩ/□ or smaller [6].Here, we demonstrate an up- scalable CNT-graphene hybrids TCE for a smart window. We employ wire-wound rod coating for the liquid dispersions of CNTs and graphene on a polyethylene terephthalate (PET) substrate. The CNT-graphene hybrid coating has 1kΩ/□ sheet resistance, 94-97% transparency in the visible spectrum with <2% standard deviation in optical uniformity across ~200cm^2. The TCEs exhibit ~15% change in resistance when bent to a radius of 3.5mm in 10 cycles, far surpassing the ~25000% increase in a 60 Ω/□ ITO sample. A 120cm^2 flexible smart window is then fabricated. The device exhibits excellent electric field induced light transmittance (~60%) even under flexion. When OFF, the device transmits <0.25%, giving a >230 contrast ratio.

[1] F. Bonaccorso, et al., *Nat Photon* **4**, 611 (2010).
[2] S. Bae, et al., *Nat Nano* **5**, 574 (2010).
[3] G. Gruner, *J. Mater. Chem*. **16**, 3533 (2006).
[4] S. De, et al., *Small* **6**, 458 (2010).
[5] J.L. Fergason US Patent 4435047, (1984).
[6] C.M. Lampert, *Sol. Energy Mater. Sol. Cells* **52**, 207 (1998)

Graphene xylophone

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We studied a mechanical resonance properties of graphene sheets and their applications. Rectangular shape of graphene sheet was prepared using O_2 plasma and suspended structure was made on the pre-patterned trench by the micro contact transfer printing method. Xylophone like structure was prepared for studying length and thickness dependence of mechanical properties of graphene resonator. Single layer graphene sheet shows nonlinear and bistable behaviors the actuation voltage was increased. The resonance frequency of graphene sheet can be tuned by applied DC bias voltage. Based on our results, we will suggest the potential application of the graphene resonator to the broadband tunable RF components

Size-homogeneous gold nanoparticle decorated on graphene via MeV electron beam irradiation

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Graphene, with its unique physical and structural properties, has recently become a proving ground for various physical phenomena, and is a promising candidate for a variety of electronic device and flexible display applications. The physical properties of graphene depend directly on the thickness. These properties lead to the possibility of its application in high-performance transparent conducting films (TCFs). Compared to indium tin oxide (ITO) electrodes, which have a typical sheet resistance of ~60 Ω/sq and ~85% transmittance in the visible range, the chemical vapor deposition(CVD) synthesized graphene electrodes have a higher transmittance in the visible to IR region and are more robust under bending. Nevertheless, the lowest sheet resistance of the currently available CVD graphene electrodes is higher than that of ITO. Here, we report an ingenious strategy, irradiation of MeV electron beam (e-beam) at room temperature under ambient condition, for obtaining size-homogeneous gold nanoparticle decorated on graphene. The nano-particlization promoted by MeV e-beam irradiation was investigated by transmission electron microscopy, electron energy loss spectroscopy elemental mapping, and energy dispersive X-ray spectroscopy. These results clearly revealed that gold nanoparticle with 10 ~ 15 nm in mean size were decorated along the surface of the graphene after 1.5 MeV-e-beam irradiation. The fabrication high-performance TCF with optimized doping condition showed a sheet resistance of ~100 Ω/sq. A chemical transformation and charge transfer for the metal gold nanoparticle were systematically explored by X-ray photoelectron spectroscopy and Raman spectroscopy. This approach advances the numerous applications of graphene films as transparent conducting electrodes.

Direct Writing of Width-tailored Graphene Nanoribbon on SiO_2 via Focused Ion Beam-assisted Chemical Vapor Deposition

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Graphene has been emerged as a fascinating material for future nanoelectronic applications due to its extraordinally electronic properties. However, their zero-band gap semimetallic nature is a major problem for applications in high performance field-effect transistors (FETs). Graphene nanoribbons (GNRs) with narrow widths ($\geq$ 10 nm) exhibit semiconducting behavior, which can be used to overcome this problem. In previous reports, GNRs were produced by several approaches, such as electron beam lithography patterning, chemically derived GNRs, longitudinal unzipping of carbon nanotubes, and inorganic nanowire template. Using these methods, however, the width distribution of GNRs was a quite broad and substantial defects were inevitably occurred. Here, we report a novel approach for fabricating width-tailored GNRs by focused ion beam-assisted chemical vapor deposition (FIB-CVD).Width-tailored phenanthrene ($C_{14}H_{10}$) templates fordirect growth of GNRs were prepared on SiO_2/Si substrate by FIB-CVD. The GNRs on the templates were synthesized at 900-1000^{o}C with introducing CH_4 (20 sccm)/H_2 (10 sccm) mixture gas for 10- 300 min. Structural characterizations of the GNRs were carried out using Raman spectroscopy, scanning electron microscopy, and atomic force microscopy.

Quantum Conductance Study On Doped Armchair Carbon Nanoribbons: First-Principles Calculations

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Electronic structure and quantum transport properties of chemically doped armchair carbon nanoribbons were studied by means of first-principles density functional theory in conjunction with Landauer-Bütiker formalism. The nanoribbons were doped in a substitutional fashion by replacing one carbon atom by boron, nitrogen, oxygen, silicon, phosphorus or sulfur atom. The dopant atoms were located in two different positions, at center and at the edge of the armchair nanoribbon. The quantum conductance, band structures, valence and conduction wave functions at the gamma point, energetic stability and current-voltage curves were analyzed. Results for boron, nitrogen and silicon doping revealed high currents exhibiting a linear currents-voltage curve; which could be used as inter-connector devices. In the case, of oxygen, phosphorus, and sulfur doping, the nanoribbons need high bias voltage to conduct; we envisage that these systems could be used in the fabrication of novel sensor devices.

High Frequency Coplanar Graphene Waveguides on Low-loss Dielectric Substrates

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Graphene is of great interest for high-frequency circuit applications, including high-f_T transistors [1,2]. High-frequency passive element applications based on gyrotropy have also been recently identified [3]. We present here our work on integration of graphene into low-loss coplanar waveguides (CPWs) using large area graphene fabrication methods. Chemical vapor deposition with a methane/hydrogen gas mixture at 900 °C was used to grow graphene on copper foils [4]. Raman spectroscopy was used to verify high-quality monolayer growth. A standard photoresist was used as the polymer handle for CVD graphene transfer to quartz substrates, where the functional diazo groups of the resist also served to heavily hole-dope the graphene [5]. A low- frequency sheet resistance of 1.1-1.3 kΩ /square was measured in the transferred graphene. Standard lithography and metal deposition techniques were used to form CPWs, after which graphene was patterned into signal-signal and signal-ground CPW test structures by oxygen plasma etching. The microwave scattering parameters, and thus impedance, of CVD graphene have been measured from 40 MHz to 40 GHz, with measurements up to 110 GHz underway. Great care was exercised in obtaining good calibrations and minimizing contact errors. Measurements are compared with full-wave electromagnetic field simulations. We find that the graphene aspect ratio can be easily used to control the transmitted and reflected microwave power. Our work sets the basis for high-frequency CPW circuits incorporating passive and active graphene circuit elements.

1. F. Schwiertz, "Graphene Transistors", *Nature Nanotech.*, **5**, 487-496 (2010).
2. Y. Wu, Y. Lin, A .Bol, K. Jenkins, F. Xia, D. Farmer, Y. Zhu, P. Avouris *Nature*, 472, 74-78, (2011).
3. D. Sounas, C. Caloz. *App. Phys. Lett.*, **98**, 021911:1-3, (2011).
4. A. Guermoune, T. Chari, F. Popescu, S. Sabri, J. Guillemette, H. Skulason, T. Szkopek, M. Siaj. under review.
5. D. Farmer, R. Golizadeh-Mojarad, V. Perebeinos, Y. Lin, G. Tulevski, J. Tsang, P. Avouris. *Nano Letters*, **9**, 1, 388-392 (2009).

Graphene Nano-Electrodes for DNA Sequencing: an Ab initio Perspective

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The proposal was made [1] that a graphene nanogap could be used to probe the transverse conductance of individual nucleotides in DNA to rapidly identify the associated base sequence. This approach is attractive because atomically-thin electrodes made from graphene could overcome the difficult issue of achieving single-base resolution. Experimentally, it has been demonstrated [2–4] that it is possible to measure the characteristic drop in ionic current associated with translocation events of DNA passing through a graphene nanopore. These findings make further developments of a graphene-based set-up aimed at whole-genome sequencing a highly promising direction.

Using first-principles methods, we have theoretically evaluated different aspects of the performance of two graphene nano-electrodes configurations for nucleobase identification. In the first study [5], we investigated the electronic transport properties of the four nucleotides when located in a graphene nanogap by employing density functional theory and the non-equilibrium Green's function method. In particular, we determined the electrical current variation at finite bias due to changes in the nucleotides orientation and lateral position. We explain the resulting fluctuations in the tunnelling current over several orders of magnitude, and conclude that a distinction between the four DNA bases appears in principle possible. Our second study [6] utilized molecular dynamics simulations in conjunction with electronic transport calculations to explore specifically the effect of the hydrogenated graphene edges on the translocating DNA. It is found that these edge-hydrogenated graphene electrodes can facilitate the temporary formation of H-bonds with suitable atomic sites in the nucleotides. As a consequence, compared to the case of bare graphene edges, the average conductivity is drastically raised by about three orders of magnitude while exhibiting significantly reduced statistical variance. Furthermore, we found that for narrow graphene electrodes separation, the mere hindrance due to the presence of protruding hydrogen atoms in the nanogap is deemed more important, while for wider electrode separation, the formation of H-bonds becomes the dominant effect.

[1] H. W. Ch. Postma, *Nano Lett.* **10**, 420-425, (2010).
[2] C. A. Merchant, K. Healy, M. Wanunu, V. Ray, N. Peterman, J. Bartel, M. D. Fischbein, K. Venta, Z. Luo, A. T. C. Johnson, and M. Drndić, *Nano Lett.* **10**, 2915-2921, (2010).
[3] G. F. Schneider, S. W. Kowalczyk, V. E. Calado, G. Pandraud, H. W. Zandbergen, L. M. K. Vandersypen, and C. Dekker, *Nano Lett.* **10**, 3163-3167, (2010).
[4] S. Garaj, W. Hubbard, A. Reina, J. Kong, D. Branton, and J. A. Golovchenko, *Nature* **467**, 190-193, (2010).
[5] J. Prasongkit, A. Grigoriev, B. Pathak, R. Ahuja, and R. H. Scheicher, *Nano Lett.*, published on-line (April 15, 2011), DOI:10.1021/nl200147x, preprint arXiv:1012.1669
[6] Y. He, R. H. Scheicher, A. Grigoriev, R. Ahuja, S. Long, Z. L. Huo, and M. Liu, *Adv.*

Funct. Mater., in press, DOI:10.1002/adfm.201002530, preprint arXiv:1012.0031

Graphene Logic Gates and Memories with Improved Current On/Off Ratio

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Over the past few years there has been a surge of interest in graphene, a recently isolated single sheet of graphite. From the application point of view this interest has mainly been driven by the high carrier mobility of graphene which enables fabrication of field-effect transistors (FETs) with much smaller channel resistance compared to their Si counterparts. In this manner, the ultimate limits of Si technology, which are expected at the sub-10 nm scale, may be overcome, paving the way for digital nanoelectronics. Here we demonstrate the operation of graphene logic gates and memories with a current on/off ratio much higher than this in conventional back-gated graphene devices.

The same resistance of a graphene FET can be obtained for two different gate voltages, one on either side of the Dirac point. This was exploited to fabricate four basic logic gates (XOR, NAND, OR, and NOT) with a single graphene FET. However, these logic gates require off chip resistors to operate, i.e., they are not integrated on the same graphene flake. An integrated graphene digital logic gate was obtained by integrating one p- and one n-type graphene FET on the same sheet of monolayer graphene. Both F ETs initially exhibited p-type behaviour at low gate voltages, since air contamination shifted their Dirac points from zero to a positive gate voltage. Contaminants in one FET were removed by electrical annealing, which shifted its Dirac point back and therefore restored n-type behaviour. Boolean inversion is obtained by operating the FETs between their Dirac points.

In order to improve the on/off ratio of graphene F ETs an alternative gate stack was fabricated. Incorporation of such graphene FETs in logic gates resulted in an increase in small-signal voltage gain of around two orders of magnitude in comparison to conventional back-gated devices. Use of these FETs in a complementary inverter eliminated need for current annealing and ensured a gain larger than unity under ambient conditions. Such a high gain is a main prerequisite for direct cascading of logic gates.

An alternative promising strategy to increase the on/off ratio relies upon patterning of graphene nanoribbons (GNRs), wherein quantum confinement and edge effects open a bandgap inversely proportional to the ribbon width. Here we demonstrate a high performance GNR memory cell based on a nondestructive storage mechanism, i.e., gate voltage pulses of opposite polarity are used to switch between the distinct on and off states of the device. The devices were fabricated by patterning graphene into nanoribbons using V_2O_5 nanofibres as etching masks. A pronounced memory effect is observed under ambient conditions, which is attributed to charge traps in the vicinity of the GNRs. Reliable switching between two conductivity states is demonstrated for clock frequencies of up to 1 kHz and pulse durations as short as 500 ns (tested limits) for $> 10^7$ cycles. The durable and stable memory cell can be rendered nonvolatile upon exclusion of oxygen and humidity. GNRs thus emerge as promising components of highly integrated memory arrays.

Energetics and Electronic Structures of Graphene Adsorbed on HfO_2 Surfaces

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Graphene has the great potential to advance both the low-dimensional sciences and the nano-scale electronic engineering. Recently, the integration of the graphene with a scalable gate dielectric, such as high permittivity (high-k) materials, has been the subject of the research with the goal of the realization of graphene-based electronic devices. For the fabrication of the graphene on insulating substrates, an understanding of its interactions with the substrates is critical, since they could directly affect the intrinsic electronic properties of the graphene. However, its underlying characteristics of the interaction are still far from being explained. Thus, we here study the energetics, geometry, and electronic structure of graphene adsorbed on (111) surfaces of cubic hafnia (HfO_2) using first-principles calculations in the framework of density functional theory (DFT) [1].

To simulate a hybrid structure of graphene and HfO_2, we considered an oxygen-terminated (111) surface of a cubic phase of HfO_2 possessing a triangular lattice of O atoms at the topmost layer. The surfaces were simulated using a repeated-slab model that includes five HfO_2 layers, graphene, and a 7 Å -vacuum region.

Our DFT calculations clarify that the graphene is bound to the HfO_2 surfaces with an interlayer spacing of 3.05 Å with a binding energy of about -110 meV per C atom. The electronic structure of the HfO_2-adsorbed graphene originates primarily from that of the graphene near the Fermi level. However, a detailed analysis of the electronic structure shows that the linear bands on the Dirac cone are slightly split, because of the interaction between the graphene and the HfO_2 substrate. The physical origin of this splitting is the hybridization between the π states of the graphene and the O *2p* state with Hf *d* character.

[1] K. Kamiya, N. Umezawa, and S. Okada, *Phys. Rev. B*, **83**, 153413, (2011).

Wideband Tunable, High-power Ultrafast Lasers Mode-locked By Graphene

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Ultrafast passively mode-locked lasers with spectral tuning capability and high output power have widespread applications in biomedical research, spectroscopy and telecommunications [1,2]. Currently, the dominant technology is based on semiconductor saturable absorber mirrors (SESAMs) [2,3]. However, these typically have a narrow tuning range, and require complex fabrication and packaging [2,3]. A simple, cost-effective alternative is to use single wall carbon nanotubes (SWNTs) [4-9] and graphene [9-14]. Wide- band operation is possible using SWNTs with a wide diameter distribution [5,9]. However, SWNTs not in resonance are not used and may contribute to unwanted insertion losses [9]. The linear dispersion of the Dirac electrons in graphene offers an ideal solution for wideband ultrafast pulse generation [9-13,15].
Here, we report graphene saturable absorbers (GSA) for wideband tunable and high power ultrafast laser sources. Tunable ultrafast pulses are generated with an Erbium-doped fiber laser mode-locked by GSA [11]. The output wavelength is tunable from 1525nm to 1559nm.Even wider range tunability is feasible with broader filters [11]. The full width at half maximum (FWHM) spectral bandwidth is ~3 nm. The output pulse duration is ~1 ps. High power ultrafast pulses are generated using a solid-state laser. A Nd:YVO_4 crystal is employed as gain medium. The peak output wavelength is ~1064 nm. The FWHM of the output spectrum is ~0.17nm. The average output power of the laser increases almost linearly with the pump power. The maximum average output power is ~1W at 2.6W pump power. The corresponding pulse energy is ~14nJ.

[1]Martin E. Fermann et.al., Ultrafast Lasers Technology and Applications, (2003) .
[2]U. Keller, Ultrafast solid-state lasers. (Elsevier, Amsterdam, 2004).
[3]U. Keller,*Nature* **424**, 831 (2003).
[4] S. Y. Set et al., in *Optical Fiber Communication Conference* (OFC), 2003.
[5] F. Wang et al.*Nat. Nanotechnol*. **3**, 738 (2008).
[6] Z. Sun et.al., *Appl. Phys. Lett*. **95**, 253102 (2009)
[7] V. Scardaci et al.,*Adv. Mater*. **20**, 4040 (2008).
[8] E. J. R. Kelleher et al., *Appl. Phys. Lett.* **95**, 111108 (2009).
[9] T. Hasan et.al., *Adv. Mater*. **21**, 3874 (2009).
[10] Z. Sun et.al., *ACS Nano* **4**, 803(2010).
[11] Z. Sun et.al., *Nano Res*. **3**, 653(2010).
[12] F. Bonaccorso et.al., *Nat. Photonics* **4**, 611(2010).
[13] D. Popa et.al.,*Appl. Phys. Lett*. **97**, 203106 (2010).
[14] D. Popa et al., *Appl. Phys. Lett*. **98**, 073106 (2011).
[15] A. K. Geim et al.,*Nat. Mater*. **6**,183(2007).

Selective Edge Functionalization of Graphene by Room Temperature Mild Plasma Treatment

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Room-temperature controllable edge functionalization and doping of graphene by a NH_3 plasma has been developed [1]. Based on a detailed Raman mapping analysis and an electrical measurement, a direct correlation between carrier doping and selective edge functionalization has been revealed for the first time. The Raman mapping analysis shows that the D-peak near the edge of the graphene sheet is selectively increased after NH_3 mild (m)-plasma treatment. The electrical measurement reveals that the Dirac point position of the graphene nano ribbon (GNR) device clearly shifts toward a negative gate-bias voltage after NH_3 m-plasma treatment. This selective edge functionalization and doping by controlled plasma treatment could yield outstanding benefits in realizing graphene-based high- performance nanoelectronic device applications.

[1] T. Kato, L. Jiao, X. Wang, H. Wang, X. Li, L. Zhang, R. Hatakeyama, and H. Dai, *Small* **7**, 574 (2011).

Fabrication of Graphene-based Electronic Devices by Selective Electrochemical Reduction in Air.

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While graphene application in digital electronics does require very high performance, there are other promising sectors (packaging, plastic electronics etc.) where, more than high charge mobility, cost reduction will be fundamental. This can be achieved by bulk production and chemical processing of graphene in liquids or air, at room temperature.

Here we describe a simple approach to fabricate graphene-based field-effect-transistors (FETs), starting from aqueous solutions of graphene-oxide (GO), processed entirely under ambient conditions. The process relies on the site-selective reduction of GO sheets deposited in between micro- or nano-electrodes. The same electrodes are first used for voltage-induced electrochemical GO reduction, and then as the source and drain contacts of FETs, allowing for the straightforward production and characterization of ambipolar devices. The nano-scale morphology and electric properties of the devices are then studied by conductive and Kelvin Probe scanning microscopy.

An overview of potential applications of graphene deposited on or embedded into different organic materials will also be given

Epitaxial CVD Growth of Single-Layer Graphene over Metal Films Crystallized on Sapphire and MgO

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Graphene is emerging as a new building block of future nanoelectronics and microelectromechanical systems. Recently, catalytic CVD growth has attracted considerable interest as an effective means to produce large-area graphene films. However, because most of the CVD growth has been done over polycrystalline metal foils/films, as-grown graphene has relatively s mall grain size and its orientation is not controlled. We studied the growth of graphene films over crystalline metal films deposited on single crystalline substrates and reported the formation of square and triangular-shaped graphene films on such crystalline metal catalyst [1].
Here, we performed atmospheric CVD growth over crystalline Co and Cu films deposited on c-plane sapphire or MgO(111) substrates. Large-area, uniform single-layer graphene was obtained on the Co film in spite that Co metal has high carbon solubility at high CVD temperature [2]. The low-energy electron diffraction (LEED) measurements revealed that the orientation of single-layer graphene matches with underneath Co(111) (or Cu(111)) lattices indicating epitaxial CVD growth of graphene [2,3]. This enables us to determine the graphene orientation from the sapphire's crystallographic orientation. Furthermore, the as-grown graphene was found to have very large domain size from the low-energy electron microscope (LEEM) analysis. We also demonstrate that amorphous carbon can be converted to uniform single-layer graphene by simply annealing it on crystalline Co or Ni films deposited on sapphire [4]. Our study offers a new route to grow high-quality single-layer graphene even on different metal films and gives new insights into the growth mechanism of graphene.

[1] H. Ago, I. Tanaka, C. M. Orofeo, M. Tsuji*, Small*, **6**, 126 (2010).
[2] H. Ago, Y. Ito, N. Mizuta, K. Yoshida, B. Hu, C. M. Orofeo, M. Tsuji, K. Ikeda, S. Mizuno, *ACS Nano*, **4**, 7407 (2010).
[3] B. Hu, H. Ago, Y. Ito, M. Tsuji, E. Magome, K. Sumitani, N. Mizuta, K. Ikeda, S. Mizuno, submitted.
[4] C. M. Orofeo, H. Ago, B. Hu, M. Tsuji, *Nano Res.*, in press.

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Graphene Technology: Production, Assembly & Applications

Multifunctional Composite Membranes Based on Graphene and Graphene Oxide Sheets

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Pristine graphene sheets, both single-layer and fewer-layer, have attracted much recent attention for their unique and/or superior properties, such as high mechanical strength, large carrier mobility and ballistic transport, and extreme thermal conductivity. For the preparation of single-layer graphene in a popular wet chemical exfoliation route, pristine graphite is exhaustively oxidized under harsh conditions to yield readily exfoliated graphene oxide (GO), which can be subsequently converted to reduced graphene. Recently, there is an emerging recognition on the excellent properties of GO themselves for material applications. In particular, GO presents some amphiphilic character and has demonstrated enhanced capability in homogeneously dispersing carbon nanotubes to form relatively stable aqueous suspensions for subsequent device fabrication and other purposes. In this reported work, we used aqueous GO to effectively disperse mono- and few-layer graphene sheets in suspension for facile wet-processing into nanocomposite membranes having a wide range of GO weight fraction (10- 100 wt%). The resulting lightweight and flexible nanocomposite materials remained structurally stable even at high loadings of pristine graphene, whereas their mechanical behavior was found to depend on the GO/graphene ratio. As an example of their superior properties, these lightweight plastic-like materials were found to be highly efficient as dry preforms for the impregnation of epoxy resin in the porous galleries of the macroscopic membrane. The reported work serves to demonstrate the great potential of GO as a unique class of two-dimensional polyelectrolyte material, for the fabrication of multifunctional carbon-based nanocomposites, which may find technological applications independent of those widely proclaimed for graphene sheets.

[1] L. Tian, et al., *ACS Appl. Mater. Interf.* **2**, 3217–3222 (2010).
[2] Z. Spitalsky et al., *Mater. Sci. Engin. B* **165**, 135-138 (2009).
[3] Z. Spitalsky et al., *Progr. Pol. Sci.* **35**, 357-401 (2010).

Synthesis and Characterization of PET/Expanded graphite Nanocomposites

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Graphene has emerged as a subject of enormous scientific interest due to its exceptional electron transport, mechanical properties, and high surface area. These atomically thin two-dimensional sheets of carbon has a high basal plane elastic modulus, E ≈1 TPa, and ultimate strength of ~ 130 GPa [1], and extraordinary high room temperature carrier mobility (200 000 cm^2/V s) [2], and also high thermal conductivity (5000 W/(m K)) [1]. Adding of highly exfoliated carbon layers can significantly alter mechanical and electrical properties of polymers at extremely small loading. Graphene can be derived directly from naturally occurring graphite via top-down methods such as mechanical cleavage and liquid-phase exfoliation [3-4]. In these work, we reported an efficient method to prepare poly(ethylene terephthatale)/expanded graphite (PET/EG) nanocomposites by in situ polymerization of PET in the presence of exfoliated graphite. By adjusting the feed ratio of PET to EG, various composites with 0.025-0.4 wt% content of graphite were obtained. The effect of the presence of exfoliated graphite in PET matrix on electrical, thermal, mechanical was studied by using dielectric spectroscopy, differential scanning calorimetry (DSC), dynamic mechanical-thermal analysis (DMTA), thermogravimetric analysis (TGA) and tensile testing. Morphologies of the nanocomposites were examined using both SEM and TEM. Our studies have shown that electrical conductivity and thermal stability of PET were notably enhanced by the introduction of EG. The electrical percolation threshold values is 0.05 wt% (EG). The crystallization behaviour of PET/EG nanocomposites was not significantly influenced by the presence of the graphite in PET matrix.

[1] H .Kim, A. A. Abdala, C. W. Macosko, *Macromolecules*, **43**, 6515-6530 (2010).
[2] Z. Xu and C. Gao, *Macromolecules* **43**, 6716–6723 (2010).
[3] J.R. Potts et al. *Polymer* **52**, (2011). Y. Hernadez et al.,*Nature Nanotechnology* **3**, 563-568 (2008).

Ab initio quantum transport in defective and chemically-modified graphene

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In the present work, quantum transport properties of disordered graphene with structural defects (Stone-Wales and divacancies) are investigated using a realistic $\pi \rightarrow \pi^*$ *tight-binding* model elaborated from accurate ab initio calculations [1]. Mean free paths and semi classical conductivities are computed as a function of the nature and density of defects (using an order- *N* real-space Kubo-Greenwood method). By increasing the defect density, the decay of the semiclassical conductivities is predicted to saturate to a minimum value over a large plateau of carrier density ($> 0{,}5 \times 10^{14}$ cm^{-2}). Additionally, strong contributions of quantum interferences suggest that the Anderson localization regime could be experimentally measurable for a defect density as low as 1%. The effects of extended line of defects on the electronic properties of graphene are also briefly described [2].

The electronic and transport properties of graphene after epoxide functionalization via ozone treatment is also studied using the same numerical method [3]. The orbital rehybridization induced by the epoxide groups triggers a strong intervalley scattering and changes dramatically the conduction properties of graphene. By varying the coverage density of epoxide defects from 0.1 to 4%, charge conduction can be tuned from a diffusive to a strongly localized regime, with localization lengths down to a few nanometers long. Our theoretical predictions provide a physical interpretation to the metal-insulator transition observed experimentally.

[1] A. Lherbier, S.M.-M. Dubois, X. Declerck, S. Roche, Y.M. Niquet, and J.-C. Charlier *Phys. Rev. Lett*. **106**, 046803 (2011).
[2] A. Botello-Mendez, X. Declerck, M. Terrones, H. Terrones, and J.-C. Charlier *Nanoscale*, in press (2011).
[3] N. Leconte, J. Moser, P. Ordejon, H. Tao, A. Lherbier, A. Bachtold, F. Alsina, C.M. Sotomayor Torres, J.-C. Charlier, and S. Roche, *ACS Nano* **4**, 4033-4038 (2010).

Large-grain Graphene Synthesis and Graphene-based Nanoelectronics

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Graphene has been reported as a promising material due to the fascinating electronic properties of ideal two-dimensional carbon. Tremendous efforts have been made on the synthesis of large-area, single-layer graphene with high quality. Chemical Vapor Deposition (CVD) method has been utilized most to achieve scalable, single-layer graphene synthesis. However, the grain size of CVD graphene is usually limited to a few tens of micrometers. The grain boundaries in CVD graphene have been found to degrade the mobility of graphene devices, hence increasing the grain size of graphene is of great importance for high- performance graphene-based electronics. Here we report a novel CVD method for the synthesis of large-grain graphene on copper foils. We were able to transfer the as-grown graphene onto Si/SiO$_2$ substrate, and micro-Raman spectroscopy and optical microscopy were applied for film characterization. In addition, back-gate graphene transistors were fabricated and electrical measurements were performed to evaluate the transport properties of the synthesized graphene. Our approach demonstrates that the large-grain CVD graphene transferred onto Si/SiO$_2$ is a promising material for wafer- scale silicon-compatible fabrication of graphene electronics.

Due to large current densities, very high carrier mobility and high saturation velocity, graphene transistors are of primary interest for high-performance radio frequency (RF) electronics. Based on the synthesized CVD graphene films, we developed scalable, self- aligned methods for fabrication of graphene field-effect transistors (FETs). This approach provided simplified and reliable way for fabrication of large number of graphene devices and/or very wide channel transistors. Additionally, the self-aligned approach allows us to improve design of graphene FET by reducing the effect from parasitic capacitances and resistances. Based on this approach, we obtained graphene FETs with gates lengths in the range of 200 nm to 130 nm with scaled transconductances up to 0.5 mS/μm. The improved device design allowed achieving actual transistor RF performances with cut-off frequencies up to 20 GHz and maximum oscillation frequencies up to 10 GHz. These results illustrate steps toward practical implementation and integration of graphene devices for radio frequency electronics.

Spectroelectrochemistry of Single and Double Layered Graphene

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The latest advances in chemical vapor deposition (CVD) synthesis have now allowed the preparation of large and uniform monolayer graphene monolayers. The CVD prepared graphene thus significantly simplifies the materials processing and more detailed studies with such samples can be readily performed. The successful application of graphene requires a detailed understanding of its electronic properties, both in its neutral and doped states. The doping of graphene leads to a shift of the Fermi level and for this reason doping provides a simple way to control the transport and optical properties. In our study the electrochemical charging has been applied to study the influence of doping on the intensity of the various Raman features of chemical vapor deposition –grown graphene. Three different laser excitation energies have been used to probe the influence of the excitation energy on the behavior of both the G and G' modes regarding their dependence on doping. The intensities of both the G and G' modes exhibit a significant but different dependence on doping. While the intensity of the G' band monotonically decreases with increasing magnitude of the electrode potential (positive or negative), for the G band a more complex behavior has been found. The striking feature is an increase of the Raman intensity of the G mode at a high value of the positive electrode potential, due to partial canceling of interfering transitions, which is an important breakthrough in the understanding of the Raman process in graphene.

Plasmonic Enhanced Graphene Photodetector

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The electrical and optical properties of graphene make it an ideal material for photonics and optoelectronics [1]. Graphene based photodetectors with a bandwidth up to 16 GHz have been demonstrated [2]. In these detectors, the separation of the photo-generated electron-hole pairs relies on the formation of a pn-junction in the vicinity of the metal contacts. The metal contacts lead to a Fermi level shift underneath the contacts, due to the difference in work function of metal and graphene [3]. However, the electrical signal produced when shining light on the graphene-based photodetector is small compared to traditional semiconductor based detectors [2,4], due to the small 2.3% absorption of graphene [5]. In order to increase the effective light absorption, we integrate plasmonic nanostructures into the devices, so to collect light over a larger area and concentrate the light energy into the near-field region right where the pn-junction is located. Metal nanogratings and nanodots are fabricated on graphene by e-beam lithography. Photovoltage mapping is then carried out at different gate voltages, laser powers, polarizations and wavelengths. Raman spectroscopy [6] is used to confirm monolayer thickness, probe doping levels [7,8] and confirm absorption enhancement [9]. We detect up to 20 times photovoltage enhancement in the device with metal nanostructures. Also, we find a wavelength dependent response, tuneable by the geometry of the applied metal nanostructures. Further, the polarization dependence of the incident light with respect to the nanostructures orientation strongly influences the magnitude of the generated photovoltage, being maximum for polarization parallel to the axis of our nanogratings.

[1] F. Bonaccorso, Z. Sun, T. Hasan, A.C. Ferrari, *Nat. Photonics* **4**, 611 (2010).
[2] T. Mueller, F. Xia, P. Avouris, *Nat. Photonics* **4**, 297 (2010).
[3] G, Giovanetti et. al., *Phys. Rev. Lett.* **101**, 026802 (2008).
[4] F. Xia et. al., *Nano Lett.* **9**, 1039 (2009).
[5] R.R. Nair et. al., *Science* **320**, 5881 (2008).
[6] A.C. Ferrari et. al., *Phys. Rev. Lett.* **97**, 187401 (2006).
[7] A. Das et. al., *Nat. Nanotech.* **3**, 210 (2008).
[8] S. Pisana et. al., *Nat. Mater.* **6**, 198 (2007).
[9] F. Schedin et. al., *ACS Nano* **4**, 5617 (2010).

Graphene Coplanar Waveguides

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Graphene is a promising material for high frequency applications, such as transistors, passive circuit elements and interconnects, and optoelectronic devices [1-4]. An example of a RF interconnect is the coplanar waveguide (CPW), the two-dimensional planar equivalent of the coaxial transmission line[5-7]. This is usually realized by placing three in-line planar copper conductors [5,6]. The central one carries the signal, while the other two are the ground conductors, thus enabling guided electromagnetic wave propagation between them [6]. CPWs are widely exploited to integrate passive and active components into complete systems-on-chip or microwave monolithic integrated circuits (MMIC) [6]. Compared to the traditional microstrip, a CPW offers numerous advantages, such as quasi-transverse electromagnetic wave propagation [6], low dispersion [8], compact MMIC integration [6,9], low cross-talk[10] and broadband operation[5,6]. Here we realize and characterize a graphene coplanar waveguide (G-CPW). Exfoliated graphene flakes are patterned using e-beam lithography and contacted with Cr/Au electrodes suitable for ground-signal-ground (G-S-G) probing. The graphene conductors of the CPW are 20μm in length, 30 μm wide and are spaced 4 μm apart. The Au electrodes conformally overlap the patterned graphene conductors and taper out to G-S-G pads of pitch suitable for microwave probes interfaced to a vector network analyzer. We show that the back-gate modulated scattering-parameters of a G-CPW have two distinct regions of frequency-response up to 13.5GHz. The first shows a frequency independent behavior at low gate bias but changes to 1/f for gate bias up to ±50V and at frequencies below 1GHz due to substrate loss. The second region shows a $1/f^2$ response at all gate bias for frequencies higher than 1GHz, indicating the impact of inductance and capacitance on the electromagnetic transport properties of a G-CPW at higher frequencies. This intrinsic impedance of the G-CPW demonstrates significantly improved RF performance compared to a similar design CPW based on conventional materials [6].

[1] Avouris P., et al., *Nature Nanotech.*, **2** (2007), 605.
[2] Xia F., et al., *Nano Lett.*, **10** (2010), 715.
[3] Lemme M. C., et al., Solid-*State Electron.,* **52** (2008), 514.
[4] Bonaccorso F., et al., *Nature Photon.,* **4** (2010), 611.
[5] Wen C. P., *IEEE Trans. MTT*, **17** (1969), 1087.
[6] Wolff I., ‘Coplanar Microwave Integrated Circuits’, Wiley-Interscience, 2006.
[7] Awan S. A., et al., ‘Coaxial Electrical Circuits for Interference-Free Measurements’, Institution of Engineering and Technology, 2011.
[8] Becker J. P. and Jager D., *Electronics Lett.*, **15** (1979), 109.
[9] Heinrich W., *IEEE Trans. MTT,* **38** (1990), 1468.
[10] Papapolymerou J., et al., *IEEE Trans. MTT*, **52** (2004), 1292.

Ultrafast Non-Thermal Electron Dynamics In Single Layer Graphene

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The dynamics of elementary excitations in graphene has been the object of a great deal of studies, aimed at understanding the fundamental relaxation mechanisms[1,2]. Following ultrafast photoexcitation, a strongly non-equilibrium (athermal) distribution of electrons in the conduction band (and holes in the valence band) is established. This then rapidly thermalizes due to electro-electron interaction, giving rise to an electron distribution with a well defined temperature, which in turn reaches thermal equilibrium with the colder lattice via electron-phonon scattering [3]. These equilibration processes change the transient absorption spectrum over a broad range of energies and an ultrafast timescale. Their time- domain observation calls therefore for the combination of very short pulsewidths with wide spectral tunability.

Here we perform pump-probe spectroscopy on graphene using two-color few-optical-cycle pulses, thus combining high time resolution with broad spectral coverage [4]. Differential transmission experiments are carried out on graphene deposited on a fused silica substrate. We impulsively excite optical transitions with an ultra-broadband 6-fs pulse centered at 2.3 eV (2-2.5 eV bandwidth) and probe with a red-shifted 13-fs pulse covering the 1.4-1.6 eV range. The overall time resolution of our apparatus (width of the pump-probe cross- correlation) is 15 fs. We find that the delay in the formation of the photo bleaching signal in the probe spectral window is shorter than our time resolution, suggesting that the early scattering dynamics are extremely fast. The photo bleaching signal then relaxes on the 200-fs timescale at all the probe photon energies, that in our system are simultaneously recorded by an optical multichannel analyzer.

By studying the dependence of the dynamics on the pump pulse energy we could observe that at high fluencies the build-up of the photobleaching signal remains “instantaneous”, but a new ultrafast decay channel (around 20 fs time constant) is detected.

[1] Z. Sun et al., *ACS Nano* **4**, 803 - 810, (2010).
[2] F. Bonaccorso et al., *Nature Photonics* **4**, 611 - 622 (2010).
[3] M. Breusing et al., *Phys. Rev. B* **83**, 153410 (2011).[
[4] D. Brida et al., *J. Opt.* **12** 013001 (2010).

Microwave Impedance Measurements of Graphene and Graphene Oxide

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Non-invasive measurement methods for assessing the quality of graphene films are important for future applications of this remarkable material. We are developing a microwave impedance measurement method for this purpose. Large scale graphene layers have been deposited at Imperial College, by a number of routes, including graphene oxide liquid phase preparation as well as CVD deposition on a range of substrates. Transport properties of these samples are being investigated at NPL, without the need for electrical contacts, by making microwave surface impedance measurements. A graphene or graphene oxide sample deposited on a low microwave loss dielectric such as quartz perturbs both the microwave resonant frequency and quality factor Q of a high Q dielectric resonator. Modelling of the combined dielectric resonator, graphene layer and substrate properties enable these measurements to estimate the real and imaginary dielectric constants of the graphene layer. The variation of microwave resonant frequency and loss with heat treatment can then reveal the removal of adsorbed or intercalated water from the graphene samples. Further modifications, including operation of this system at cryogenic temperatures should reveal more details of temperature dependent mobility. In addition we have begun investigating the mechanical properties of suspended graphene oxide films using substrates with pre-patterned wells over which a graphene sheet can be deposited. We may then use a modification of the high Q dielectric resonator system as a microwave near-field scanning microscope to measure both the electromagnetic and the mechanical responses of suspended graphene films.

Spin-Orbit Coupling And Weak Localisation In Graphene

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We model the influence of spin-orbit coupling on electronic transport in graphene, particularly on the weak localisation correction to conductivity. As is often the case in semiconductors, the presence of spin-orbit coupling in graphene will tend to produce an anti-localization effect. As temperature is lowered, this would be manifest as a change in the sign of the magnetoconductivity $\delta\sigma(B) < 0$ as the dephasing length increases beyond the relevant spin-orbit length scale. An alternative scenario is that the spin-orbit coupling conserves the out-of-plane (z) component of electronic spin. This type of spin-orbit coupling leads to a random precession of the electron spin around the z axis, causing the relaxation of the in-plane polarization of electrons. It also distinguishes between up and down spin electrons, generating, for each, an effect equivalent to time-reversal symmetry breaking for Dirac electrons, and, therefore, it suppresses weak localization. We discuss the possible origin of such spin-orbit coupling in graphene, including intrinsic effects and the role of disorder, and we explain how measurements of magnetoconductivity in mesoscopic devices may shed light on sources of spin decoherence in graphene.

Towards Chiral Angle Control of SWNT's: Insights from a Hybrid MD/MC Modelling Approach

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One of the major obstacles in making SWNTs applicable in everyday (electronic) applications on the large scale, is our current inability to control the exact properties, and specifically the chirality of the tube. On a fundamental level, the mechanism of chirality determination is indeed not yet known. While many researchers have worked on the growth of SWNTs using atomistic simulation techniques, these works have always resulted in highly defected structures, due to the neglect of long time scale effects, preventing the study of the chirality during the growth. Recently, we have demonstrated the importance of taking these long time scale effects into account (by combining MD and MC simulations), in generating a SWNT with a definable (12,4) chirality [1]. In the first part of the presentation, we focus on the growth mechanism as well as on the exact mechanism of chirality formation using this novel simulation methodology. The observed SWNT growth process is found to proceed through a number of distinct steps, viz. the dissolution of carbon in the metallic particle, the surface segregation of carbon with the formation of aggregated carbon clusters on the surface, the formation of graphitic islands that grow into SWNT caps, a restructuring process of the carbon network in which many topological defects are healed, and finally continued growth of the SWNT. Furthermore, it is demonstrated that it is possible that the chirality still changes after the initial cap formation, through a metal-mediated restructuring process. Specifically, we observe the SWNT chirality to change from (11,0) (i.e., zigzag type) to finally (7,7) (i.e., armchair type). In the second part of the talk, the effect of applying electric fields on the growth of SWNTs will be demonstrated. Indeed, while SWNT's are traditionally grown in arc discharges, laser ablation sources or in catalytic chemical vapor deposition (CCVD), SWNT's can now also be grown by means of plasma-enhanced chemical vapor deposition (PECVD). Besides the lower growth temperature, PECVD has additional advantages over thermal CVD such as alignment of the SWNTs during the growth (instead of forming spaghetti as in thermal CVD). Using small, surface bound nickel nanoparticles as catalysts, we demonstrate how the electric field can enhance the phase separation between the carbon and the nickel. When applying weak electric fields, phase separation is barely enhanced and typical thermal CVD growth results emerge. Applying higher electric fields, however, enhances the phase separation and forces the nucleation of the SWNT cap to occur in alignment with the field, resulting in aligned SWNT growth. Finally, when applying very strong electric fields, SWNT caps can no longer nucleate, and amorphous carbon is formed instead.

[1] Neyts et al., *ACS Nano* **4** , 6665, (2010).

Charge Transfer between Metal Clusters and Growing Carbon Structures in Chirality-Controlled Single Walled Carbon Nanotube Growth

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Synthesis of single walled carbon nanotubes (SWCNTs) with specific chirality has been a great challenge. The detailed role of catalyst clusters in chirality-selective growth of SWCNT is still unclear. We studied armchair (5,5), chiral (6,5) and zigzag (9,0) nanotube growths on a relaxed Ni55 cluster. Although adhesion energies and chemical potentials of growing carbon structures only show small differences, charges are evidently transferred (or redistributed) from Ni atoms to the growing end-edges of nanotubes, which enhance the reactivity of carbon edges. Different chiral nanotubes exhibit distinct reaction active sites. (5,5) has five identical double-carbon active sites, while (9,0) has nine single-carbon active sites. (6,5) has a kink site with the highest reaction activity. These findings imply the structure of metal clusters strongly correlate with nanotube growth sites through charge transfer (or redistribution). Potential opportunities exist in enabling (n,m) selective growth by engineering charge transfer between metal clusters and growing carbon structures.

[1] Wang, Q.;Yang, S. W.; Yang, Y. H.; Chan-Park, M. B.; Chen, Y., *Journal of Physical Chemistry Letters*, **2**, 1009-1014, (2011).
[2] Wang, Q.; Lim K. H.; Yang, S. W.; Yang, Y. H..; Chen, Y., *Theoretical Chemistry Accounts*, **128**, 17-24, (2011).
[3] Wang, Q.; Ng M. F.; Yang, S. W.; Yang, Y. H..; Chen, Y., *ACS Nano*,**4**(2), 939–946, (2010).

Mechanism of the Initial Stages of N-SWCNT Growth

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Substitutional doping with nitrogen atoms has been proposed as a possible way for controlling the electronic properties of carbon nanotubes (CNTs). A variety of methods are available for the synthesis of nitrogen-doped multiwalled carbon nanotubes(N-MWCNTs). However, synthesis of single-walled nitrogen-doped carbon nanotubes (N-SWCNTs) has struggled to overcome difficulties foreign to the synthesis of pristine material[1]. Efforts to master the synthesis of N-SWCNTs have been hindered by an acute lack of knowledge about the chemistry involved and the growth mechanism [1,2]. We have studied for the first time the mechanism of the initial stages of N-SWCNT growth [3] illustrated for the case of a floating catalyst chemical vapor deposition system, which uses carbon monoxide (CO) and ammonia (NH_3) as precursors and iron as catalyst [4]. We performed first-principles electronic-structure calculations, fully incorporating the effects of spin polarization and magnetic moments [5], to investigate the bonding and chemistry of CO, NH_3, and their fragments on a model Fe_{55} icosahedral cluster. A possible dissociation path for NH_3 to atomic nitrogen and hydrogen was identified, with a reaction barrier consistent with an experimentally determined value we measured by tandem infrared and mass spectrometry. Both C–C and C–N bond formation reactions were found to be barrierless and exothermic, while a parasitic reaction of HCN formation had a barrier of over 1 eV.

[1] P. Ayala, R. Arenal, A. Loiseau, A. Rubio and T. Pichler, *Rev. Mod. Phys.*,**82**, 43, (2010).
[2] C. P. Ewels et al.,in *Chemistry of Carbon Nanotubes*, (2008).
[3] T. Susi et al., *Physical Chemistry Chemical Physics*,submitted, (2011).
[4] T. Susi et al., *Chemistry of Materials, article ASAP*, doi: 10.1021/cm200111b, (2011).
[5] G. Lanzani et al., J. Phys. Chem. C, 113, 12939, (2009).

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CCTN11

Numerical Modelling Of Metal-Catalyzed Growth Process Of Carbon Nanotube And Related Properties Of Catalytic Metal Nanoparticles

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Thanks to a lot of efforts to understand formation mechanism of carbon nanotubes during metal-catalyzed growth process, there has been a broad consensus that the initial cap structure is nucleated on the surface of the metal nanoparticle, followed by subsequent longitudinal growth. One of the remaining issues is to understand a key factor determining a chirality of the carbon nanotube. Here, recent numerical approaches on this issue, which focus on the orientation relationship between the graphite and metal surface and the structure of catalytic- metal nanoparticle at the high temperature, will be discussed.

Rims Of Carbon Nanotubes: A Possible Path To Chiral Selective Growth ?

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The chirality of a carbon nanotube determines its electronic and mechanical properties. To control the properties of a carbon nanotube sample it is necessary to control the chiralities within the sample. Chirality control is desired in the growth process, as nanotubes could be directly grown into devices instead of using post processing methods. The growth can be divided into two stages. The nucleation phase and the elongation stage. The nucleation phase is especially important, as the cap nucleated in this phase determines the chirality of the tube. [1] Almost all studies on the nucleation process model the nucleation without taking into account chiral selectivity. Liu et al attempted to describe chiral selectivity in the nucleation phase concentrating on the rim of the nanotubes. [2] The study, however, did not consider pentagons, needed for the inclination of the cap, and neglected the change in the rim structure with every carbon addition.[3,4] To understand the chiral selectivity in the nucleation process we determine the interaction between the cap and the catalytic particle. We calculate the atomic binding energies of the atoms in carbon nanotube caps with various chiralities on metallic clusters using density functional theory. The rim is directly connected to the cluster forming carbon-metal bonds. We find that carbon-metal bonds are the main influencing part for the cap-cluster interaction, as they have the weakest binding energies. The armchair and zigzag parts of the rim have varying bond energies depending on their neighboring atoms. Especially rim atoms in pentagons have lower bond energies. Small changes of the atom positions between rim and catalytic particle can influence the bond energies significantly. We conclude that the chiral selective carbon nanotube nucleation phase cannot be modeled by only considering the rim of a nanotube. It is necessary to consider the rim atoms of the cap structure and the neighboring atoms of the catalytic particle to model the nucleation phase. But this leads to the conclusion that chiral selective growth of a single chirality is not possible, as experimental evidence suggests that catalytic particles have a dynamic structure. [5] Our study will help to improve/rethink the models for chiral selective growth of carbon nanotubes.

[1] Stephanie Reich, Lan Li, and John Robertson, *Chemical Physics Letters*, **421**, 469 , (2006).
[2] Yuanyue Liu, and Alex Dobrinsky, and Boris I. Yakobson, *Phys. Rev. Lett*,. **105**, 235502, (2010).
[3] Heiko Dumlich and Stephanie Reich, *Phys. Rev. B*, **82**, 085421, (2010).
[4] Heiko Dumlich and Stephanie Reich, *Phys. Stat. Solidi B*, **247**, 2722, (2010).
[5] Stephan Hofmann, Renu Sharma, Caterina Ducati, Gaohui Du, Cecilia Mattevi, Cinzia Cepek, Mirco Cantoro, Simone Pisana, Atlus Parvez, Felipe Cervantes-Sodi, Andrea C. Ferrari, Rafal Dunin-Borkowski, Silvano Lizzit, Luca Petaccia, Andrea Goldoni, and John Robertson, *Nano Lett*,. **7**, 602, (2007).

Electron beam knock-on damage in graphene and white graphene

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Recent advances in high resolution transmission electron microscopy (HRTEM) have allowed the imaging of atomic-scale defects in graphene [1], carbon nanotubes and other nanoscale objects. We have combined state-of-the-art HRTEM with atomistic computer simulations to study the effects of the electron beam on these structures.

Specifically, we have investigated the possible reason for the formation of the triangular vacancy structures in hexagonal boron nitride (h-BN) mono-layers [2], and noted that the likely reason for their appearance is the asymmetric displacement thresholds for nitrogen and boron atoms in this structure. Due to the asymmetry, boron atoms are much more likely to sputter via a knock-on displacement event between an electron and a target atom, which leads to nitrogen-terminated multi-vacancy structures.

Since graphene is a monatomic structure consisting only of carbon, the situation for it is quite different to h-BN. Moreover, as carbon chemistry allows for many different polygonal arrangements for the atoms, a variety of different defect structures exist in this case [1,3]. Using TEM at different voltages, we have been able to differentiate between two different electron irradiation-induced structural changes in graphene, namely bond rotations (Stone-Wales transformations) and atomic ejections [3]. We show that electron irradiation at moderate energies (~100 keV) tends to amorphize graphene instead of perforating it due to the higher probability for bond rotations. In the most recent study [4], we have demonstrated that the bond rotations in carbon nanostructures are caused by single electron impacts, unlike what has previously been assumed. This explains the frequency of experimental observations of Stone-Wales defects, which is at odds with equilibrium thermodynamics due to the high formation energy and energy barrier for bond rotations. We also show that another way of forming these defects is via incomplete Frenkel defect annihilations, similar to Wigner defects in silicon.

[1] F. Banhart, J. Kotakoski, and A.V. Krasheninnikov, *ACS Nano*, **5**, 26-41, (2011).
[2] J. Kotakoski, C.H. Jin, O. Lehtinen, K. Suenaga and A.V. Krasheninnikov, *Phys. Rev. B*, **82**, 113404, (2010).
[3] J. Kotakoski, A.V. Krasheninnikov, U. Kaiser and J.C. Meyer, *Phys. Rev. Lett.*, **106**, 105505 (2011).
[4] J. Kotakoski, J.C. Meyer, S. Kurasch, D. Santos-Cottin, U. Kaiser and A.V. Krasheninnikov, submitted for publication, (2011).

Understanding Carbon Nanotube Chirality through Molecular Dynamic and Kinetic Monte Carlo Simulations

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We are going to present a theoretical study on carbon nanotube growth mechanism through both molecular dynamic (MD) simulation and kinetic Monte Carlo (KMC) simulation. From 2003, we have successfully simulated the nucleation and growth of carbon nanotubes (CNTs) by a MD simulation and have revealed two necessary conditions for catalytic CNT growth: the strong tube edge-catalyst interaction [1] and the weak tube wall-catalyst interaction [2]. While the MD simulated CNTs suffer a drawback of numerous defects and thus we can't use it to explore the origin of CNT chirality, (*n*,*m*), and potential means of tube chirality control.
On the other hand, a KMC method has been developed to deal with the coalescence of fullerenes and perfect CNT formation has been seen in a KMC simulation [3]. By combining the MD and KMC, methods together, we are now able to simulate defect free CNTs and thus the origin of tube chirality and means of CNT chirality control by changing the tube-catalyst interaction has been emerged[4].

[1] F. Ding*, et al. Nano. Lett.*, **8**, 463-368, (2008)
[2] Ribas MA, *et al. J. Phys. Chem*., **131**, 224501, (2009)
[3] Ding F, *et al. Phys. Rev. B,* **82**, 041403, (2010)
[4] Xu ZW, Ding F, submitted, (2011)

Dynamic And Charge Doping Effects On The Phonon Dispersion Of Graphene And Metallic Carbon Nanotubes: A Theoretical Study

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The dynamic and charge doping effects on the phonon dispersion of graphene and metallic carbon nanotubes were studied within a non-orthogonal tight-binding model. We found that the dynamic corrections are largest for the in-plane optical phonon branches in the vicinity of the Γ point and K point of the Brillouin zone of these systems and that they essentially depend on the doping level. We reproduced previous results of the dynamic and doping effects on the G-modes of graphene and selected metallic carbon nanotubes. In addition, we obtained new results for these effects for the phonon dispersion of graphene [1] and the G-modes of a large number of metallic nanotubes [2].

[1] V. N. Popov and Ph. Lambin, *Nano Res*., **3**, 822–829, (2010).
[2] V. N. Popov and Ph. Lambin, *Phys. Rev. B*, **82**, 045406/1-9, (2010).

Modification Of The Electronic Structure In Single-walled Carbon Nanotubes With Aromatic Amines

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We investigated the interactions of two aromatic amines,N,N,N'N'-tetramethyl-p-phenylenediamine (TMPD) and tetramethylpyrazine (TMP) with single-walled carbon nanotube (SWNT) networks. Adsorption and intercalation of amine molecules in bundled SWNTs is expected to modify electronic structure of nanotubes in a similar way as has already been observed for alkali metals. Our ab initio density functional calculations demonstrate that TMPD donates electron to the nanotube and produces donor-like states below the conduction band whereas the effect of the TMP treatment is very weak. The electron transfer to the nanotubes has been supported experimentally by the XPS valence band spectra which show strongly modified spectral features. Especially an increase of the electronic density at the Fermi level upon adsorption of TMPD and TMP is clearly demonstrated. Rather intensive feature between π* and σ* transitions in the NEXAFS spectrum of the pristine SWNTs attributed to the oxidized carbon functional groups are chemically modified upon adsorption of amines on the networks. This fact suggests that the aromatic amines evidently react with the defects, remove or replace oxygen species responsible for the p-type doping of SWNTs, and thus acting also as a de-doping agent for the naturally p-type doped semiconducting SWNTs.

Carbon Nanotubes As Substrates For Molecular Switches

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The adsorption of molecules to the surface of carbon nanostructures opens a new field of hybrid systems with distinct and controllable properties. Carbon nanotubes (CNTs) consisting of a single layer of carbon atoms show a high sensitivity to changes in their surrounding medium, which makes them optimal substrates. In particular, the functionalization with photochrome molecules, such as spiropyrans, is promising for engineering switches on the molecular level. First experiments have been realized illustrating how the spiropyran molecules can be used to switch the conductance of carbon nanotube transistors [1]. Here, we present a microscopic study on optical properties of pristine and spiropyran-functionalized carbon nanotubes. Our approach is based on a combination between the density matrix formalism (CNT optics) and quantum-chemical DFT calculations (molecule geometry). Spiropyrans can be reversibly switched between two different conformations: planar merocyanine (MC) and orthogonal spiropyran (SP). The conversion is induced by visible and ultraviolet light, respectively, and is accompanied by a significant change in the molecular dipole moment. As a result, the attached molecule has - depending on its conformation - an unique influence on the carrier mobility and the optical transitions in the substrate CNT.

We derive many-particle Bloch equations for hybrid nanostructures including excitonic effects and dipole-induced molecule-substrate coupling. Applied to spiropyran-functionalized nanotubes, we observe considerable red-shifts of transition energies in excitonic absorption spectra of functionalized CNTs. In particular, the MC molecule with its large dipole moment (13.9 Debye) significantly influences the optical properties of the substrate CNT leading to a red-shift of up to 65 meV [2]. In contrast, the SP molecule (6.2 Debye) only slightly changes the absorption spectrum (approx. 5 meV). This clear difference between the spectra of MC- and SP-functionalized CNTs suggests the possibility of an unambiguous optical read-out of spiropyran-based molecular switches.

To assure that the observed red-shift of the transition energy is stable and to find optimal functionalization scenarios, we performed calculations for different dipole densities, distributions, and orientations [2]: We observe the largest shift in the case of perpendicularly oriented dipoles with respect to the CNT axis. The distribution of molecules along the CNT surface turns out to have no measurable influence on the peak position. Furthermore, we find a surprising non-linear dependence of the observed red-shift on the dipole density predicting an optimal molecule coverage with respect to the design of spiropyran-based molecular switches.

Our microscopic investigations offer new insights, which can guide future optical experiments and help realize efficient nanotube-based molecular switches. The developed many-particle Bloch equations describing the coupling mechanism between excitons in the one-dimensional nanosubstrate and the externally induced molecular dipole field can be applied to other hybrid structures.

[1] X. Guo et al., *J. Am. Chem. Soc.* **127**, 15045, (2005).
[2] E. Malic et al., *Phys. Rev. Lett.* **106**, 097401 (2011).

The intercalation and diffusion of lithium ions in a bundle of carbon nanotubes (CNTs)

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The intercalation and diffusion of lithium ions in a bundle of carbon nanotubes (CNTs) are investigated via an ab initio molecular dynamics simulation method based on the density functional theory. We found that lithium ions quickly penetrate into the CNTs and the space between neighboring CNTs. With a low Li ion density, the Li ions tend to stay close to the nanotube ends. Interestingly, Li ions are able to penetrate through the carbon nanotube and move from one end to the other. We also discovered that Li ions may remain between two neighboring CNTs, which presents a new approach for Li ion intercalation and storage. Importantly, Li ions located among three neighboring CNTs have very strong adsorption potentials that are a factor of four larger than those of Li ions located along the central axis of a single-walled nanotube (SWNT). This indicates that Li ions located among three neighboring CNTs would be very difficult to remove from a nanotube bundle, which suggests that Li storage capacity in this case is possibly irreversible, and that keeping the nanotubes apart with an appropriate distance would hinder or promote the formation of irreversible intercalation. Our findings contribute to the understanding of lithium intercalation and diffusion in CNTs, which has implications for the experimental development and application of rechargeable Li ion batteries.

[1] Bo Song, Junwei Yang, Jijun Zhao, and Haiping Fang, *Energy & Environmental Science*, published on line, DOI: 10.1039/c0ee00473a, (2011).

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Modelling Solvent Interaction with Carbon-based Nanomaterials

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While carbon-based nanomaterials display an array of exciting material properties, their entry into application has been hindered by the lack of suitable solvent systems for their dispersal and subsequent manipulation. Here, we investigate the interaction of several solvents with single-walled carbon nanotubes (SWCNTs) through molecular dynamics simulations. The nanotubes are seen to experience a solvent dependent in-plane contraction that results in considerable bond-strain. However, in contradiction to the solvent pressure model, no meaningful correlation between the cohesive energy density (CED) values of the pure liquids and the in-plane deformation of the SWCNT could be observed. Instead, we find excellent correlation between the relative difference in the Gibbs free energy of solvation between different solvent systems and the bond-strain. This observation has important implications for the choice of solvent systems for the dispersal of SWCNTs and other carbon nanostructures.

Monte Carlo Simulation of Water Nanosorption in Carbon Nanotubes

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A Grand Canonical Monte Carlo (GCMC) algorithm has been developed for studying the nano-scale sorption of water molecules inside smooth single wall carbon nanotubes (SWCNTs) with different diameters. Armchair (n,n) SWCNTs with indices n = 6, 8, 10, 12 and 20 (corresponding to tube radii of 4.07, 5.43, 6.79, 8.14 and 13.57 Å, respectively) and length equal to 40 Å were used. Atomistic interactions among water molecules were computed by making use of the accurate three-site SPC/E forcefield [1]; interactions between the oxygen atom of the water and the SWCNT carbon atoms (which were assumed fixed during the simulations) were modelled by a Lennard-Jones 12-6 potential with parameters taken from the work of Liu et al. [2]. All simulations were conducted in the Grand Canonical (μVT) ensemble where the water chemical potential (μ), the temperature (T = 298K) and the volume (V) of the SWCNT were kept fixed. The water chemical potential was set equal to that of bulk water at the same temperature (T = 298 K) and pressure P = 1 atm; its value was computed via the direct particle deletion method [3]. The initial configuration consisted of an empty SWCNT which was gradually filled up with water molecules in the course of the MC simulation based on appropriate energetic (Metropolis) criteria. Results will be presented for the local density and local packing of the water molecules in the CNT, as a function of the CNT diameter. Our simulations indicate strong ordering of the water molecules which depends on CNT diameter. For example, inside the (6,6) SWCNT we observe the formation of a single water layer, but inside an (8,8) SWCNT one water ring and one water layer are formed.

[1] H.J.C. Berendsen, J.R. Grigera, T.P. Straatsma, *J. Phys. Chem*., **91**, 6269-6271 (1987).
[2] Y. Liu, Q. Wang, T. Wu, L. Zhang, *J. Chem. Phys.*, **123**, 234701, (2005).
[3] M.G. De Angelis, G.C. Boulougouris, D.N. Theodorou, *J. Phys. Chem. B*, **114**, 6233–6246, (2010).

Investigation Of The Chirality Control Through Tight-Binding Computer Simulations.

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Although significant efforts have been directed towards nanotubes synthesis, the diameter and chirality distribution is still disparate and its control remains a great challenge. Thus, the mechanism under which chirality (diameter) control has been partially achieved in some processes is not well understood. This is not surprising since the detailed microscopic mechanisms involved in the growth of carbon nanostructures are still lacking. An atomic scale investigation of the nanotube – catalyst particle interface and of the way carbon atoms get incorporated in the tube, under the conditions of the experiments is then highly desirable. However, whether the employed method is empirical or semi-empirical, all final configurations are plagued by a high concentration of atomic-scale defects making impossible the modelization of tubes with defined chirality.

In the present work, we investigate the healing processes of defective carbon nanotubes at atomic scale. We have developed a tight-binding (or semi-empirical) model for nickel and carbon that uses Monte Carlo simulations in the grand canonical ensemble to study the formation of carbon structures (graphene and nanotubes) from a metallic substrate [1,2]. In particular, we have recently discussed the key role played by metallic atoms in the reconstruction of a defected graphene sheet by annealing defects [3].

Here, we use our approach to study the evolution at finite temperatures of defected nanotubes. Different lengths and diameters of nanotubes have been investigated at various temperatures demonstrating that defects can thermally be activated and that high temperatures are able to heal the structure. We have also investigated the role played by the metal catalyst and a vapor of carbon atoms in the healing process. The building up of the tube chirality is analyzed and discussed through electron diffraction patterns. The approach proposed here could help identify individual healing mechanisms during growth that produces perfect tube structures and those favouring a definite chirality [4].

[1] H. Amara *et al.*, *Phys. Rev. Lett.*, **100**, 056105, (2008).
[2] H. Amara *et al.*, *Phys. Rev. B*, **79**, 014109, (2009).
[3] S. Karoui *et al., ACS Nano*, **4**, -10-, 6114-20, (2010).
[4] M. Diarra *et al.,* (in preparation)

Plasmon Generation By Optically Excited Excitons In Individual Single Wall Carbon Nanotubes

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Optical properties of semiconducting carbon nanotubes (CNs) originate from excitons and may be tuned by either electrostatic doping[1], or via the quantum confined Stark effect (QCSE) by means of an electrostatic field applied perpendicular to the CN axis [2]. In both cases exciton properties are mediated by surface plasmon excitations [2,3,4]. We have shown recently that the QCSE allows one to control the exciton-interband-plasmon coupling in individual CNs and their optical absorption, accordingly [2]. Here, we extend our studies to demonstrate the possibility of low-energy localized surface plasmon generation by optically excited excitons in small-diameter (~1nm) semiconducting single wall nanotubes. The phenomenon is similar to the known SPACER effect (Surface Plasmon Amplification by Stimulated Emission of Radiation) reported previously for a number of metallic nanosystems [5]. The stimulated character of the exciton-to-plasmon energy transfer causes the buildup of the macroscopic population numbers of coherent localized surface plasmons. As a consequence, high-intensity coherent localized optical-frequency fields are created at nanoscale across the nanotube diameter along the nanotube surface. These strong local fields can be controlled and manipulated by fine tuning the exciton-plasmon coupling by means of the QCSE and by changing the sample temperature. The effect can be used in a variety of new optoelectronic applications of CNs, including exciton photoluminescence control and enhanced electromagnetic absorption, optical switching, near-field nonlinear-optical probing and sensing, materials nanoscale modification.

[1] M.Steiner, M.Freitag, V.Perebeinos, et al., *NanoLetters*, **9**, 3477, (2009).
[2] I.V.Bondarev, L.M.Woods, and K.Tatur, *Phys. Rev. B*, **80**, 085407, (2009).
[3] C.D.Spataru and F.Leonard, *Phys. Rev. Lett.*, 104,177402, (2010).
[4] A.Popescu, L.M.Woods, and I.V.Bondarev, *Phys. Rev. B*, **83**, 081406(R), (2011).
[5] D.J.Bergman and M.I.Stockman, *Phys. Rev. Lett.*, **90**, 027402, (2003).

Asymptotic Exchange Coupling Of Quasi-One-Dimensional Excitons in Carbon Nanotubes

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An analytical expression is derived for the biexciton binding energy as a function of the binding energy of constituent quasi-one-dimensional excitons in small-diameter (~1 nm) single wall carbon nanotubes (CNs). This allows one to trace biexciton energy variation and relevant non-linear absorption under external conditions whereby the exciton binding energy varies. The non-linear absorption lineshapes calculated exhibit characteristic asymmetric (Rabi) splitting as the exciton energy is tuned to the nearest interband plasmon resonance[1,2]. This effect may be used in tunable optoelectronic device applications of small-diameter semiconducting CNs in areas such as nanophotonics, nanoplasmonics, and cavity quantum electrodynamics, including the strong excitation regime with optical non-linearities. In the latter case, the experimental observation of the non-linear absorption line splitting predicted would help identify the presence and study the properties of biexcitonic states (including biexcitons formed by excitons of different subbands[3])in individual single wall CNs, due to the fact that when tuned close to a plasmon resonance (see Ref.[4] for details) the exciton relaxes into plasmons at a rate much greater than the exciton-exciton annihilation rate (~1ps, Ref. [5]), totally ruling out the role of the competing exciton-exciton annihilation process.

[1] I.V.Bondarev, *Superlattices and Microstructures*, **49**, 217, (2011).
[2] I.V.Bondarev, *Phys. Stat. Solidi B*, **248**, 468, (2011).
[3] D.J.Styers-Barnett, S.P.Ellison, B.P.Mehl, B.C.Westlake, R.L.House, C.Park, K.E.Wise, and J.M.Papanikolas, *J. Phys. Chem. C*, **112**, 4507, (2008).
[4] I.V.Bondarev, L.M.Woods, and K.Tatur, *Phys. Rev. B*, **80**, 085407, (2009).
[5] F.Wang, G.Dukovic, E.Knoesel, L.E.Brus, and T.F.Heinz, *Phys. Rev. B*, **70**, 241403(R), (2004).

Changing Chirality During SWNT Growth: A Reactive Molecular Dynamics / Monte Carlo Study

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One of the major obstacles in making SWNTs applicable in everyday electronic applications on the large scale, is our current inability to control the exact properties, and specifically the chirality of the tube. On a fundamental level, the mechanism of chirality determination is indeed not yet known. While many researchers have worked on the growth of SWNTs using atomistic simulation techniques, these works have always resulted in highly defected structures, due to the neglect of long time scale effects. These simulations therefore do not allow to study the chirality determination during growth. Recently, we have demonstrated the importance of taking these long time scale effects into account, in generating a SWNT with – for the first time – a definable (12,4) chirality [1]. In the present work, we focus on the growth mechanism as well as on the exact mechanism of chirality formation during the growth using this novel simulation methodology.

The observed SWNT growth process was found to proceed through a number of distinct steps, viz. the dissolution of carbon in the metallic particle, the surface segregation of carbon with the formation of aggregated carbon clusters on the surface, the formation of graphitic islands that grow into SWNT caps, a restructuring process of the carbon network in which many topological defects are healed, and finally continued growth of the SWNT.

Usually, it is assumed that the chirality is determined during the initial cap formation, and that this chirality subsequently remains invariant. However, we here demonstrate that it is possible that the chirality still changes after the initial cap formation, through a metal-mediated restructuring process. Specifically, we observe the SWNT chirality to change from (11,0) (i.e., zigzag type) to finally (7,7) (i.e., armchair type). These calculations demonstrate for the first the simulated growth of an armchair SWNT with a definite chirality on a surface-bound catalyst.

[1] Neyts et al., *ACS Nano,* **4**, 6665, (2010).

Simulated PECVD Growth Of Aligned Single Walled Carbon Nanotubes

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Traditionally, carbon nanotubes (CNTs) are grown in arc discharges, laser ablation sources or in catalytic chemical vapor deposition (CCVD). Since about 10 years, CNTs are also grown by means of plasma-enhanced chemical vapor deposition (PECVD). PECVD allows the formation process to occur at lower temperatures, which is beneficial for e.g. deposition on temperature sensitive polymeric substrates. Very recently, it has also become possible to generate SWNTs in a PECVD process. Besides the lower growth temperature, PECVD for SWNT growth has additional advantages over thermal CVD such as alignment of the SWNTs during the growth (instead of forming spaghetti as in thermal CVD). Furthermore, using PECVD, freestanding SWNTs can be produced, and most importantly, it offers perspective on controlling the chirality of the growing SWNTs. Because these are very recent developments, until now there has been very little fundamental research on the precise PECVD-based SWNT growth process.
Here, we investigate the fundamental mechanisms of SWNT growth in a PECVD- setup using state-of-the-art atomistic simulations. The simulation technique that we use is a hybrid molecular dynamics / force biased Monte Carlo (MD/fbMC) model. Recently, we have demonstrated its effectiveness by simulating a chiral (12,4) SWNTs [1]. Using small, surface bound nickel nanoparticles as catalysts, we demonstrate in this work how the electric field can enhance the phase separation between the carbon and the nickel. When applying weak electric fields, phase separation is barely enhanced and typical thermal CVD growth results emerge. Applying higher electric fields, however, does enhance phase separation and forces the nucleation of the SWNT cap to occur in alignment with the field, resulting in aligned SWNT growth. Finally, when applying very strong electric fields, SWNT caps can no longer nucleate, and amorphous carbon is formed instead.

[1] E. C. Neyts, Y. Shibuta, A. C. T. van Duin, A. Bogaerts, *ACS Nano*, 4 (2010) 6665

Large Hyperfine Enhancement At Lattice Defects In Single-Walled Carbon Nanotubes

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We present a first principles study of the hyperfine interaction in 13 C enriched achiral single-walled carbon nanotubes (SWCNTs). We show that while the hyperfine constant is extremely small in pristine nanotubes, it is significantly enhanced near lattice defects such as vacancies and Stone-Wales pairs. We argue that this hyperfine enhancement is due to electron localization around the defect sites. Using this argument we give a qualitative explanation of recent measurements on the hyperfine coupling in SWCNT- based double quantum dots which showed a larger than expected hyperfine coupling.

Magnetization in Carbon Nanotubes under Ion Irradiation

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Carbon materials including nanotubes and graphene are known to exhibit magnetic properties. It is conjectured that the localized states at the zig–zag edge of the single walled nanotubes (SWNTs) and graphite sheets can induce magnetic polarization. Defects are also known to induce localized spin moments in carbon materials. Here we report ferromagnetic–like ordering in multi–walled carbon nanotubes (MWCNTs) under ion irradiation that arise from topological defects and mechanical strain. We have performed X-ray photoelectron spectroscopy measurements and *ab initio* simulations to support our magnetic measurement data.
MWCNTs grown by chemical vapor deposition technique were irradiated by 70 MeV Ni^{6+} ions at the Inter–University Center for the Accelerators, New Delhi. DC magnetization data were recorded using a vibrating sample magnetometer. The magnetic moments of the virgin MWCNTs were then subtracted from those of the irradiated samples. The measured magnetization, which is similar to that of the conventional ferromagnetic materials, strongly indicates the presence of ferromagnetic moments in the irradiated MWCNTs.
We have further performed x-ray photon spectroscopy on the virgin and irradiated MWCNTs. It is observed that the percentage of sp3 bonded carbon atom increases with irradiation fluence. The mixing of sp2 and sp3 bonds gives further evidence for magnetic ordering in the defected carbon nanotubes. In order to verify our experimental results we have performed *ab initio* simulations using density functional theory (DFT). Our results show a small net magnetic moment in the defected carbon nanotubes. By investigating the σ-π orbitals admixture, we attribute the origin of magnetism in MWCNTs to the presence of topological defects and the attendant mechanical strain introduced by ion irradiation.

Growth Mechanisms Of Single Wall Carbon Nananotube From Tight Binding Computer Simulations

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Selectively growing single wall carbon nanotubes is quite a challenging task and a number of papers recently reported significant steps forward in this direction. An atomic scale understanding of the nanotube – catalyst particle interface and of the way carbon atoms get incorporated in the tube, under the conditions of the experiments is then highly desirable.
Using a carefully parameterized order N tight binding model [1], we could identify the temperature and carbon chemical potential conditions for the nucleation of a tube cap on nickel particles. We could show that the nucleation takes place after the outer Ni layer(s) are saturated with carbon [2, 3]. We also discussed the role of Ni in the healing of defected carbon structures [4].
Recent technical improvements [5] of the algorithm of our tight binding Monte Carlo code made it significantly faster and make it now possible to address the tube growth by varying the growth parameters. Working in the Grand Canonical ensemble enables one to control the carbon incorporation in the open system made of an initial tube butt located on a Ni particle. The chirality of the initial tube structure and the diameter of the Ni particle are varied, as well as the growth conditions (temperature, carbon chemical potential, “feeding rate” characterized by the number of relaxation steps performed between two successful C insertions or destructions). In this parameter space, we identify two growth termination mechanisms, either by encapsulation of the catalyst particle by a graphitic layer, or by detachment of the growing tube from the catalyst. We also evidence the need for a correct matching between the tube and catalyst particle diameter. Finally, we characterize the conditions to grow tubes and focus on keeping the chirality of the initial tube butt during the growth (i.e. : growing a defectless tube). In agreement with other computer simulation studies [6] our calculations emphasize the role of short carbon (polyyne) chains that are attached to the tube lip and lead to the formation of ring structures.

[1] H. Amara et al., *Phys. Rev. Lett.*, **100**, 056105, (2008).
[2] H. Amara et al., *Phys. Rev. B*, **79**, 014109, (2009).
[3] M. Moors et al., *ACS Nano*, **3** (3), 511-516, (2009).
[4] S. Karoui et al.,*ACS Nano*, **4**, -10-, 6114-20, (2010).
[5] J. H. Los et al., submitted
[6] A. Page et al., *J. Phys. Chem. C*, **114**, 18, 8206-11, (2010).

Possible CVD Synthesis Region of Single-walled Carbon Nanotube in the Bachmann Diagram

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Considering the massive-scale synthesis of single-walled carbon nanotube (SWCNT), chemical vapor deposition (CVD) has become a standard process for synthesizing CNTs, because it is an economical and a fast process. In most of these processes, oxygen and hydrogen atoms were included originally or added later; these atoms were expected to have important roles such that they helped in the removal of amorphous carbon from catalysts and prevented SWCNTs from containing metal particles. However, whole perspectives for suitable carbon source or ideal balance among carbon, hydrogen, and oxygen have not been reported. Therefore, we performed experiments from the point of view of determining the appropriate C-H-O components ratio in raw materials could be used to synthesize CNTs by CVD processes. In this study, we employed a C-H-O ternary diagram, which was known as the Bachmann diagram for diamond synthesis, to clearly understand the most important relationship among the components of each raw material. We examined a variety of raw materials in our newly developed round-trip-type vacuum furnace in order to determine whether they could be used to synthesize a carbon nanotube. We used Raman spectroscopy to identify the developed carbon nanotube, and we plotted the component ratios of effective and ineffective materials on a C-H-O ternary diagram. In this study, we employed two kinds of catalyst supporters such as aluminum oxide and zeolite (USY type). We confirmed a kind of affinity between catalyst supporters and carbon sources, but this affinity did not lead to inconsistency in the tendency on the C-H-O ternary diagram. Some carbon sources are shown in the same position on this diagram; for example, ethanol and DME (C2H5OH and CH_3OCH_3) or hydrocarbon gases and hydrocarbon gases with hydrogen (C_2H_6 and $C_2H_4 + H_2$), there is no contradiction.

As a result, in this diagram, the growth region became highly apparent. It should be noted that for the growth of the carbon nanotube, this region should satisfy the equation $O < C < (H + O)$ in molar ratio. Furthermore, it was observed that adjusting the component ratios by mixing raw materials did not cause an inconsistency in the growth region.

Molecular Orbital Calculations of Small Graphene-Like Species to Interpret Their Site-Dependent EELS

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Electron energy -loss spectroscopy of coronene ($C_{24}H_{12}$), perchlorocoronene ($C_{24}Cl_{12}$), and graphene was compared with the theoretical calculation of those derivatives. The contributions of individual carbon atoms to the carbon K-edge spectrum is evaluated, which roughly approximates the site-dependent electronic properties.

The first principle calculations provide information of a specific carbon site that is mainly influenced by surrounding chemical environment. Real -space molecular orbital (MO) calculations, based on the density functional theory (DFT), can determine both the energy levels and the density of states after self-consistent field (SCF) calculations. Some results of theoretical calculations will be shown based on the model structures of coronene, perchlorocoronene [1] and other graphene-like derivatives that assumingly possess zigzag- edge ($C_{150}H_{30}$), armchair- edge ($C_{114}H_{30}$), and Klein- edge ($C_{120}H_{24}$) structures [2]. When focusing on the π^* peak of peripheral carbon sites, the chlorine- terminated carbon site relatively shift to higher energy level compared to hydrogen- terminated carbon. The chlorine atom pulls the valence electron from the carbon site which is positively charged and accordingly binds the inner 1s energy level of carbon atom much deeper (lower) energy level. The hydrogen- terminated peripheral carbon atoms of coronene do not show significant energy shift compared with other carbon atoms inside the coronene molecule. In graphene derivatives with zigzag- edge, armchair- edge, and Klein- edge structures, the peripheral hydrogen-terminated carbon atoms do not show significant energy shift compared to the observed experimental energy shift of graphene edge. The distribution of unoccupied 2p orbitals on the peripheral edge of carbon, however change drastically to show the characteristic fine structures. Indeed, there are numbers of parameters that must be considered in the calculations, for instance, the precise structure of the materials of interest (whether the termination should be hydrogen, other elements, or perhaps no termination should be applied), valency (or charge) of carbon atoms, size effect of model structures (cluster size), etc. As the building block comparison is not suitable to predict the electronic properties of new materials like a graphene edge, the theoretical calculation still plays an important role to interpret or explain what we experimentally see.

[1] M. Koshino, H. Kurata, S. Isoda, *Ultramicroscopy*, **110**, 1465-1475, (2010).
[2] Kazu Suenaga & M. Koshino, *Nature*, **468**, 1088-1090, (2010).

Birth-Death Markov Modeling for Single Molecule Counting using Single-Walled Carbon Nanotube Fluorescent Sensor Arrays

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Functionalized SWNTs could be used as local concentration sensors for the biological community. In recent work we have shown that d(AT)$_{15}$ DNA-wrapped single-walled carbon nanotubes (SWNT) are able to detect the adsorption and desorption of single molecules of nitric oxide (NO) from their surfaces by quenching of the near-infrared fluorescence [1]. This work employs an exact solution to the Birth-Death Markov model to estimate the local concentration from the stochastic dynamics. Analytical expressions are derived for the intrinsic variance displayed by identical sensor elements, and the homogeneity of the environment is assessed by comparing experimental sensor-to-sensor variance with this limit. d(AT)$_{15}$ DNA-wrapped SWNTs are found to demonstrate variances that are close to the idealized limit at relatively high NO concentrations (19.4 μM). At 780 nM, the sensor-to-sensor variance is double the idealized value, which indicates marginal variation in the SWNT array. We outline how to predict the local analyte concentration from sensor dynamics, and identify an NOadsorptionratecoefficient 2.6×10^{-4} s^{-1} μM^{-1}.

[1] Zhang, J.; Boghossian, A.A.; Barone, P.W.; Rwei, A.; Kim, J.-H.; Lin, D.; Heller, D.A.; Hilmer, A.J.; Nair, N.; Reuel, N.F.; Strano, M.S.; J. *Am. Chem. Soc.*, **133**(3), 567–581, (2010).

Spin-Related Novel Optical Phenomena in Single-Walled Carbon Nanotubes

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The interplay between conduction electrons and localized spins is one of fundamental and important problems in modern condensed matter physics giving us unexpected phenomena: It is well known that they induce resistivity minimum phenomena, known as the Kondo effect. Besides the conducting electrons, the fundamental question arises whether the interplay between photo-excited electrons and localized spins leads novel phenomena. In this regard, semiconducting single-walled carbon nanotubes (CNTs) provide us an interesting research field of spin-related optical phenomena. Because of their quasi-one- dimensional structure, photo-excited electrons and holes in CNTs are strongly correlated and form a bound electron-hole pair, called an exciton, which has large binding energy, leading to remarkable stability up to room temperatures. Therefore, when there are localized spins in CNTs, optical phenomena are expected to exhibit wide variety. In this paper, we demonstrate two interesting examples of novel optical properties of CNTs that are induced by localized spins based on the theoretical investigations:(1) Recent experiments have shown the evidence in which the excitons correlate with localized spin induced by the defects in CNTs those are essential in the bipartite lattice of CNTs. However, unfortunately, the fundamental theory for this problem has not been addressed yet. We thus propose a theory that expresses the interaction between excitons and localized spins in CNT system [1]. Our theory solves one of the most important issues regarding the optically activated triplet dark excitons and first successfully provides a unified explanation for all the experimental conditions [2,3,4].(2) It has been pointed out that ultrathin magnetic nanowires encapsulated in carbon nanotubes are potential candidates for constituent elements in the next-generation spintronics and electronics devices with nanometer scal e[5]. For the device application, the evaluation methods for detecting the magnetic state of the nano-wires are essential and important. For such methods, we theoretically propose a non-contacted optical probing method based on the optical response from such magnetic nanomaterials encapsulated in carbon nanotubes. Due to the exchange interaction between excitons and polarized spins in ferromagnets, triplet excitons acquire finite oscillator strength and can thus be excited by light [6]. This mechanism certainly detects magnetic ordering of nano-materials encapsulated in carbon nanotubes.

[1] S. Konabe and S. Okada, submitted.
[2] H. Harutyunyan et al. *Nano Lett.*, **9**, 2010, (2009).
[3] R. Matsunaga et al. *Phys. Rev. B.*, **81**, 033401, (2010).
[4] K. Nagatsu, S. Chiashi, S. Konabe, Y. Homma, *Phys. Rev. Lett.*, **105** 157403, (2010).
[5] R. Kitaura et al. *Angew. Chem. Int. Ed.* **48**, 8298, (2009).
[6] S. Konabe and S. Okada, *Appl. Phys. Lett.*, **98**, 073109, (2011).

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Graphene Nano-Electrodes for DNA Sequencing: an Ab initio Perspective

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The proposal was made [1] that a graphene nanogap could be used to probe the transverse conductance of individual nucleotides in DNA to rapidly identify the associated base sequence. This approach is attractive because atomically-thin electrodes made from graphene could overcome the difficult issue of achieving single-base resolution. Experimentally, it has been demonstrated [2–4] that it is possible to measure the characteristic drop in ionic current associated with translocation events of DNA passing through a graphene nanopore. These findings make further developments of a graphene-based set-up aimed at whole-genome sequencing a highly promising direction. Using first-principles methods, we have theoretically evaluated different aspects of the performance of two graphene nano-electrodes configurations for nucleobase identification. In the first study [5], we investigated the electronic transport properties of the four nucleotides when located in a graphene nanogap by employing density functional theory and the non- equilibrium Green's function method. In particular, we determined the electrical current variation at finite bias due to changes in the nucleotides orientation and lateral position. We explain the resulting fluctuations in the tunnelling current over several orders of magnitude, and conclude that a distinction between the four DNA bases appears in principle possible.

Our second study [6] utilized molecular dynamics simulations in conjunction with electronic transport calculations to explore specifically the effect of the hydrogenated graphene edges on the translocating DNA. It is found that these edge-hydrogenated graphene electrodes can facilitate the temporary formation of H-bonds with suitable atomic sites in the nucleotides. As a consequence, compared to the case of bare graphene edges, the average conductivity is drastically raised by about three orders of magnitude while exhibiting significantly reduced statistical variance. Furthermore, we found that for narrow graphene electrodes separation, the mere hindrance due to the presence of protruding hydrogen atoms in the nanogap is deemed more important, while for wider electrode separation, the formation of H-bonds becomes the dominant effect.

[1] H. W. Ch. Postma, *Nano Lett.* **10**, 420-425, (2010).
[2] C. A. Merchant, K. Healy, M. Wanunu, V. Ray, N. Peterman, J. Bartel, M. D. Fischbein, K. Venta, Z. Luo, A. T. C. Johnson, and M. Drndić, *Nano Lett.* **10**, 2915-2921, (2010).
[3] G. F. Schneider, S. W. Kowalczyk, V. E. Calado, G. Pandraud, H. W. Zandbergen, L. M. K. Vandersypen, and C. Dekker, *Nano Lett.* **10**, 3163-3167, (2010).
[4] S. Garaj, W. Hubbard, A. Reina, J. Kong, D. Branton, and J. A. Golovchenko, *Nature* **467**,

190-193, (2010).
[5] J. Prasongkit, A. Grigoriev, B. Pathak, R. Ahuja, and R. H. Scheicher, *Nano Lett.*, published on-line (April 15, 2011), DOI:10.1021/nl200147x, preprint arXiv:1012.1669
[6] Y. He, R. H. Scheicher, A. Grigoriev, R. Ahuja, S. Long, Z. L. Huo, and M. Liu, *Adv. Funct. Mater.*, in press, DOI:10.1002/adfm.201002530, preprint arXiv:1012.0031

Effect of Variations in Carbon-Carbon Bond Lengths on the Optical Absorption Properties of Different Carbon Nanotubes

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The electronic and optical properties of carbon nanotubes are known to be highly dependent on their diameters. For small-diameter nanotubes, the curvature of the nanotube sidewall has shown to significantly influence their electronic structures. One effect of this curvature is the change in the carbon-carbon bond length after geometry relaxation. In this theoretical work, we show the importance of geometry optimization in the prediction of the band structure and optical absorption spectra of nanotubes. We first study the effect of geometry relaxation on the carbon-carbon bond length along and perpendicular to the nanotube axis. For this purpose, we simulate three zigzag nanotubes with considerably different diameters ((4,0), (8,0) and (16,0) nanotubes with diameters of ~0.34, ~0.63, and ~1.27 nm, respectively) and calculate the bond length change resulting from the geometry optimization with different density functional theory (DFT) and hybrid methods. For example, after geometry optimization with the hybrid method of HSEH1PBE/6-31G,the carbon-carbon bond length along the nanotube circumference increases by about 4.37%, 0.92% and 0.27% from the original value of 1.42 nm in graphene for the (4,0), (8,0) and (16,0) nanotubes, respectively. In the next step, we show how this bond length change can affect the band structure and consequently the optical absorption spectra of carbon nanotubes. For instance, the first optical transition energy of the (4,0) nanotube decreases by 50% after geometry optimization (0.8 eV for a non- relaxed and 0.4 eV for a relaxed structure). For an (8,0) nanotube the first optical transition energy increases by 14% and for a (16,0) nanotube it decreases by 9%. We also perform a systematic study to separate the effects of the perpendicular bond length and the parallel bond length on the electronic bands and absorption spectra of nanotubes.

Energetics and Electronic Structure of Encapsulated Single-Stranded DNA in Carbon Nanotubes

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Nanometer-scale tubular-spacing inside single-walled carbon nanotubes (SWCNTs) is inherently capable of accommodating foreign atoms molecules, leading to novel one- dimensional phases with unusual physical properties. Recently, single-stranded DNA (ssDNA) has been experimentally demonstrated to be encapsulated into the inside of SWCNTs. ssDNA is an amphiphilic biopolymer consisting of aromatic bases polymerized via hydrophilic backbone of sugar-phosphate groups. The energetics and electronic structures of the ssDNA-SWCNT hybrid systems are, however, still unclear. In order to provide theoretical insight into this novel bio/nano hybrid material, we here study the energetics of encapsulation of ssDNA in SWCNTs and electronic structures of the resulting ssDNA- SWCNTs hybrid systems on the basis of the density functional theory (DFT) [1]. As a structural model for the hybrid system, we consider infinite length of ssDNAs (poly- adenine, poly-guanine, poly-thymine, and poly-cytosine) encapsulated into SWCNTs. Our DFT calculations clarify that the encapsulation reaction is exothermic for nanotubes with diameters greater than 1.33 nm. The energy gain is calculated to be in the range of 0.8–1.5 eV/nm, depending on tube diameter, base sequences, and ssDNA structure. In optimal ssDNA-SWCNT hybrid-system geometries, the polar groups of ssDNA, i.e. the POH moiety in its backbone, are located adjacent to the wall of the nanotube. The electronic structure of the hybrid system is qualitatively similar to a simple sum of those of an isolated ssDNA molecule and an empty SWCNT. However, detailed analysis of the electronic structure of the hybrid system reveals that the encapsulation of ssDNA into a SWCNT affects the electronic structures of both the ssDNA and the SWCNT.

[1] K. Kamiya and S. Okada, *Phys. Rev. B* in press.

Fluid Flow Induced Voltage Generation In Single Wall Nanotubes -Simulation, Analysis And Application

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Initially water flow through SWCNT was simulated in LAMMPS with a finite temperature difference at its ends. The snapshot of MD simulation was analysed using Gaussian for charge accumulation on the ends of the CNT by Natural Population Analysis (NPA).The exact potential difference was computed using coulombs electrostatic equation in Matlab. The voltage difference fluctuated between 45mV and 490mV for various iterations. An energy harvesting assembly is proposed in which the nanotube array is placed in the vapour- liquid cavity of a heatpipe. By selecting suitable working fluid and temperature range, energy conversion is made possible. The advantage of temperature difference over pressure (which is widely considered for such type of simulation [1]) is that the temperature difference causes: 1. The water or working fluid to get agitated and flow through the Nano pore resulting in dragging of surface electron due to their highly polar nature. 2. The nanotube gets heated up, forcing phonon vibrations from hot to cold end which in turn causes the dragging of the surface electrons of the nanotube.
The 2nd phenomena cannot be observed when only pressure is applied. Even though the pressure difference may lead to temperature variation build up, the prevalent existence of waste thermal energy may find interesting applications in industries. It is suitable for space applications were the entire electromagnetic spectrum can be used to heat up the working fluid resulting high fluid flow rate hence higher voltage generation. We don't know how the nanotube bundle incorporated in heatpipe can be simulated to show the nanoscale phenomena in micro/macro scale. Even though the nanotube bundles with length ranging up to several centimetres showed such voltage generation effect in practise. Combining the heatpipe which so far mechanical engineers modelled using FEM and nanotube which involves Newtonian and quantum dynamics is a computational challenge. Further simulation was carried out with bundle of SWCNT (4 CNT in 2X2 array) using NAMD. The nanotubes were fixed along the axial direction but free to move in the radial direction. When the water flow was initiated along the axial direction majority of the water molecules tend to flow through the inner cavity of nanotube but only few molecules passed the cavity between the nanotubes. This shows that the voltage generation in the nanotube was due the interaction between the molecules inside nanotube cavity and the surface electrons of the nanotube as opposed to the phonon induced dragging from the surface adsorbed molecules [2]. When nanotube in an array were moved apart and placed at distance larger than their equilibrium distance they tend to come closer and find the equilibrium position. Hence it is highly improbable for the surface absorbed molecules to induce electron drifting in a nanotube bundle. So new understanding of the flow induced dragging of electrons should be formulated to take into account the above mentioned phenomena.

[1] Quanzi Yuan; Ya-Pu Zhao, *Journal of American Chemical Society*, **131**, 6374-6376, April , (2009).
[2] Král P.; Shapiro M., *Physical Review Letters*, **86**, 131-134, (2001).

Magnetic ordering in the fluorinated graphene

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Electronic and magnetic properties of fluorinated graphene were studied depending on the fluorine concentration within the density functional approach. Polyene carbon chains were created in a fully fluorinated graphene fragment, where fluorine atoms were subsequently attached to the opposite sides of the sheet. Two parallel zigzag- or armchair-type chains with a length varied from 1 to 7 atoms were located in a center of the fragment. The models were calculated using hybrid B3LYP method with the Jaguar package. Calculations showed that models with even-numbered chains are more preferable energetically. Although as soon as odd bare carbon chains are formed the ferromagnetic ordering appears in the fluorinated graphene. Spin density is determined by highest occupied molecular orbitals, where π-electrons are distributed along the chains. The model with a single polyene odd-numbered chain showed an anti-ferromagnetic ordering. Our calculations show that the exchange spin interaction decreases with the separation of the bare carbon atoms and thus one could expect ferromagnetic or anti-ferromagnetic ordering in the fluorinated graphene depending on the atomic structure and stoichiometry of a layer.

Carbon Nanomaterials as Catalysts for Hydrogen Desorption from Complex Metal Hydrides

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A key issue of complex metal hydrides for their application as hydrogen storage materials is the requirement of a catalyst to facilitate hydrogen uptake and release. One promising new class of such catalysing agents is constituted by carbon nanomaterials, in particular nanotubes and fullerenes. In a close collaboration with experimentalists, we have have explored [1] how carbon nanostructures can act as catalysts for hydrogen release in the complex metal hydride sodium alanate ($NaAlH_4$). The stability of the AlH_4 moiety is due to the charge transfer from Na, resulting in an ionic bond between Na^+ and AlH_4^- and a strengthening of the covalent bond between Al and H. Interaction of $NaAlH_4$ with any electronegative substrate, such as a carbon nanotube or fullerene, affects the amount of charge donated from Na to AlH_4 and thus weakens the Al−H bonds, causing hydrogen to desorb at lower temperatures. Further experiments [2] concentrated on the catalysing effects of fullerenes (C_{60}) for the hydrogen uptake and release in lithium borohydride ($LiBH_4$). In an effort to better understand the involved mechanism, we have carried out a detailed computational study of the interaction between $LiBH_4$ and C_{60}. Considering a stepwise removal of the hydrogen from $LiBH_4$, we find that the presence of C_{60} can lead to a substantial reduction of the involved H- removal energies. This effect is explained as a consequence of the interaction between the negatively charged borohydride complex and the C_{60} entity [3]. Finally, graphitic nanofibres (GNFs) represent another new promising class of materials for catalysing the dehydrogenation and rehydrogenation process in complex metal hydrides. Experiments considering both planar GNFs (PGNFs) and helical GNFs (HGNFs) have been carried out [4−6] and the results show that HGNFs posses superior catalytic activity over other carbon nanomaterials in improving the desorption kinetics and decreasing the desorption temperature of certain H-storage materials. We are again employing density functional theory calculations in an attempt to better understand this catalysing effect from first principles.

[1] P. A. Berseth, A. G. Harter, R. Zidan, A. Blomqvist, C. M. Araújo, R. H. Scheicher, R. Ahuja, and P. Jena, *Nano Lett.* **9**, 1501-1505, (2009).
[2] M. S. Wellons, P. A. Berseth, and R. Zidan, *Nanotechnology*, **20**, 204022, (2009).
[3] R. H. Scheicher, S. Li, C. M. Araúo, A. Blomqvist, R. Ahuja, and P. Jena, *Nanotechnology*, under review, preprint arXiv:1102.2435
[4] M. S. L. Hudson, H. Raghubanshi, D. Pukazhselvan, and O. N. Srivastava, *Int. J. Hydrogen Energy*, **35**, 2083-2090, (2010).
[5] H. Raghubanshi, M. S. L. Hudson, and O.N. Srivastava, *Int. J. Hydrogen Energy*, **36**,

4482-4490, (2011).
[6] M. S. L. Hudson, H. Raghubanshi, D. Pukazhselvan, and O. N. Srivastava, *Int. J. Hydrogen Energy*, in press, DOI:10.1016/j.ijhydene.2011.03.006

Preparation of Iron Catalyst Nanoparticle for Single-Walled Carbon Nanotube Forest from Various Iron Compounds

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Catalysts are one of the most important factors that govern the structure of single wall carbon nanotube (SWNT). When SWNTs are synthesized in high yield on substrates, in most cases, pure iron thin films sputtered or e-beam deposited on an Al_2O_3 support layer are annealed in hydrogen to form small catalytic nanoparticles [1-3].In this presentation, we have studied this pre-annealing process, denoted as the “formation process”, of Fe/Al_2O_3 catalyst for SWNT growth. Various Fe compounds, such as iron nitrate, iron chloride, bucky ferrocene, and chemically prepared colloidal iron nanoparticles, deposited on sputtered Al_2O_3 layer by spin-coating or bar-coating, could serve as a catalyst for highly efficient SWNT growth. This generality was explained by subsurface diffusion of Fe atoms into the Al2O3 support invoked by hydrogen annealing. As a result, the majority of the deposited Fe left the surface and the remaining Fe reconfigured into small nanoparticles suited to grow SWNTs. Additionally, the average diameter of the SWNTs (and the size of Fe catalysts) grown from all iron compounds studied fell in an unexpectedly narrow range of 2.8-3.1 nm. From experimental observation including XPS, AFM, and SEM-EELS observations, we interpret that interplay between Ostwald ripening that eliminated smaller nanoparticles and subsurface diffusion that reduced the size of larger nanoparticles resulted in a fairly uniform assembly of small catalysts regardless the initial Fe compound.

[1] D. N. Futaba, K. Hata, T. Namai, T. Yamada, K. Mizuno, Y. Hayamizu, M. Yumura, S. Iijima, *J. Phys. Chem. B*, **110**, 8035, (2006).
[2]Y. Q. Xu, E. Flor, M. J. Kim, B. Hamadani, H. Schmidt, R. E. Smalley, R. H. Hauge, *J. Am. Chem. Soc.*, **128**, 6560, (2006).
[3] G. Zhong, T. Iwasaki, J. Robertson, H. Kawarada, *J. Phys. Chem. B*, **111**, 1907, (2007).

Directed Motion Of Carbon Nanotube In Water Driven By Non-uniform Electric Field

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The carbon nanotubes (CNTs) have been used as nanoelectromechanical systems (NEMS) components widely because of their superior mechanical properties, ideal geometry, and chemically inertia. In addition, due to their one-dimensional nature, they are regarded as a promising and powerful tool for molecules transportation. To this end, a variety of novel mass conveyors in molecular scale was proposed experimentally or theoretically.

In this work, a novel type of molecular linear motor in water based on molecular dynamics (MD) simulations is reported. The physical model is composed of two coaxial armchair single-walled CNTs (5,5) and (10,10) immersed inside water cluster and the outer SWCNT(10,10) is shorter than the inner SWCNT(5,5). The axis of CNTs is along the Z direction and a non-uniform electric field is applied in X direction with a linear gradient along the Z axis. The strength is expressed as $E_x = a.z$, where z is coordinate in Z axis and a is the gradient coefficient. The results show that the outer SWCNT starts to move just as the electric field is applied and finally it reaches the end of inner SWCNT where the electric field strength is lower within some nanoseconds. In addition, the velocity of movement dependent remarkably on the gradient coefficient a, but due to the thermal fluctuations the velocity value is no more than 10nm/ns. To study the physical mechanism of this phenomenon, we calculate the VdW interaction energy of the outer SWCNT with water along the Z direction. The results demonstrate that as the strength of electric field decreases the VdW energy also decreases and so the outer SWCNT is forced to the areas where the VdW energy is lower. Also, when the strength of electric field is low, the gradient of the VdW energy is also low and even the trend has a little reverse. We think the inertia could overcome the barrier and the model could be designed exactly to avoid this problem.

Synthesis, Characterization, and Theoretical Studies of Hybrid ZnO Nanoparticles and Nitrogen-Doped Carbon Nanotubes

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We have synthesized ZnO nanoparticles (ZnO-NPs) anchored on the surface of nitrogen-doped multiwalled carbon nanotubes (CN_x-MWNTs). The anchoring process consisted in adding CN_x-MWNTs (previously synthesized using chemical deposition method) in a solution containing dimethylformamide, zinc acetylacetonate, and thiophene. The thiophene solvent was used as a capping agent. Different samples were obtained by varying the thiophene concentration. Scanning and transmission electron microscopy characterizations revealed that ZnO-NPs are homogeneously distributed along the CN_x-MWNTs. X-ray diffraction analysis demonstrated that the ZnO-NPs exhibit a Wurtzite crystal structure with an average diameter equal to 5 nm. We found that the ZnO-NPs does not exhibit a preferential grown direction respect to the nanotube surface, and its growth is controlled by the concentration of passivating agent. First- principles density functional calculations in the local spin density approximation were performed to understand the role of the sulfur atoms (coming from the passivating agent) during the formation of ZnO-NPs and the interaction with CNx-MWNTs. Our theoretical results on different nanoparticle sizes revealed the presence of unpaired spins on the isolated ZnO-NPs passivated with sulfur. The obtained magnetic moments were located mainly at the surface and on the sulfur atoms. In addition, a ZnO-NP was set on the surface of a N-doped (10,0) single walled carbon nanotubes. After geometry relaxation, the ZnO-NP was attached to the nanotube surface exhibiting a net total magnetic moment. The ZnO-NP was preferentially bonded to the surface of carbon nanotubes via oxygen atoms.

Modelling the Effects of High Exciton Density on the Optical Properties of Carbon Nanotubes

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It is now widely accepted that exciton effects play an important role in the optical processes of carbon nanotubes [1]. Recent experimental studies, investigating the photoluminescence process, have demonstrated optical pumping of carbon nanotubes over a wide range of intensities [2]. These experiments are expected to produce excitons at sufficiently high densities that exciton-exciton interactions, and the screening by excitons, should be significant. However, previous theoretical investigations have typically modelled the optical properties of carbon nanotubes only at vanishing exciton density, and by considering screening effects only within a static approximation. It has been demonstrated elsewhere that, for semiconductor quantum wires, these approximations are insufficient at high exciton densities [3]. In this work we use a fully dynamical theory to investigate the effects of varying exciton density on the optical response of carbon nanotubes. We use the Bethe-Salpeter Equation to describe the exciton and many-body effects. The many-body interaction is built upon a tight- binding framework. Dynamical screening is modelled through a multiple Plasmon Pole Approximation and plasmon dispersions are extracted from a fully dynamical calculation of the dielectric function, in the Random Phase Approximation. Our calculations show that as the exciton density increases, the exciton binding energy and the band-gap renormalisation both decrease significantly. However, due to a partial cancelling of these effects, we see only a small shift in the positions of the exciton emission peaks.

[1] M. S. Dresselhaus, et al., *Annu. Rev. Phys. Chem.*, **58**, 719, (2007).
[2] Y. Murakami, J. Kono, *Phys. Rev. Lett.*, **102**, 037401, (2009).
[3] S. Das Sarma and D. W. Wang, *Phys. Rev. Lett.*, **84**, 2010, (2000).

How do Carbon Atoms Assemble at The sp2-edge?

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It spite of the importance in determining the growth rate and chirality changes, it still remains unclear how carbon atoms are incorporated into the edge of growing carbon nanotube or graphene. We perform atomistic calculations to evaluate the free energy changesaccompanying thecarbon attachment to different growth sites: armchair (A) or zigzag (Z) edges [1], and the corresponding kinks (KA or KZ) sites, at the interfacewith various metals, i.e. Ni, Co, Fe, or Cu. It appears that the K sites are most energetically favorable for carbon incorporation, validating the screw-dislocation model [2] for the near-equilibrium growth. With the metal atoms in proximity, the defects (pentagons, heptagons, etc.) are efficiently annealed at the carbon incorporation stage, resulting in defect-free growth of nanotube or graphene. This in-situ annealing model can explain why the nanotubes and graphene have much lower defect density than typically observed in rapidMD simulations [3].

[1] Y. Liu, A. Dobrinsky, and B.I. Yakobson, *Phys. Rev. Lett*., **105**, 235502, (2010).
[2] F. Ding, A. Harutyunyan, and B. I. Yakobson, *PNAS*, **106**, 2506, (2009).
[3] M.A. Ribas, et al.*J. Chem. Phys*., **131**, 224501, (2009).

Abstract 622
CCTN11

Ab initio simulations of carbon nanotube bundles used as gas sensors

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Carbon nanotubes present great potential for applications due to many interesting properties such as the possibility to be either metal or semiconducting depending on the chiral vector. One could also mention its high surface area to volume ratio which leads to one of the possibilities which raises the highest hopes: the area of nanotube-based gas sensors. One, for instance, envisions the possibility of combining high sensitivity with room temperature operation, surpassing more commonly used semiconductor-based sensors. At the same time, from the technological point of view, one is probably going to use bundles of CNTs instead of a single tube due to commercial viability.

In this work we use density functional theory (DFT) calculations to determine the electronic structure properties of different molecules interstitially positioned between the nanotubes in a bundle. From the most stable structures we couple the DFT calculations to a recursive Green's function method to simulate the electronic transport properties of nanotube bundles containing a large number of molecules randomly distributed along the different tubes forming the ropes. This way one is able to simulate a realistic sensor based on three- dimensional nanotube bundles taking into consideration the effects of disorder. Our results show that both ammonia and CO when trapped between the tube walls show high sensitivity.

Abstract 623
CCTN11

Ab initio simulations of electronic transport of nanotube bundles used as gas sensors

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Carbon nanotubes present great potential for applications due to many interesting properties such as the possibility to be either metal or semiconducting depending on the chiral vector. One could also mention its high surface area to volume ratio which leads to one of the possibilities which raises the highest hopes: the area of nanotube-based gas sensors. One, for instance, envisions the possibility of combining high sensitivity with room temperature operation, surpassing more commonly used semiconductor-based sensors. At the same time, from the technological point of view, one is probably going to use bundles of CNTs instead of a single tube due to commercial viability. In this work we use density functional theory (DFT) calculations to determine the electronic structure properties of different molecules interstitially positioned between the nanotubes in a bundle. From the most stable structures we couple the DFT calculations to a recursive Green's function method to simulate the electronic transport properties of nanotube bundles containing a large number of molecules randomly distributed along the different tubes forming the ropes. This way one is able to simulate a realistic sensor based on three- dimensional nanotube bundles taking into consideration the effects of disorder. Our results show that both ammonia and CO when trapped between the tube walls show high sensitivity.

Abstract 675
CCTN11

Ab initio simulations of electronic transport of nanotube bundles used as gas sensors

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Carbon Nanotubes (CNTs) are interesting materials from the viewpoint of applications due to some of their astounding properties such as the possibility of being metal or semiconductor - depending on its chirality - as well a large Young's Modulus (about 1TPa). Because of these properties the CNTs could be used in nanosensors, nanodevices and reinforcements in polymer matrices. Experimental studies have shown that low doses of ion irradiation can create links between the walls of nanotubes and consequently modify their proprieties even further, in particular their mechanical and electrical ones. In this work we theoretically address the possibility of building an electromechanical device using double-wall carbon nanotubes (DWCNTs) connected by different cross-links. For this study we have investigated the Wigner Defect – consisting of the Frankel pair composed by a vacancy-interstice with connections between the walls of the DWCNTs.

We investigate two distinct systems: first we study a device composed by two different electrodes, one (10,10) and other (5,5) CNT in a telescope-type arrangement connected by a defect within a double wall segment. The second arrangement considers a weight-type arrangement where an (5,5) nanotube connects two (10,10) CNTs via a double-wall region that contains the defect. Using Density Functional Theory with Non-equilibrium Green's Function we show how the mechanical properties could alter the electronic transport in these systems. For all systems we will show that the transmittance has several resonances, which depend on the particular relative positions of the atoms in the nanotubes. Thus we will demonstrate how small displacements of the inner tube can alter the position of these peaks for the above systems leading to a device that could be used as a mechanical sensor for length scales in the nanometer and subnanometer range.

Using Raman Spectroscopy and Electron Microscopy as Metrological Tools in the Study of Graphene and Other Carbon Nanostructures

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Graphene is a promising material in the development of future nanodevices. Developing methods of characterization and creating metrological standards is an issue of great relevance in this process. Here we present different approaches in the study of defects and deformations in graphene done at the Division of Materials in Inmetro. Raman is the most common technique used to study carbon materials and it is also the most suitable to study the presence of defects in graphene. We have done a thorough analysis of the Raman spectrum of a monolayer graphene as we increase the disorder in the system by a systematic and controlled ion bombardment. In special, the evolution of the intensity ratio between the G band (1585 cm^{-1}) and the disorder-induced D band (1345 cm^{-1}) with ion dose is accurately determined, providing a spectroscopy-based method to quantify the number of defects in that system

When two graphene are placed on top of each other, they can form the Moiré pattern, a super lattice structure generated by a mismatch angle between the top and bottom layer. Recently was demonstrated that twisted graphene layers can generate low energy van Hove singularities in the density of electronic states. Here, a study of intravalley and intervalley double-resonance Raman processes mediated by static potentials in rotationally stacked bilayer graphene is presented. The peak properties depend on the rotation angle and can be used as an nanometrology tool for super lattices in bilayer graphene. A lattice resolution atomic force microscopy system is used to identify a specific rotationally stacked bilayer graphene that, together with Raman spectroscopy data demonstrates the validity of our model.

Annealed graphene layers samples at 2800 °C shows an excellent contrast under 80 kV TEM observations. We have studied the propagation of vacancies assisted by the presence of Fe and Pt nanoparticles deposited by sputtering in an ultra-high vacuum scanning tunneling microscope (STM). Our experiments show a difference in the dynamics of vacancies creation in the presence of Fe. We observed the formation of holes in the graphene layers, and as the honey- comb network thinned between two holes (below 1 nm) we identified the formation of carbon chains. Also, during one of these experiments the formation of large vacancies allowed us to observe in detail the morphology of a double loop formed at the edges of four layers of graphene.

How to Improve Interference Substrates for the Exploration of Graphene and Nanotubes

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Progress on single layer graphene can be attributed to making graphene visible using optical microscopes. Using interference colour changes on oxidized Si surfaces makes single layer graphene visible [1]. This can be explained using a Fresnel law based model. We use the transfer matrix method to calculate the local filed across the oxidized Si substrate showing that the maximum of optical surface standing waves fall at the surface of the substrate. This means that the interference substrate acts as a half cavity. We have calculated the broadening of the interference maximum due to the numerical aperture of the illumination optics. Adding a highly reflecting metal layer improves the performance of the half cavity and one can enlarge the amplitude of the surface standing wave increasing optical contrast. The fact that the maximum of the surface standing wave falls on the surface makes that the Raman signal is enhanced [2]. The maximum amplitude at the substrate surface corresponds to four times the amplitude in vacuum. We show how plasmon coupling combined with the enhanced field at the surface of the substrate contributes to the observed enhancement in graphene enhanced Raman spectroscopy [3].

[1]. P. Blake, W. Hill, A.H. Castro Netoet al., *App. Phys. Lett*,. **91**, 063124,(2007) [2]. W.S. Bacsa, J. Lannin, *Appl. Phys. Lett.,* **61**, 19-21, (1992)
[3]. X. Ling, L. Xie, H. Xu, H. Zhang, J. Kong, M.S. Dresselhaus, J. Zhnag, Z. Liu, *Nano Letters*, **10**, 553-561, (2010)

Raman Metrology Of Uniaxially Strained Graphene

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The presented work summarizes various aspects of uniaxial deformation in single- and bilayer graphene studied by means of Raman spectroscopy. Graphene flakes were subjected to tension - compression uniaxial loading using the cantilever beam technique [1-4]. The evolution of the Raman single-resonance (G) and double-resonance (2D, G*) bands is monitored at strain levels < 1%. The position of all peaks redshifts under tension and blueshifts under compression. The G peak splitting into two sub-bands (G^- and G^+) which is caused by symmetry lowering, is observed in both strain directions. The sub-bands' intensities are used to calculate the crystal lattice orientation of the measured graphene flakes with respect to the strain axis [2,5]. The nature and splitting of the 2D band even in the unstrained flakes, when excited by the 785 nm (1.58 eV) laser line, is interpreted as the interplay between two distinct double resonance scattering processes [3].

Finally, it will be shown, that the flake geometry and the presence of residual strain strongly influence the deformation behavior of the individual flakes, which is then reflected in the Raman shift rates and slopes [2-4]. Most importantly, the observed differences between experiments using flakes firmly fixed in the substrate or simply laid on its surface are mainly due to slipping and non-uniform stress transfer at various stages of the loading cycles [4]. The stress transfer to graphene flakes from under- and/or overlying polymers as well as large-scale buckling [2] is monitored by detailed Raman mapping.

[1] O. Frank, G. Tsoukleri, I. Riaz, K. Papagelis, J. Parthenios, A.C. Ferrari, A.K. Geim, K.S. Novoselov, C. Galiotis*, Nature Communications* **2**, DOI: 10.1038/ncomms1247 (2011).
[2] O. Frank, G. Tsoukleri, J. Parthenios, K. Papagelis, I. Riaz, R. Jalil, K.S. Novoselov, C. Galiotis, *ACS Nano* **4**, 3131-3138 (2010).
[3] O. Frank, M. Mohr, J. Maultzsch, C. Thomsen, I. Riaz, R. Jalil, K.S. Novoselov, G. Tsoukleri, J. Parthenios, K. Papagelis, L. Kavan, C. Galiotis, *ACS Nano* **5**, 2231–2239 (2011).
[4] G. Tsoukleri, J. Parthenios, K. Papagelis, R. Jalil, A.C. Ferrari, A.K. Geim, K.S. Novoselov, C. Galiotis, *Small* **5**, 2397-2402 (2009).
[5] T.M.G. Mohiuddin, A. Lombardo, R.R. Nair, A. Bonetti, G. Savini, R. Jalil, N. Bonini, D.M. Basko, C. Galiotis, N. Marzari, K.S. Novoselov, A.K. Geim, A.C. Ferrari*, Physical Review B* **79**, 205433-8 (2009).

Resonant Raman Spectroscopy on ^{13}C Enriched Carbon Nanomaterials

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Isotopically enriched single wall carbon nanotubes (SWCNTs) and graphene were investigated via Resonance Raman spectroscopy. The effect of the reduced mass variation of the isotope mixture on the phonon frequencies is described through a simple harmonic oscillator approximation. For ^{13}C modified SWCNTs linear reductions of the Raman frequencies with an increase of ^{13}C concentration are observed for the different nanotube Raman modes. In addition to the frequency dependence, the Raman linewidths as a function of the concentration of ^{13}C were also investigated and an expression describing this is presented. We observed a reduction of the G band linewidth, associated with the isotopic mass variation and a decrease of the phonon lifetime, when the isotope mix ratio has increased. Through an analysis of the Raman spectra of the radial breathing modes (RBM) obtained with different excitation energies, and the optical absorption spectra of the isotope samples, a relation between the RBM frequency and the diameter of ^{13}C enriched nanotubes was also established. Measurements with different excitation energies were performed and the frequency dispersions of the D and G' bands with laser energy were observed to be the same for ^{12} C and ^{13}C nanotubes, suggesting no changes in the electronic structure after isotope enrichment.

A sample of graphene containing a spatially varying mixture of ^{13}C-graphene vs. normal graphene (having 1.1 at% ^{13}C) grown by chemical vapor deposition of methane on Cu foil was interrogated using different laser energies. A comparison between isotopically labeled SWCNTs and isotopically labeled graphene will be presented.

Molar Extinction Coefficient of Single-Wall Carbon Nanotubes

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The molar extinction coefficient of single-wall carbon nanotubes (SWNTs) is determined using fluorescence tagging, as well as AFM imaging, to correlate nanotube concentrations with absorption spectra. Tagging of SWNTs is achieved using fluorescence labeled single strand DNA oligomers as dispersion additive, while AFM imaging is used to determine the mass of SWNTs in the retentate of vacuum filtered colloidal SWNT suspensions. The resulting absorption cross section for the first exciton transition of (6,5) nanotubes of $1.7 \cdot 10^{-17}$ cm^2 per C-atom corresponds to an extinction coefficient of (4400±1000) $M^{-1} \cdot cm^{-1}$ which is equivalent to an oscillator strength of 0.010 per carbon atom. In combination with the measurement of radiative lifetimes this also allows a determination of the first subband exciton size of (6,5) SWNTs which is here found to be 3.2 nm.

Gate-Induced Blueshift and Quenching of Photoluminescence in Suspended Single-Walled Carbon Nanotubes

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Understanding of electric-field effects on optical emission properties in single-walled carbon nanotubes is a key to the development of carbon-based nanoscale optoelectronics. In particular, gate-fields are expected to cause redshifts through screening and Stark effects, allowing for voltage-tuning of emission wavelengths. Here we report on gate-voltage dependence of photoluminescence spectra in individual suspended single-walled carbon nanotubes. As-grown nanotubes within field-effect transistor structures are identified by photoluminescence imaging using a home-built laser scanning confocal microscope. Excitation spectroscopy is used to determine their chirality, and photoluminescence spectra are collected as a function of gate voltage. Surprisingly, we fnd that the emission blueshifts when the gate voltages are applied. The blueshifts occur in nanotubes with different chiralities and types, suggesting that it is an extrinsic effect. Furthermore, the photoluminescence intensity decreases exponentially with gate voltage, and we find that a model assuming doping-induced exciton relaxation proportional to carrier density cannot account for all of the quenching observed.

Tip Enhanced Raman Scattering & Multiprobe Scanned Probe Imaging & NanoLithography of Carbon Nanotubes & Graphene

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Research will be described that has focused on optimizing the essential components of instrumentation and probes for carbon nanotubes and Graphene functional imaging.

One important such probe is for tip enhanced Raman scattering (TERS) and associated techniques based on full integration of scanned probe microscopy with microRaman spectroscopy. The results of this research effort have allowed for a general TERS solution that can be applied for both opaque and transparent samples and employing exciting developments of multiprobe scanned probe microscopy. It also permits for integration with all upright, inverted and dual 4 Pi microscope solutions. The probes that have worked best have been those that are based on single gold nanoparticles at the exposed tip of a low dielectric glass probe (see diagrammatic representation below). These probes were originally designed for use in tip enhanced non-linear optical microscopy (TEN)[1]. Such probes will be compared to other solutions in the literature especially those based on etched wires of gold or silver or coated silicon probes. The data indicate that single gold nanoparticle probes provide artifact free TERS results. As part of this research it has been necessary to define samples which have specific properties to demonstrate the nature of the TERS effect. This aspect of the research has identified the factors that maximize enhancement and minimize the optical interference that can be parasitic to the TERS signal.

In addition it will be shown that these TERS developments are compatible with exciting new directions in multiprobe scanned probe microscopy measurements (see above) with probes that include not only those for TERS but also those that can be applied to multiprobe electrical, thermal and Kelvin probe scanned probe microscopy.

The results indicate that these developments together with their full integration with Raman spectroscopy are powerful techniques for such carbon based fundamental and applied developments.

[1] Barsegova et al, *Applied Physics Letters* **81**, 3461-63 (2002)

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Femtonewton Force Sensing and Optical Trapping of Nanotubes and Graphene

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Optical Tweezers, instruments based on a tightly focussed laser beam, have been used to trap, manipulate, control and assemble dielectric particles, single atoms, cells, metal and semiconducting nanostructures, leading to a real optical revolution in Physics, Biology and Nanotechnology. In particular, optical trapping of one-dimensional nanostructures has great potential for top-down organization of complex nano-assemblies [1-7] and increased space and force resolution in photonic force microscopy [1,5,8]. Their small transverse size is the key to achieve nanometric resolution, while an axial dimension in the micron range ensures stable trapping and force sensing in the femtonewton regime. Here we discuss our recent results on optical trapping and force sensing with nanotubes and graphene [3-6,9]. We show how to extract the distribution of both centre-of-mass and angular fluctuations from three- dimensional tracking of optically trapped nanotubes [5]. The optical force and torque constants can be measured from auto and cross-correlation of the tracking signals [5,6]. This allows us to isolate the angular Brownian motion [5]. We demonstrate that nanotubes enable nanometer spatial, and femto-Newton force resolution in photonic force microscopy [1,5,8] by accurately measuring the radiation pressure in a double frequency optical tweezers. Furthermore we use correlation function analysis to study the rotational dynamics of light driven nanorotors made of nanotube bundles [6]. We then extend our results to study trapping and dynamics of individual graphene flakes in solution. Finally, we show how to integrate optical trapping with Raman and photoluminescence spectroscopy. We demonstrate the use of these Raman and photoluminescence Tweezers to study nanotubes and graphene flakes in solution [9].

[1] O.M Maragò, P.H. Jones, P.G. Gucciardi, Photonic Force Microscopy: From Femtonewton Force Sensing to Ultra-Sensitive Spectroscopy, in “Scanning Probe Microscopy in Nanoscience and Nanotechnology”, ed. B. Bushan, Springer-Verlag (2010).
[2] Y Nakayama et al. *Nature* **447**, 1098-1102 (2007).
[3] F. Borghese et al. *Phys. Rev. Lett*. **100**, 163903 (2008).
[4] O.M. Maragò et al., *Physica E* **40**, 2347-2351 (2008).
[5] O.M. Maragò et al. *Nano Lett*. **8**, 3211-3216 (2008).
[6] P.H. Jones et al. *ACS Nano* **3**, 3077 (2009).
[7] A.A.R. Neves et al., *Opt. Express* **18**, 822 (2010).
[8] E. L. Florin et al*., J. Struct. Biol*. **119**, 202 (1997).
[9] O.M. Maragò et al., *ACS Nano* **4**, 7515 (2010) .

Pristine, Empty Nanotubes Have Enhanced Electronic and Vibrational Properties

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In this talk we show that both empty and water-filled single-walled carbon nanotubes (SWCNTs) coexist in aqueous solutions, that the solutions of chemically purified or sonicated SWCNTs (as are generally used in the literature) contain mainly water-filled tubes and, more importantly, that the intact, empty nanotubes possess quite different and far superior electronic and vibrational properties with ~2 times higher fluorescence quantum efficiencies and ~4-5 times larger resonant Raman cross-sections (compared to the commonly used filled tubes).

We have previously shown that the water-filling of SWCNTs can be experimentally observed by a blue shift and broadening of the radial breathing mode (RBM) frequency and a red-shift and broadening of the electronic transitions and that even a very limited sonication can already open a majority of the tubes.[1,2] Starting from carefully solubilized solutions (i.e. no sonication), the pristine, closed SWCNTs can be sorted out by density gradient ultracentrifugation.[3] These empty nanotube solutions yield by far the most resolved Raman spectra ever observed for SWCNTs, with RBM line widths down to 1.16cm^{-1}, which implies very long phonon lifetimes (setting a lower limit of 4.6ps for the (6,4) tube), suggesting improved thermal conductivities for the intact tubes. Also their electronic transitions are much narrower compared to the water-filled ones. This indicates that also the electronic properties are much less perturbed, which is further confirmed by dramatically improved fluorescence efficiencies and Raman cross-sections, which, combined with the much narrower RBM lines, yields extraordinarily strong peak intensities in Raman spectroscopy.

Clearly, the filling state of SWCNTs is an important variable that needs to be taken into account when using optical spectroscopy for quantitative analysis of carbon nanotube samples.

[1] W. Wenseleers et al., *Adv. Mater*. **19**, 2274-2278, (2007).
[2] S. Cambré et al., *Phys. Rev. Lett*. **104**, 207401, (2010).
[3] S. Cambré and W. Wenseleers, Angew. *Chem. Int. Ed*. **50**, 2764-2768, (2011).

In situ NEXAFS study of Initial Growth Process of Carbon Nanotube by Surface Decomposition of SiC

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Carbon nanotube (CNT) growth by thermal decomposition of SiC is a unique technique because CNTs grow only by heating SiC substrates above 1200 ºC in a vacuum. By this method, aligned zigzag-type CNTs with fairly uniform tube diameters can be produced without any catalysts. So far, it has been reported that nanosized cap structures ("carbon nanocap") are initially formed and that these nanocaps determine the CNT structures. However, formation process of carbon nanocaps has never been clarified, although elucidation of growth mechanism would lead to control of structural parameters of CNTs. In this study, we carried out in situnear edge X-ray absorption fine structure (NEXAFS)spectroscopy measurement for the initial stage of CNT growth by surface decomposition of SiC. 6H-SiC single wafers with well-polished (000-1) carbon-face were used as samples. After HF treatments, the samples were transferred into a UHV chamber and heated up to an intended temperature under a H_2 ambient atmosphere. The sample temperature was monitored with a pyrometer. Above 1000 ºC, the heating rate was kept less than 1 º C/min to form carbon nanocaps. In situ C *K*NEXAFS measurements were carried out in the UHV chamber at BL-7A in the Photon Factory of KEK. The NEXAFS spectra were measured in Auger electron yield detection mode, keeping the sample at the heating temperature. Below 1000 ºC, the C *K* NEXAFS spectra were similar to those of 6H-SiC. At 1110 ºC, a weak C-C π^* resonance peak appeared at 285 eV in the spectrum, suggesting the beginning of decomposition of SiC surface. When the sample temperature was 1360 ºC, the NEXAFS spectrum was almost the same as that of graphite, indicting the carbon nanocap formation. Polarization dependence of the NEXAFS spectra indicated that direction of C-C bonds changed during the carbon nanocap formation. Based on these results, we propose a formation model for carbon nanocaps by surface decomposition of SiC.

[1] M. Kusunoki et al., *Appl. Phys. Lett.* **77** 531 (2000).
[2] T. Maruyama et al. *Chem. Phys. Lett.* **423** 317 (2006).

Carbon Nanoubes as substrates for Surface Enhanced Raman Spectroscopy

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The surface enhanced Raman spectroscopy (SERS) has attracted great attention in the last 30 years. It can increase the Raman signal of molecules by several orders of magnitude facilitating the detection of even trace molecules. In SERS effect, the substrates play a key role, being the responsible for the intensification of the Raman signal. The substrates are obtained by conventional deposition or immobilization of metal nanoparticles on a surface. The current challenge is the gain in performance with the fabrication of nanostructured SERS substrates. Recently, it was shown that if this surface is composed by carbon nanotubes, the effect can be dramatically increased. Also very recently, single or few layers of graphene were seen to work as SERS substrate without even the presence of metallic particles. In this work we investigate the Raman spectra of Raman spectra of octadecilamine molecules bonded to the surface of single-wall carbon nanotubes. Laser excitation energy is changed from 1.92 to 3.81 eV and the dependence of the Raman signal with excitation energy is observed. We note that under special conditions of resonance, the Raman signal of octadecilamine interacting with carbon nanotubes is strongly increased, becoming even stronger than the resonant Raman signal of the carbon nanotubes.

Metrology of Single Walled Carbon Nanotubes With Engineered Defects

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One of the main issues in carbon nanotubes science and technology is nanotubes purity and quality. The majority of samples contain carbon nanotubes with defects. Therefore the investigation of the effects of defects on carbon nanotubes properties is an important task of nanotubes metrology. For the evaluation of the defects Raman spectroscopy is frequently used, since the intensity of the D band in the Raman spectra of SWCNT is related to the concentration of defects. Here we have studied long (more than 1 mm) individual single wall carbon nanotubes which were intentionally and only locally modified by defects while other parts of the tube remained defect-free. We use Raman spectroscopy and in situ Raman spectroelectrochemistry to investigate the changes in the electronic structure of a particular SWCNT by the creation of defects. We show that not only is the increased D band a signature of defects in carbon nanotubes Raman spectra, but the creation of a defect also caused a significant decrease of the intensity of other Raman features. In addition we show that defects leads to a broadening of the Raman resonance profile and also to a decrease of the resonance profile intensity maxima.[1] In addition we studied the intensity of the D band, the ratio of the intensities of the D band and the TG band (I_D/I_{TG}), and the ratio of the intensities of the D and G' band ($I_D/I_{G'}$) in the Raman spectra of SWCNT bundles and their dependence on doping level. It is shown that the D band intensity is significantly attenuated in a doped carbon nanotube sample for both semiconducting and metallic tubes. Furthermore we found that the I_D/I_{TG} ratio is weakly dependent on doping for semiconducting tubes but for metallic tubes the I_D/I_{TG} ratio exhibits a dramatic dependence on doping. The $I_D/I_{G'}$ ratio, which is most frequently used for quantification of the defects, is changed only weakly at low doping levels but at high doping levels the $I_D/I_{G'}$ ratio exhibits a significant dependence on charging and doping level.

[1] M. Kalbac, Y-P. Hsieh, H. Farhat, L. Kavan, M. Hofmann, J. Kong, and M.S. Dresselhaus, *Nanoletters*, **10**, 4619-4626 (2010).

In Situ Raman Spectroscopy Of Carbon Nanotubes During Growth By A Local Heating Technique

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Most carbon nanotube synthesis methods require temperatures that are higher than what can be used for integration of nanotubes into electronics. In this study, a local heating technique is used to grow nanotubes in a CMOS-compatible process. High temperatures are generated locally on the sample by sending a current through a small molybdenum wire/heater which is deposited on the substrate. Nanotubes are grown from catalysts deposited on top of the heater whereas the temperature rapidly decreases to room temperature outside it. Since no furnace is required in this technique a small chamber that fits under a Raman microscope is used. This allows *in situ* Raman spectroscopy of the growing nanotubes. It is found that the heater is carbonised before any growth occurs and that the growth can be well described by the model used in refs. [1-3]. The kinetics show that the process is limited by mass transport of the carbon precursor. Fast growth rates are recorded despite the use of a cold carbon precursor, which has been shown to decrease the growth rate significantly [4]. We find that the molybdenum heater creates an additional pathway for the carbon cycle from gas to nanotube formation.

[1] E. Einarsson, et al., *Carbon,* **46**(6): p. 923-930 (2008).
[2] D.N. Futaba, et al., *Physical Review Letters*, **95**(5): p. 056104 (2005).
[3] M. Picher, et al., *Nano Letters*, **9**(2): p. 542-547 (2009).
[4] A.J. Hart, et al., *Small*, **3**(5): p. 772-777 (2007).

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Evaluation of Affinity between Carbon Nanotubes and Organic Molecules

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A family of single-walled carbon nanotubes (SWNTs), though existing as a mixture of different chiralities, has unique electronic, photophysical, mechanical and thermal properties. Because these properties markedly depend on its own chirality, facile preparation of highly pure SWNT with single chirality becomes one of the most important issues in the current carbon nanotube science and technology. However, any rational materials design enabling to efficiently extract/solubilise pure SWNT with a desired chirality has yet not been demonstrated.
In this paper, we demonstrate, fort the first time, a method for the selective chiral recognition and solubilization of selected (*n*,*m*) SWNTs [1]. The approach is to use new p-conjugated copolymers which have the selective recognition and solubilization abilities of (*n*,*m*) SWNTs with a few specific chirality. The p-conjugated copolymers are polyfluorene-based copolymers carrying achiral and bulky chiral side chains. We have discovered a regulated SWNT chirality recognition/dissolution by changing the copolymer composition ratios due to the SWNT chiral angle recognition by the copolymers. A molecular mechanics simulation partially explained this behavior based on binding energies and close packing.

[1] J-T. Yoo, H. Ozawa, T. Fujigaya and N.Nakashima, *Nanoscal*e, in press.

Solvents for Nanotubes and Graphene – Why the Difference?

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The effective dispersion of nanomaterials is universally acknowledged to be critical when one wishes to harness their full potential in devices or applications. Over the past number of years much work has been carried out on overcoming the inherent difficulties associated with producing high quality dispersions of both single walled carbon nanotubes (SWNTs) and graphene. Liquid-phase exfoliation of these intractable materials in organic solvents offers high quality dispersions from a relatively simple processing route. Whilst work by these authors has discovered and chararacterised families of new solvents for both SWNTs and graphene there remains outstanding questions as to why certain solvents work and others do not [1-2].
Herein, I shall present recent findings on the critical components necessary for solvents to debundle SWNTs and/or exfoliate graphite to produce graphene. Whilst these two materials have very similar surface energies (a critical component when considering suitable solvents for materials), the set of effect solvents for both are not identical. Reasons for this variation will be presented.

[1] Bergin, S.D., et al., *ACS Nano*, **3**(8): p. 2340-2350 (2009).
[2] Hernandez, Y., et al., *Langmuir*, **26**(5): p. 3208-3213 (2010).

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Micro-Dielectric Environment Effect on the Band Gaps of (n,m)Single-Walled Carbon Nanotubes

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The electronic states of carbon nanotubes are one of the most fundamental properties of the nanotubes. We report the finding that the band gaps of (*n,m*) SWNTs are strongly affected by the change in micro-dielectric environments around the isolated nanotubes [1]. In situ photoluminescence (PL) spectroelectrochemistry of the films containing fifteen isolated (*n,m*) single-walled carbon nanotubes (SWNTs) cast on ITO electrodes in organic solvents including DMSO, acetonitrile, DMF, THF and chloroform was completed and then the oxidation and reduction potentials, and band gaps ($\Delta E_{\mathrm{electr}}$) of the (*n,m*) SWNTs in the solvents were determined. We have discovered that the $\Delta E_{\mathrm{electr}}$ of the (*n*,*m*) SWNTs become greater as the solvent dielectric constants decreased, which is in sharp contrast to the optical band gaps (ΔE_{opt}) that show virtually no solvent dependence. Such a strong solvent dependence of the electrochemical band gaps is due to the difference in the solvation energy of the charged SWNTs produced during the electrochemical processes.

[1] Y. Hirana, Y. Tanaka, Y. Niidome, N. Nakashima, *J. Am. Chem. Soc*. **132**, 13072–13077 (2010).

High-Resolution Photocurrent Microscopy of Carbon Nanotube Film Photodiodes

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Semiconducting carbon nanotubes (CNT) are a promising material for photovoltaic applications [1]. Within a photovoltaic element CNTs can take up various functionalities, e.g. as a light absorbing layer, conducting channel material or (transparent) electrode.

Here we present CNT thin film photodiodes in which CNTs act as the light absorbing layer and simultaneously promote the carrier separation and transport to the electrodes. The CNTs used in this study are highly separated (99%) semiconducting single-wall carbon nanotubes [2] that are self-assembled on a transparent substrate by an evaporation-driven process [3]. CNT thin film photodiodes are fabricated with two different contact metals, i.e. Palladium and Aluminum. The work function difference creates a built-in electric field in the device channel that transforms electron-hole pairs into free carriers at opposite contacts [4].

We use scanning oil-immersion laser microscopy in order to acquire short-circuit photocurrent and open-circuit photovoltage images of the CNT thin film photodiodes. A maximum optical resolution below 300 nm is demonstrated by comparative measurements of the local potential landscape in the same device, with and without the use of immersion oil at different excitation wavelengths. The possibility to study the underside of the device contacts provides unique insight into the coupling mechanisms at the CNT-metal interface.

[1] Avouris et al., *Nature Photonics* **2** (6) 341-350 (2008).
[2] Arnold et al., *Nature Nanotechnology* **1** (1) 60-65 (2006).
[3] Engel et al., *ACS Nano* **2** (12) 2445-2452 (2008).
[4] Chen et al., *Small* **4** (9) 1313-1318 (2008).

Challenging in Characterizing Modified SWCNT

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A great effort has been directed in recent years towards the chemistry of Single-walled carbon nanotubes (SWCNT); that is, the control of exfoliating and adding diverse chemical addends to their sidewalls. This field has matured rapidly and has reached the point were a vast array of functional moieties can be linked to SWCNT through both covalent and non-covalent interactions. Being able to "tune" the type, quantity, and location of functional groups on the SWCNT is an extremely valuable tool, particularly for applications in composite materials. Despite its obvious importance, the ability to characterize the types and quantities of functional groups attached to SWCNT has proven to be a difficult task. Here we will present our work in the characterization of functionalized SWCNT and the different tools used to identify functionalities and determine the functionalization degree.

Dispersion and Separation of Single Walled Carbon Nanotubes by Polysaccharides

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Chitosan, various neutral pH water-soluble chitosan derivatives and heparin sodium salt were investigated as dispersants of single-walled carbon nanotubes (SWNTs). Chitosan (CS) can disperse SWNTs well, but only in acidic pH condition. Our two novel derivatives, *O*-carboxymethylchitosan (OC) and OC modified by poly(ethylene glycol) at the -COOH position (OPEG), were able to produce highly effective debundling and dispersion of SWNTs in neutral pH aqueous solution. Debundling of the nanotubes into individuals was confirmed with transmission electron microscopy (TEM), atomic force microscopy (AFM), photoluminescence (PLE) and UV-vis-NIR spetroscopy. The solubilities of individually dispersed SWNTs in neutral water are 0.021 and 0.032 g/L for OC and OPEG, respectively, which are comparable to 0.038 g/L for SWNTs using CS in acetic acid. When heparin sodium salt was used as dispersant for CoMoCAT nanotubes, (8,4) tubes were preferentially extracted and enriched in the supernatant. Pristine CoMoCAT nanotubes are dominated by the (6,5) species, which has smaller diameter than the (8, 4) species. After threefold extraction, the composition percentage of (8,4) tubes, determined by PLE spectroscopy, increased from 7% to 60%. Computer modeling verified that, of the four semiconducting species abundant in CoMoCAT samples, the (8,4) species has the lowest binding energy with heparin. Nanotube solutions enriched in the (8,4) species were successfully used for fabrication of network field-effect transistors, confirming the easy removability of heparin. Polysaccharide dispersed SWNTs solution also can be used as reinforcement materials in alginate hydrogels. The results show that SWNTs can improve the mechanical and electrical properties of alginate hydrogels. In summary, we found that several polysaccharides can effectively debundle SWNTs in neutral aqueous solutions using a mild and easy-to-implement process. Also certain polysaccharide-heparin sodium salt can extract (8,4) chirality from CoMoCAT dispersion. Some polysaccharide-SWNTs solutions can be used to reinforce alginate hydrogels.

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Doping Single-Walled Carbon Nanotubes With Nitrogen: A STM And STS Investigation

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Prior to the integration of carbon nanotubes (CNTs) into nanoelectronic and C-based devices, large batches of nanotubes with reproducible and controlled properties are necessary. Because of the strong dependency of the electronic structure of carbon nanotubes with respect to geometrical parameters such as the diameter and the helicity, many efforts have been directed towards controlling the chiral indices of the tubes during synthesis or towards sorting nanotubes according to theses chiral indices. Another method to tune the nanotubes' electronic structure is to use doping, which may lead to properties that are more controlled by the chemistry than by the structure of the tubes. One of the most promising candidates for doping carbon nanotubes is nitrogen, thanks to its suitable atomic radius. Nitrogen atoms can however adopt different local environments (graphitic-like, pyridinic-like) which can have various effects on the nanotube's electronic structure.

To investigate this impact, Scanning Tunnelling Microscopy(STM) and Spectroscopy (STS), appears as a unique tool since it can provide local information regarding both the structural and electronic properties of carbon nanotubes. For instance, this technique has given experimental evidence of the correlation between the chiral indices of single-walled CNTs and their electronic structure [1-2].

Here, we present the results of a STM/STS study of nitrogen doped single-walled carbon nanotubes, prepared by two different techniques: the vaporization with a continuous laser of a C:Ni/Y target under a nitrogen atmosphere [3]and a CVD floating catalyst reactor using a hot iron wire/CO/ammonia system [4]. These techniques lead to single-walled nanotubes with a nitrogen content ranging from 0.3 to 4%, as determined by EELS.

For both synthesis methods, the STM images of nitrogen-doped CNTs reveal the presence of defects which can be assigned to the presence of N atoms since they are not observed in pure single-walled CNTs prepared in a similar way. These defects appear as large protusions (1 to 3 nm wide) at the surface of the nitrogen-doped tubes. High resolution STM images of the defects display various patterns, associated with different configurations involving one or several N atoms. Another signature of the incorporation of nitrogen is the presence of interference patterns which can be extended up to a few nanometres away from a defect.

On the STSspectra, that measure the local density of states, we observe additional sharp peaks at the N-based defects, as compared to spectra recorded in defect-free area that only display contributions associated with the van-Hove singularities (vHs). These new peaks appear at energies that are different from those of the vHs and correspond to localized states. Based on a comparison between our STM/STS data, other experimental results and theoretical studies, we will discuss the nature of the defects induced by nitrogen doping of carbon nanotubes and their consequences on the tubes' structural and electronic properties.

[1] J.W.G. Wildöer et al., *Nature*, **391**; 59 (1998)
[2] T.W. Odom et al., *Nature*, **391**; 62 (1998)
[3] H. Lin et al*., J. Phys. Chem. C*, **113**, 9509 (2009)
[4] T. Susi et al*., Physica Status Solidi B*, **246**, 2507 (2009)

Abstract 259
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Quantification of the Metallic/Semiconducting Ratio of Bulk SWCNT Samples by Cobalt Porphyrin Probe EPR Spectroscopy

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A simple, quantitative, and self-calibrating spectroscopic technique for the determination of the ratio of metallic (M) to semiconducting (SC) single-wall carbon nanotubes (SWCNTs) in a bulk sample is presented. The technique is based on the measurement of the electron paramagnetic resonance (EPR) spectrum of the SWCNTs to which Cobalt(II) octaethylporphyrin (CoOEP) probe molecules have been added. [1] This yields signals from both CoOEP molecules on M and on SC tubes, which are easily distinguished and accurately characterized in this work. The EPR intensities can be directly related to the mass fraction of M and SC tubes respectively. [2] By applying this technique to a variety of SWCNT samples produced by different synthesis methods, it is shown that these EPR signals for porphyrins adsorbed on M and SC tubes are independent of other factors such as tube length, defect density, and diameter. [2] CoOEP adsorption is checked to be unbiased towards M or SC tubes.

[1] S. Cambré, W. Wenseleers, J. Čulin, S. Van Doorslaer, A. Fonseca, J. B.Nagy, E. Goovaerts, *ChemPhysChem* **9**, 1930 (2008).
[2] S. Cambré, W. Wenseleers, E. Goovaerts, D.E. Resasco, *ACS Nano* **4**, 6717 (2010)

Wall-Selective Probing Of Double-Walled Carbon Nanotubes Using Covalent Functionalization

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Double-walled carbon nanotubes (DWNTs) present an original coaxial geometry in which the inner wall is isolated by the outer wall, while the latter is in direct interaction with the environment. Covalent functionalization, performed using an aryldiazonium salt, is presented here as an efficient tool to investigate DWNT devices. Optical and electrical properties of DWNTs are measured in pristine, functionalized and defunctionalized states. Absorption and resonant Raman spectroscopy measurements, on individual DWNTs and networks, show that the functionalization is reversible upon thermal annealing and occurs strictly at the surface of the outer wall, leaving the inner wall essentially unaltered by the chemical bonding. Individual DWNT field-effect transistors are operated in functionalized state with current flowing mainly through the inner wall, with a current intensity comparable to a pristine single-walled carbon nanotube device. Electrical transfer characteristics are demonstrated to provide unambiguous identification of the metallic or semiconducting character of both walls. Current saturation at high bias is also measured in the inner wall of functionalized DWNT, leading to novel insight on the current saturation mechanism. Finally, opportunities enabled by the wall-selectivity of the functionalization are discussed: fundamental experiments about wall to wall interactions in DWNTs are made possible, but also the design of novel environment-sensitive electronic devices in which the inner wall is used for electrical transport while the outer wall chemically interacts with external stimuli.

Engineering And Metrology Of Epitaxial Graphene

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We shall report recent progress in engineering and ultra-precise quantum Hall resistance measurements of epitaxial graphene devices on SiC. Any new material to be practically employed as an embodiment of a quantum resistance standard needs to satisfy stringent requirements not only with respect to quantisation accuracy, but also its robustness over a range of temperature, magnetic field and measurement current.
Quantisation of the Hall resistance in epitaxial graphene on silicon carbide accurate to 3 parts in a billion was previously demonstrated [1]. Now we shall show that encapsulated and photochemically gated epitaxial graphene devices [2] demonstrate extraordinary robustness of the $h/2e^2$ plateaux. We attribute it to the pinning of $\nu=2$ filling factor provided by charge transfer between the SiC surface and graphene layer [3]. This robustness makes epitaxial graphene ideally suited for quantum resistance metrology and facilitates even more precise measurements than ever before. We believe that the new results on graphene reported at this conference will help expand the horizon of quantum metrology and advance the understanding of both graphene and QHE.

[1] A. Tzalenchuk, S. Lara-Avila, A. Kalaboukhov, S. Paolillo, M. Syvajarvi, R. Yakimova, O. Kazakova, T. J. B. M. Janssen, V. Fal’ko, S. Kubatkin, *Nature Nanotechnology* **5**, 186-189 (2010).
[2] S. Lara-Avila, K. Moth-Poulsen, R. Yakimova, T. Bjornholm, V. Fal'ko, A. Tzalenchuk and S. Kubatkin, *Adv Mater* **23** (7), 878-882 (2011).
[3] S. Kopylov, A. Tzalenchuk, S. Kubatkin and V. I. Fal'ko*, Appl Phys Lett* **97** (11), 112109 (2010).

Direct Measurements of Bending Stiffness and Rippling Phenomena in Free-Standing Carbon Nanotubes

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Carbon nanotubes (CNTs) have a low mass and a high stiffness, which makes them suitable for future nano-electromechanical systems (NEMS), especially in high- frequency switching applications. In relays, the CNTs are bent during operation and a high bending stiffness is important throughout the bending sequence. Deformation modes will appear at large deflections, leading to a lower bending stiffness which in turn will influence the device performance. At relatively low bending curvatures there can be a wave-like rippling of the walls, while at higher bending curvatures there can additionally be a local collapse, buckling, of the walls.

Buckling [1] and severe rippling [2] have both been observed using transmission electron microscopy (TEM). TEM imaging is not particularly useful though for detecting the very onset of the rippling, as there are only minute distortions of the CNT-walls [3]. Various theoretical modelling [3,4] have indicated at which strain levels the rippling would emerge, and how the bending stiffness would be affected. There has been very little experimental data to compare with though, thus far.

Here we present direct measurements of the force response in freestanding carbon nanotubes. The measurements have been performed using a custom-built atomic force microscope (AFM) inside a scanning electron microscope (SEM). We have been able to detect the very onset of the rippling mode [5], which is manifested through an abrupt change in the bending stiffness of the CNTs. The stiffness drops by about a factor of two and the force response continues to be linear in the rippling phase. Critical strains for the rippling onset have been measured in nanotubes of 7-18 nm in diameter, and the obtained strain values compare well with theoretical modelling predictions. We have additionally found an indication that defects in the nanotubes will increase the critical strain value and give a reduction in Young's modulus. The present findings will have implications for the design of CNT-based NEMS, where exceeding the critical strain will influence the device performance.

[1] S. Ijima, C. Brabec, A. Maiti, and J. Bernholc, *J. Chem. Phys.* **104**, 2089 (1996)
[2] P. Poncharal, Z. L. Wang, D. Ugarte, and W. A. de Heer, *Science* **283**, 1513 (1999)
[3] M. Arroyo and I. Arias, *J. Mech. Phys. Sol.* **56**, 1224 (2008)
[4] I. Nikiforov, D.-B. Zhang, R. D. James, and T. Dumitrica, *Appl. Phys. Lett.* **96**, 123107 (2010)
[5] H. Jackman, P. Krakhmalev, and K. Svensson, Accepted for publication in *Appl. Phys. Lett.* (2011)

Abstract 680
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STM Images of Carbon-Nanotube Quantum Dots:Seeing a Wigner Molecule of Correlated Electrons

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The paradigm of few-electron complexes in quantum dots (QDs) relies on the idea that the lowest- energy quantized levels are filled according to Pauli's exclusion principle. If Coulomb repulsion is sufficiently strong to overcome the kinetic energy cost of localization, a different scenario is predicted: a “Wigner” molecule (WM) forms, made of electrons frozen in space according to a geometrical pattern. Despite considerable experimental effort, evidence of the WM in semiconductor QDs has been elusive so far. Here we demonstrate theoretically that WMs occur in gate-defined QDs embedded in typical semiconducting carbon nanotubes (CNTs). The unambiguous signatures of the WM state must be searched in the scanning tunneling microscopy (STM) images of the electrons. Through exact diagonalisation (ED) calculations, we unveil the inherent features of the electron molecular states. We show that, like nuclei in a usual molecule, electrons have localized wave functions and hence negligible exchange interactions [1, 2]. ED results for single and double QDs provide a simple interpretation for transport experiments in ultraclean CNTs [3, 4].

[1] A. Secchi and M. Rontani, *Phys. Rev. B* **80**, 041404(R) (2009).
[2] A. Secchi and M. Rontani, *Phys. Rev. B* **82**, 035417 (2010).
[3] V. V. Deshpande and M. Bockrath, *Nature Phys.* **4**, 314 (2008).
[4] F. Kuemmeth et al., *Nature* **452**, 448 (2008).

Quantum Conductance in Carbon Nanotube Systems

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Quantum conductance in carbon nanotube systems has been under investigation since the seminal publication by Frank *et al* announced a micrometre-scale room- temperature phase coherence length in multi-wall carbon nanotubes (MWNTs): one thousand times greater than those typically observed in metal nanowires [1]. This observation points to the application of carbon nanotubes as dissipationless interconnect for CMOS micoelectronics as well as single-molecule detection using coupled-wall MWNTs.

Quantum conductance is described by the Landauer formalism and expressed as multiples of the conductance quantum, $G_0=2e^2/h$; theory predicts that a single-wall nanotube (SWNT) will exhibit a conductance of $2G_0$. This work aims to tackle the open questions that followed the *Frank et al* publication, namely: i) is a direct measurement of the SWNT quantum conductance possible, ii) why do MWNTs exhibit only $1G_0$ of conductance rather than the ideal $2G_0$ per wall, and iii) can the quantum conductance of a sample be characterised by unique numbers of current-carrying 'modes' (m) and the associated transmission coefficients (T)?

Mechanically controllable break-junction (MCBJ) methods were used to probe the quantum conductance of freestanding nanotubes not subject to any chemical modification: SWNTs; the simplest multi-wall system, namely the double-wall carbon nanotube (DWNT); and MWNTs. Ideal (m=2, T=1) behaviour was observed in some SWNT systems but non-ideal m=2, T= 0.88 was also observed, sometimes in mixed ideal/non-ideal samples. In DWNTs produced by the coalescence method, one metallic channel contributes to quantum transport and additional field- and temperature-dependent two-channel contributions were observed. The electronic conductance of chemical vapour deposition grown DWNTs comprising two populations of inner- and outer-wall diameter showed two discrete conductances, $0.24G_0$ and $0.91G_0$ with non-ideal corresponding transmission coefficients of 0.12 and 0.45, respectively, were identified as those of the lowest-energy metallic subbands in outer walls. High-bias injection was dominated by two discrete conductance values for a wide range of excitation energy. Conductance in MWNT systems was found to comprise ballistic (1 G_0 contribution from the outer-wall) and diffusive contributions. Covalent functionalisation of the MWNTs was found to increase the diffusive nature of the electron transport whereas π-stacked chemical modification increased the number of scattering centres per nanotube but electron transport remained ballistic. In conclusion, ideal behaviour was observed in some SWNT systems but highly non- ideal behaviour was observed in multi-wall systems. The physical origin of the discrete values of the observed transmission coefficients emerged as question for future work.

[1] S. Frank, P. Poncharal, Z. L. Wang, W.A.de Heer, *Science* **280**, 1744, (1998).
[2] M. Baxendale, M. Melli, Z. Alemipour, I. Pollini, T.J.S. Dennis, *J. Appl. Phys*. **102**, 103721, (2007).

[3] M. Baxendale, P. Battini, I. Pollini, M. Endo, Y.A. Kim, T. Hayashi, H. Muramatsu, *Phys. Rev. B*, **80**, 125411, (2009).

Combining Independent Measurements on Individual Carbon Nanotubes

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We have studied the individual properties of freely suspended carbon nanotubes (CNTs) using three different measurement techniques: electronic transport measurements, Raman spectroscopy and electron diffraction measurements in a transmission electron microscope. The two latter techniques give two independent methods to determine the chirality of the nanotube [1,2]. CNTs with determined chiral indices are then studied, allowing us to tie the optical and electronic response to a known lattice structure. We have e.g. recently performed the first time-resolved (femtosecond) four-wave-mixing (FWM) measurements on individual (8,4), (24,14) and (28,14) CNTs [3], directly probing both exitonic and vibrational dynamics.
We will present those measurement, as well as transport and Raman measurements of known individual CNTs down to cryogenic temperatures.

[1] J. Rintala et al*., J. Phys. Chem. C*, **113**, 15398, (2009)
[2] H. Jiang et al., *Carbon*, **45**, 662, (2007)
[3] P. Myllyperkiö, et al., *ACS Nano*, **4**, 6780, (2010)

Abstract 684
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Graphene at High Pressure: Dimensionality Transition, Mechanical and Doping Effects Under Biaxial Strain

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The pressure-induced evolution of exfoliated graphene samples of n =1, 2 and 3 layers supported in silica on top of silicon substrates has been studied by Raman spectroscopy up to a maximum pressure of 9.8 GPa using different pressure transmitting media (PTM). The pressure derivative of the G-band strongly depends on both the number of layers and of the PTM. We show that the dependence on the number of layers is explained through the biaxial strain of graphene samples by the substrate compression which leads to a transition between a 2D towards a 3D mechanical response to biaxial strain when going from the bilayer to the trilayer sample. The dependence on PTM is on its side to be related to chemical interactions between the carbon layers and the compression fluid.

The Use of Ga$^+$ Focused Ion Beam to Modify Graphene for Device Applications.

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Graphene, a two dimensional carbon structure, is a model system that comprises exciting possibilities for demonstrating new physics and novel electronic applications, [1-3] many of which can be appreciated only by making nanoscale modifications in its structure. [4,5] Therefore, the study of defects, impurities and nanoconfinement in a single layer graphene is of great importance to understand, predict and tune the behavior of such material. Normally, such structures are on the 5 to 100 nanometer scale up to micrometer scale and many applications are predicted and demonstrated, for instance: Ballistic room-temperature transistors, carbon-based spintronic devices and permeation membranes. Graphene nanostructures have already been fabricated by electron beam lithography followed by reactive ion etching, scanning tunneling microscopy lithography, and atomic force microscopy anodic oxidation, and by chemically derived techniques. In this study we demonstrate well controlled etching of single layer graphene by using a Ga$^+$ focused ion beam. Using this technique, we obtain different structures such as graphene nanoribbons and periodic array of scratches. Using charge injection and electrical force microscopy the ion fluence that cuts the graphene in two parts are obtained. By means of polarized Raman spectroscopy the quality of the graphene edges at the scratches are studied. The Raman spectroscopy studies show that the graphene is resilient under the etching conditions, indicating that commercial Ga$^+$ ion column is a powerful technique to produce graphene nanocircuits with defined graphene edges.

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science*, **306**, 666-669 (2004)
[2] A. K. Geim, K.S. Novoselov, *Nature Materials*, **6**, 183-191 (2007)
[3] R. V. Noorden, *Nature* **442**, 228–229 (2006)
[4] C. H. Park, L. Yang, Y. W. Son, M. L. Cohen, S. G. Louie, *Nature. Phys.* **4**, 213 (2008)
[5] I. Deretzis, A.Magna, G.Forte, R. Pucci, *Physical Review B*, **80**, 195413 (2009)

Abstract 321
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Novel Testing Method Of Carbon Nanotube-Array Actuators

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Mats of randomly oriented carbon nanotubes, known as Bucky papers, show in contact with an ionic electrolyte an active strain based on the capacitor-like mode of operation [1]. The mats are manufactured by a filtration of an aqueous dispersion. The dispersion is made of commercially available CNT-powder. Various investigations show low reliability and reproducibility of powder-based structures because of the low powder-quality [2]. Furthermore the random orientation of the papers does not allow using the excellent properties of a single CNT. That is the reason why great efforts are made to align the free movable CNTs in the dispersion. Other aligned CNT-based structures like yarns or CNT- array-based papers suffer from low conductibility, low stiffness or bad alignment according to the manufacturing process. The mechanism of strain generation still remains undefined but there is a controversial discussion. Either it is a quantum-mechanical lengthening of C-bonds [3] or an electrostatic repulsion between charged CNTs [4]. Maybe it is a superposition of both mechanisms.

The presented paper focuses on a method for measuring the free strain of as produced vertically aligned CNT-arrays. The advantage of this approach is the analysis of a highly oriented CNT-based structure. The analysed arrays are provided by the working group of Schulte (Polymer Composites, Technical University of Hamburg-Harburg, Germany). The tubes have an average diameter of 20 nm therefore they can be identified as multi walled carbon nanotubes (MWCNTs). The average length depends on the CVD-processing time and differs between 500µm and 1300 µm. The basic substrate is silicon.

The cell of the set-up is designed for testing small volumes (15 ml) of ionic electrolytes. The tested specimens are 10 x 10 mm in size. The specimen used as working electrode is fixed at the bottom of the cell by two PTFE-clamps. The clamps are electrical conductible because of inner Pt-electrodes. A CNT-mat or CNT-arrays positioned in the cell will be used as counter electrode. The calomel-reference electrode completes the three-cell set-up. A glass-cylinder, placed on the top of the CNTs transfers the deflection external of the electrolyte. The deflection of the glass-cylinder is measured by a confocal sensor.

The tests show a similar quadratic correlation between activation voltage and free strain like it is found using CNT-mats within aqueous electrolytes. A maximum strain of 0.14% could be achieved. In comparison the cation-induced strain (negative charged electrode) has a dominant character.

This presented test set-up, the way of analysis and the used specimen avoid on the one hand measuring secondary effects and allow on the other hand recording the reaction of one MWCNT standing in parallel as an array. Therefore the analysed effect must be dominated by a quantum-mechanical character.

[1] R. H. Baughman et al., *Science*, **284**, 1340-1344 (1999).
[2] N. Grobert, *Materials Today*, **9**, 64, (2006).
[3] S. Ghosh, et al., *Chem.Phys. Lett*., **406**, 10-14, (2005).
[4] D. Suppiger, et al*., Phys. Chem.,* **11**, 5180-5185, (2009).

Isolated and shape defined graphene layers in a single litographic step

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Graphene layers produced by micromechanical cleavage are always surrounded by thicker, unwanted graphitic material that could interfere with the fabrication of electronic devices as it results in shorts or compromises lithography. Also, they are randomly shaped, while shape control is required for application.

Here we present a technique that allows, in a single and quick lithographic step, the production of fully isolated graphene samples of defined shape. Graphene flakes are first obtained by micro-mechanical exfoliation on a Si + SiO_2 substrates and characterized by optical microscopy and Raman spectroscopy. PMMA is spin-coated onto them and patterned via e-beam lithography in order to define on the graphene sample the contour of the desired shape. After resist development, oxygen plasma is used to etch the uncovered part of the graphene. This results in an island (graphene covered in PMMA) of desired shape isolated from the rest of the polymer film. The latter is then removed by immersion in de-ionized water, while the lithographically defined island remains on the substrate. All the graphitic material is removed from the substrate together with the polymer film. PMMA is eventually dissolved leaving a completely isolated and shaped graphene sample. The frame width is few microns wide and requires only seconds to be e-beam written. The plasma is very mild, as just part of the monolayer has to be etched, and does not affect the polymer-covered part of the flake. Raman spectroscopy shows the process does not induce any structural defects in the resulting shape-defined flakes.

In Situ TEM Investigations of Electronic and Mechanical Properties Of Nanotube Architectures

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Nanotubes have attracted great research interest due to their unique structure, novel properties and potential applications. However, it is important to have them connected via suitable interfaces for achieving specific functions and applications. While many studies have been conducted on the individual nanotube level, there are still only a few investigations on the complex architectures and the influence of interfaces on the device performance. In this contribution, we applied an *in situ* transmission electron microscopy (TEM) technique to investigate the electronic and mechanical properties of nanotube architectures. With the aid of atomically-resolved TEM imaging the interface structure and nanotube architecture properties were correlated.

The first example is the electronic properties of fabricated carbon nanotube (CNT)-clamped metal atomic chains (MAC) [1]. This hybrid nanostructure was prepared by *in situ* machining a metal-filled CNT, which included peeling off carbon shells by a spatially positioned and energy selective electron beam and further elongating the exposed metal nanorod. First-principles calculations indicated that strong covalent bonds had been formed between the CNT and MAC. The electrical transport properties of the CNT-clamped MAC were experimentally measured, and quantized conductance was observed. The second example is the effects of a homogeneous interface on the mechanical properties of boron nitride (BN) nanobamboos, an assembly of short BN nanotubes [2].

By combining *in situ* TEM mechanical tests and molecular dynamics simulations, it was demonstrated that the interface geometry had an important influence on the mechanical properties. Under a geometry strengthening effect, the BN nanobamboos showed fracture strength and Young' modulus up to 8.0 GPa and 223 GPa, respectively.

[1] D.-M. Tang, L.-C. Yin, F. Li, C. Liu, W.-J. Yu, P.-X. Hou, B. Wu, Y.-H. Lee, X.-L. Ma, H.-M. Cheng, *Proceedings of the National Academy of Sciences* **107**, 9055 (2010).
[2] D.-M. Tang, C.-L. Ren, X. Wei, M.-S. Wang, C. Liu, Y. Bando, D. Golberg, *Submitted*, (2011).

Optical Heterodyne Detection Visualizes the Spatial Resonance of Multilayer Graphene Cantilevers

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Graphene resonator is anticipated as ultrasensitive mass detectors and biosensors. To investigate the vibration of the graphene cantilever in various environments toward mass sensors of biological molecules, we developed the optical actuation and optical heterodyne detection based on the opto-mechanical heterodyne technique.[1]The graphene flakes were mechanically exfoliated over predefined 9μm-wide trenches on SiO_2 (300nm)/Si wafer to fabricate cantilevered graphene resonators. The length and width of the typical cantilevered graphene used in this study were 7μm and 7.5μm, respectively. For optical actuation of graphene resonators, we irradiated the graphene with a red laser (660nm, 300W) for thermal expansion by modulating the laser intensity, and with a blue laser (406nm, 1μW) to detect vibration amplitude by the optical detection technique. The modulation frequencies of two lasers were set with a small difference, Δf, resulting in the detection of the resonance at the frequency of Δf. First, to investigate the effects of gaseous dissipation of the graphene vibration, we measured the Q factors of the graphene vibration at the pressure of $1\sim10^4$ Pa. The Q factor at the pressure over 500 Pa was inversely proportional to the pressure, indicating that the graphene cantilever acts as in the free molecular flow. In contrast, the Q factor at the pressure below 500 Pa remained constant, implying that the energy loss induced by the collision of gas molecules was much smaller than the intrinsic energy loss of the graphene resonator. One of the advantages of our excitation/detection technique is that the vibration amplitude of the graphene can be spatially visualized over the surface of the graphene by changing the position of the laser that detects the vibration. This vibration mode analysis was examined using a combination of experiments and finite element method. In contrast, by changing the position of the laser that excites the vibration, thermal propagation of the graphene can also be estimated in order to determine where induces the vibration efficiently. This is crucial in the application using graphene-based nanoelectromechanical resonators in liquid.

[1] A. Yoshinaka et al., *Appl. Phys. Lett.* **98**, 133103 (2011).

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Collection-Mode Near-Field Nanoscopy of Individual CNTs

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Applications of luminescent single-wall carbon nanotubes (CNTs) in nanosized optoelectronics and photonics devices envisioned for the next future [1] require suitable optical characterization methods addressing individual CNTs. Within this frame, the abilities exhibited by nonpropagating electromagnetic fields in overcoming the diffraction limits offer unique possibilities. For instance, photoluminescence (PL) from emitting CNTs adsorbed on transparent samples has been imaged and analyzed by tip-enhanced microscopy several years ago [2].

We are presently using a collection-mode, polarization-controlled scanning near-field optical microscope (SNOM) to analyze PL and scattering from individual CNTs. Collection is accomplished in near-field by an aperture-probe, whereas excitation is provided in far-field by an optical fiber-focuser. Since the focuser is placed on the same side of the sample where near-field collection takes place, the system can be adopted for both transparent and opaque substrates. Moreover, the polarization status of the excitation radiation can be reliably controlled by polarizing optics put in front of the optical fiber. Since the focuser holder is mounted on a piezoelectric translator driven independently from the sample scanner, the excitation spot can be freely adjusted on the sample surface with respect to the probe. Thus, effects of the optical interaction between the CNT and any neighboring nanostructures such as surface plasmon waveguides and concentrators can be easily analyzed.

Preliminary results indicate a spatial resolution in the few tens of nanometer range and sensitivity suitable to collect optical scattering from individual CNTs with a photon-counting detector.

[1] P. Avouris, M. Freitag, and V. Perebeinos, “Carbon-Nanotube Optoelectronics”, in Carbon Nanotubes, *Topics Appl. Physics* **111**, 423-454 (2008); A. Jorio, G. Dressehlhaus, M.S. Dresselhaus,(Eds.), Springer-Verlag Berlin Heidelberg 2008.

[2] A. Hartschuh, H. Qian, A.J. Meixner, N. Anderson, and L. Novotny, *NanoLett*. **5**, 2310-2313 (2005).

An inner look into biscrolled CNT yarns: Studies on their different typical internal morphologies by microscopic analyses of their cross sections

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The biscrolling process is a suitable way to produce multifunctional weavable yarns of otherwise unspinnable nanofibers or particulate materials using twisted aligned CNT sheets as host. In brief, the biscrolling technique involves the deposition of guest material over one or several CNT sheets and their subsequent scrolling into a biscrolled yarn. Applications of this technique are broad and some of them have been shown by making yarns of superconductors, lithium-ion batteries, catalytic nanofibers for fuel cells and of particulate titanium oxide for photocatalysis.[1] During the scrolling process, nanometric-thick CNT host sheets produce complex irregular galleries along the yarn that act as confinement sacks for the guest material. Aiming to understand the general relation between the complex inner yarn morphology generated by the biscrolling process itself, microscopic studies were made on biscrolled yarn cross-sections prepared by focused ion-milling (FIB). Mechanisms such as pleating and additional folding during twist derive into the complex inner yarn morphologies found. However, general trends in the resulting morphology of biscrolled yarns were identified to depend upon factors such as (1)the deposition method used for the guest material and (2) the liquid-densification of the host CNT sheets or its absence either before or during the twisting process. The lateral migration of CNT sheets during the scrolling process was studied with patterned guest material deposition used as contrast marker on the CNT host sheets. This resulted in ways to engineer the location of guest material along the radius of a biscrolled yarn achieving production of core-shaft morphologies. Understanding the main causes of internal morphology variations in biscrolled yarns (apparent void space, guest location, etc.) could lead to a development of new feasible applications and encourage more studies of the mechanisms involved in yarn formation by twisting and spinning.

[1] M.D.Lima, S. Fang, X. Lepró, C. Lewis, R. Ovalle Robles, J. Carretero González, E. Castillo Martínez, M. Kozlov, J. Oh, N. Rawat, C.S.Haines, M.H.Haque, V. Aare, S. Stoughton, A.A. Zakhidov, and R.H. Baughman, *Science*, **331**, 51-55 (2011).

Resonant Raman Spectroscopy on ^{13}C Enriched Carbon Nanomaterials

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Isotopically enriched single wall carbon nanotubes (SWCNTs) and graphene were investigated via Resonance Raman spectroscopy. The effect of the reduced mass variation of the isotope mixture on the phonon frequencies is described through a simple harmonic oscillator approximation. For ^{13}C modified SWCNTs linear reductions of the Raman frequencies with an increase of ^{13}C concentration are observed for the different nanotube Raman modes. In addition to the frequency dependence, the Raman linewidths as a function of the concentration of ^{13}C were also investigated and an expression describing this is presented. We observed a reduction of the G band linewidth, associated with the isotopic mass variation and a decrease of the phonon lifetime, when the isotope mix ratio has increased. Through an analysis of the Raman spectra of the radial breathing modes (RBM) obtained with different excitation energies, and the optical absorption spectra of the isotope samples, a relation between the RBM frequency and the diameter of ^{13}C enriched nanotubes was also established. Measurements with different excitation energies were performed and the frequency dispersions of the D and G' bands with laser energy were observed to be the same for ^{12} C and ^{13}C nanotubes, suggesting no changes in the electronic structure after isotope enrichment.

A sample of graphene containing a spatially varying mixture of ^{13}C-graphene vs. normal graphene (having 1.1 at% ^{13}C) grown by chemical vapor deposition of methane on Cu foil was interrogated using different laser energies. A comparison between isotopically labeled SWCNTs and isotopically labeled graphene will be presented.

Dispersion and Separation of Single Walled Carbon Nanotubes by Polysaccharides

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Chitosan, various neutral pH water-soluble chitosan derivatives and heparin sodium salt were investigated as dispersants of single-walled carbon nanotubes (SWNTs). Chitosan (CS) can disperse SWNTs well, but only in acidic pH condition. Our two novel derivatives, *O*-carboxymethylchitosan (OC) and OC modified by poly(ethylene glycol) at the -COOH position (OPEG), were able to produce highly effective debundling and dispersion of SWNTs in neutral pH aqueous solution. Debundling of the nanotubes into individuals was confirmed with transmission electron microscopy (TEM), atomic force microscopy (AFM), photoluminescence (PLE) and UV-vis-NIR spetroscopy. The solubilities of individually dispersed SWNTs in neutral water are 0.021 and 0.032 g/L for OC and OPEG, respectively, which are comparable to 0.038 g/L for SWNTs using CS in acetic acid. When heparin sodium salt was used as dispersant for CoMoCAT nanotubes, (8,4) tubes were preferentially extracted and enriched in the supernatant. Pristine CoMoCAT nanotubes are dominated by the (6,5) species, which has smaller diameter than the (8, 4) species. After threefold extraction, the composition percentage of (8,4) tubes, determined by PLE spectroscopy, increased from 7% to 60%. Computer modeling verified that, of the four semiconducting species abundant in CoMoCAT samples, the (8,4) species has the lowest binding energy with heparin. Nanotube solutions enriched in the (8,4) species were successfully used for fabrication of network field-effect transistors, confirming the easy removability of heparin. Polysaccharide dispersed SWNTs solution also can be used as reinforcement materials in alginate hydrogels. The results show that SWNTs can improve the mechanical and electrical properties of alginate hydrogels. In summary, we found that several polysaccharides can effectively debundle SWNTs in neutral aqueous solutions using a mild and easy-to-implement process. Also certain polysaccharide-heparin sodium salt can extract (8,4) chirality from CoMoCAT dispersion. Some polysaccharide-SWNTs solutions can be used to reinforce alginate hydrogels.

Element Mapping of Coated Multiwall Carbon Nanotubes

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To facilitate any real application in the nm-range, be that using graphene or carbon nanotubes, it is vital to have means to characterise the element distribution with high spatial resolution. Modern energy-dispersive X-ray spectroscopy (EDS) in electron microscopy is a straightforward method for chemical analysis. Scanning transmission electron microscopy (STEM) using high brightness electron sources and aberration correction in combination with modern spectroscopy techniques such as electron energy loss spectroscopy and liquid nitrogen free silicon drift detectors (SDD) for EDS allows the characterisation on micrometer, nm and even atomic scale [1]. As one example coated multiwall carbon nanotubes, to be used as flexible interconnects [2], were investigated. 2-D element maps of the as grown carbon nanotubes containing Co and Ni catalysts and of CuO-coated tubes will be shown. Aberration corrected STEM and EELS at 80kV allows to count the number of tube walls and to judge the quality of the coating film produced by atomic layer deposition (ALD) [3]. EDS in SEM and conventional STEM reveals within minutes the whereabouts and type of the catalyst particles and the element distribution in the ALD coating. A combination of SEM- and TEM-spectroscopy techniques can provide reliable data on the structure and element composition of nanotube arrays in a reasonable amount of time.

[1] M. Falke, *Imaging & Microscopy*, **11**, 35-38, (2009).
[2] S. Hermann, et al.,*Microelectronic Engineering*, **87** (3), 438-442, (2010).
[3] T. Waechtler, et al.,*J. Electrochem. Soc.*, **156** (6), H453-H459, (2009).

Metrology of Single Walled Carbon Nanotubes With Engineered Defects

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One of the main issues in carbon nanotubes science and technology is nanotubes purity and quality. The majority of samples contain carbon nanotubes with defects. Therefore the investigation of the effects of defects on carbon nanotubes properties is an important task of nanotubes metrology. For the evaluation of the defects Raman spectroscopy is frequently used, since the intensity of the D band in the Raman spectra of SWCNT is related to the concentration of defects. Here we have studied long (more than 1 mm) individual single wall carbon nanotubes which were intentionally and only locally modified by defects while other parts of the tube remained defect-free. We use Raman spectroscopy and in situ Raman spectroelectrochemistry to investigate the changes in the electronic structure of a particular SWCNT by the creation of defects. We show that not only is the increased D band a signature of defects in carbon nanotubes Raman spectra, but the creation of a defect also caused a significant decrease of the intensity of other Raman features. In addition we show that defects leads to a broadening of the Raman resonance profile and also to a decrease of the resonance profile intensity maxima.[1] In addition we studied the intensity of the D band, the ratio of the intensities of the D band and the TG band (I_D/I_{TG}), and the ratio of the intensities of the D and G' band ($I_D/I_{G'}$) in the Raman spectra of SWCNT bundles and their dependence on doping level. It is shown that the D band intensity is significantly attenuated in a doped carbon nanotube sample for both semiconducting and metallic tubes. Furthermore we found that the I_D/I_{TG} ratio is weakly dependent on doping for semiconducting tubes but for metallic tubes the I_D/I_{TG} ratio exhibits a dramatic dependence on doping. The $I_D/I_{G'}$ ratio, which is most frequently used for quantification of the defects, is changed only weakly at low doping levels but at high doping levels the $I_D/I_{G'}$ ratio exhibits a significant dependence on charging and doping level.

[1] M. Kalbac, Y-P. Hsieh, H. Farhat, L. Kavan, M. Hofmann, J. Kong, and M.S. Dresselhaus, *Nanoletters*, **10**, 4619-4626 (2010).

Gate-Induced Blueshift and Quenching of Photoluminescence in Suspended Single-Walled Carbon Nanotubes

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Understanding of electric-field effects on optical emission properties in single-walled carbon nanotubes is a key to the development of carbon-based nanoscale optoelectronics. In particular, gate-fields are expected to cause redshifts through screening and Stark effects, allowing for voltage-tuning of emission wavelengths. Here we report on gate-voltage dependence of photoluminescence spectra in individual suspended single-walled carbon nanotubes. As-grown nanotubes within field-effect transistor structures are identified by photoluminescence imaging using a home-built laser scanning confocal microscope. Excitation spectroscopy is used to determine their chirality, and photoluminescence spectra are collected as a function of gate voltage. Surprisingly, we find that the emission blueshifts when the gate voltages are applied. The blueshifts occur in nanotubes with different chiralities and types, suggesting that it is an extrinsic effect. Furthermore, the photoluminescence intensity decreases exponentially with gate voltage, and we find that a model assuming doping-induced exciton relaxation proportional to carrier density cannot account for all of the quenching observed.

Characterization, Standardization and Industrial Quality of Multiwall Carbon Nanotubes

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We have undertaken review of the scientific literature and industrial requirements for the characterization of multiwall carbon nanotubes.[1]. Methods for sampling and determination of size, area, density, color, crystallinity, as well as purity compared to characteristics of non-MWCNT carbon and catalyst metals were compiled. As with single-wall carbon nanotubes, one measurement tool alone does not provide a complete characterization. We review characterization methods that include scanning electron microscopy, transmission electron micrsoscopy (TEM), fast Fourier transform of high- resolution TEM, Raman spectroscopy, reflectance, thermogravimetric analysis, Fourier transform infrared spectroscopy and Brunauer Emmett Teller (BET) analysis. We extend the review by presenting taxonomy of defects present in MWCNTs. It is clear that reference samples characterized by standard protocols are needed. Arguably, TEM is the most significant tool for the researcher attempting to characterize structural properties of MWCNTs; it is the only way to verify the existence of multiple tube walls and to verify that MWCNTs exist in a sample batch. We have presented a case for FFT as an adjunct to HRTEM to evaluate nanotube crystallinity and presence of defects. SEM is sufficient to approximate nanotube diameter and thus infer the presence of MWCNTs. In the industrial setting, however, MWCNTs are produced in multi-ton quantities, and TEM or SEM may not be economically competitive for routine characterization. Raman spectroscopy, TGA, and near infrared spectroscopy provide a picture of material purity after one has established the presence of MWCNTs in a bulk sample. Density and area measurements of bulk samples answer some fundamental questions for making engineering and economic decisions for a given application. In this review we discuss an ensemble of measurements to characterize MWCNT samples such that a basis for quality control can be achieved. Such information is also perhaps pertinent to evaluation MWCNTs for environment, health and safety requirements. We propose that some of this information may be useful for establishing documentary standards for MWCNT characterization.

[1] J. H. Lehman, M. Terrones, E. Mansfield, K.E. Hurst, V. Meunier, *Carbon*, **49**, 2581 – 2602 (2011).

Optical response of single-walled carbon nanotubes in far-infrared region

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A carbon nanotube (CNT) is one-dimensional and hollow cylindrical structure formed by wrapping a graphene sheet, and becomes either metallic or semiconducting depending on its geometry. Usually, single-walled carbon nanotubes (SWCNTs) have the order of a few nanometers in diameter and the order of several micrometers in length. Optical spectroscopy such as Raman scattering and photoluminescence is well-known to be effective technique to characterize their properties for electronic and optoelectronic applications. In addition, using infrared (IR) spectroscopy and terahertz time domain spectroscopy (THz-TDS), there has been reported the small band-gap and antenna effects of metallic SWCNTs [1-4]. The former has so far been reported theoretically and experimentally [1-3,5]. The small gaps in a few tens of meV at Fermi level were induced by the curvature effect and intertube interactions [5]. The latter, antenna effects by plasmon resonance have been predicted theoretically that frequency in far-IR spectroscopy and THz-TDS is proportional to the inverse tube length that has been one of the on-going themes in CNTs [4]. We here report optical response of SWCNTs by using FT-IR spectroscopy in mid- and far-IR range. Several types of SWCNTs were used and prepared on silicon wafer and polyethylene sheet. In case of arc discharge SWCNTs, the IR spectra exhibit a broad band around 100 cm^{-1} in low-frequency range and a sharp peak near 5580 cm^{-1} in high-frequency range. The latter is thought to be S1 interband transition of semiconducting SWCNTs. The former is considered to be a small gap or antenna effects-induced signal of metallic SWCNTs. To clarify the origin of this signal, we have investigated the doping dependence with F4TCNQ dopant and treatment time dependence by using tip ultrasonication which cut long SWCNTs into short pipes. Upon doping, the absorption intensity was enhanced or not decreased depending on a substrate in low-frequency region along with the strong reduction of the peak of S1 interband transitions. In addition, depending on treatment time of tip ultrasonication, the signals in low-frequency region were shifted upward, whereas no peaks of S1 interband transitions were shifted. The possible mechanisms for the experimental observations will be discussed in detail.

[1] M. E. Itkis, S. Niyogi, M. E. Meng, M. A. Hamon, H. Hu, and R. C. Haddon, *Nano Lett.*, **2**, 155 (2002).
[2] H. Nishimura, N. Minami, and R. Shimano, *Appl. Phys. Lett.,* **91**, 011108 (2007).
[3] N. Akima, Y. Iwasa, S. Brown, A. M. Barbour, J. Cao, J. L. Musfeldt, H. Matsui, N. Toyota, M. Shiraishi, H. Shimoda and O. Zhou, *Adv. Mater.* **18**, 1166 (2006).
[4] T. Nakanishi, T. Ando, *J. Phys. Soc. Jpn.,* **78**, 114708 (2009). 18, 1166.
[5] M. Ouyang, J.-L. Huang, C. L. Cheung and C. M. Lieber, *Science*, **292**, 702 (2001).

Length Analysis of Single-Wall Carbon Nanotubes Cut by Sonication

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Single-wall carbon nanotubes (SWCNTs) were frequently dispersed into suspension by sonication with the help of various dispersing reagents (detergents), not only for fundamental but also for applied research. Although the dispersing process using sonication was thought to cut SWCNTs, to date its detailed effect has not been fully clarified yet. In this work, we have investigated the differences in length distribution of SWCNTs against various detergents and dispersing conditions. In addition, we have fabricated thin film transistor (TFT) devices by using length-determined SWCNTs and investigated the consistency of the device performance because it was suggested that the length of SWCNTs largely affects the reliability on performances of SWCNT-TFTs [1]. Four detergents, sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfate (SDBS), sodium cholate (SC), and ethylene glycol (100) stearyl ether (Brij700) have been intentionally selected to explore the effect of cutting SWCNTs during their dispersing. The length of SWCNTs in each sample, deposited on the aminopropyltriethoxysilane (APTES) functionalized silicon substrate, were statistically characterized by the analysis of topographic images taken by atomic force microscope (AFM). For fabricating TFTs, the extraction of semiconducting SWCNTs was carried out by electric-force-induced layer formation (ELF) method [2]. The average length and percentage of extracted semiconducting SWCNTs were 336 nm and 97 %, respectively, characterized by AFM and Raman. For the shortened semiconducting SWCNTs, the device performances of TFTs fabricated on silicone substrates with SiO_2 layer of 100 nm thickness were measured. As a result of dispersing by bath sonication at 70 W, while the length distributions of SWCNTs, especially in SDS dispersing, highly depended on the dispersing process, dispersing by using SC and Brij700 showed shorter length distributions compared with SDS and SDBS. In particular, the detailed analysis proved the considerable decrease in the longer part of SWCNTs (> 1mm) in the sample dispersed by Brij700. Furthermore, when SWCNTs were dispersed by using Brij700 with the horn-type sonication homogenizer at 300 W for 10 hours, all measured SWCNTs were even shorter and in the range less than 600 nm with the average length of 119 nm. To investigate the dependence on SWCNT diameter, we have analyzed lengths of three different SWCNTs with mean diameters of 1, 1.4, and 2.2 nm dispersed by using SC and Brij700. In SC dispersions, average lengths of SWCNTs with diameters of 1, 1.4, and 2.2 nm were 528, 794, and 905 nm, respectively, and the dependency according to the diameter was observed. On the other hand, SWCNTs of Brij700 dispersions were shortened in the average length of less than 400 nm without showing the diameter dependence. These results suggest that Brij700 possesses the considerably strong ability that effectively cuts SWCNTs in their dispersing process. TFTs of shortened SWCNTs exhibited high performances in mobility and on/off ratio with extreme uniformity. Detailed characteristics of devices will be discussed in the presentation.

[1] M. Ishida and F. Nihey, *Appl. Phys. Lett.* **92**, 163507 (2008).
[2] K. Ihara, et. al., Abstract NT10, CT-38.

Quantum Conductance in Carbon Nanotube Systems

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Quantum conductance in carbon nanotube systems has been under investigation since the seminal publication by Frank *et al* announced a micrometre-scale room- temperature phase coherence length in multi-wall carbon nanotubes (MWNTs): one thousand times greater than those typically observed in metal nanowires [1]. This observation points to the application of carbon nanotubes as dissipationless interconnect for CMOS micoelectronics as well as single-molecule detection using coupled-wall MWNTs.

Quantum conductance is described by the Landauer formalism and expressed as multiples of the conductance quantum, $G_0=2e^2/h$; theory predicts that a single-wall nanotube (SWNT) will exhibit a conductance of $2G_0$. This work aims to tackle the open questions that followed the *Frank et al* publication, namely: i) is a direct measurement of the SWNT quantum conductance possible, ii) why do MWNTs exhibit only $1G_0$ of conductance rather than the ideal $2G_0$ per wall, and iii) can the quantum conductance of a sample be characterised by unique numbers of current- carrying 'modes' (m) and the associated transmission coefficients (T)?

Mechanically controllable break-junction (MCBJ) methods were used to probe the quantum conductance of freestanding nanotubes not subject to any chemical modification: SWNTs; the simplest multi-wall system, namely the double-wall carbon nanotube (DWNT); and MWNTs. Ideal (m=2, T=1) behaviour was observed in some SWNT systems but non-ideal m=2, T= 0.88 was also observed, sometimes in mixed ideal/non-ideal samples. In DWNTs produced by the coalescence method, one metallic channel contributes to quantum transport and additional field- and temperature-dependent two-channel contributions were observed. The electronic conductance of chemical vapour deposition grown DWNTs comprising two populations of inner- and outer-wall diameter showed two discrete conductances, $0.24G_0$ and $0.91G_0$ with non-ideal corresponding transmission coefficients of 0.12 and 0.45, respectively, were identified as those of the lowest-energy metallic subbands in outer walls. High-bias injection was dominated by two discrete conductance values for a wide range of excitation energy. Conductance in MWNT systems was found to comprise ballistic (1 G_0 contribution from the outer-wall) and diffusive contributions. Covalent functionalisation of the MWNTs was found to increase the diffusive nature of the electron transport whereas π-stacked chemical modification increased the number of scattering centres per nanotube but electron transport remained ballistic. In conclusion, ideal behaviour was observed in some SWNT systems but highly non- ideal behaviour was observed in multi-wall systems. The physical origin of the discrete values of the observed transmission coefficients emerged as question for future work.

[1] S. Frank, P. Poncharal, Z. L. Wang, W.A.de Heer, *Science* **280***,* 1744, (1998).
[2] M. Baxendale, M. Melli, Z. Alemipour, I. Pollini, T.J.S. Dennis, *J. Appl. Phys*. **102**, 103721, (2007).
[3] M. Baxendale, P. Battini, I. Pollini, M. Endo, Y.A. Kim, T. Hayashi, H. Muramatsu, *Phys. Rev. B*, **80**, 125411, (2009).

Photocurrent Imaging Of Ultra Clean Suspended Carbon Nanotubes

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Carbon nanotubes have been found to be an excellent system for studies of optoelectronics, due to their high carrier mobility and direct bandgap [1]. Photoluminescence as well as electroluminescence from a single walled semiconducting carbon nanotube have been demonstrated [2,3] and have paved the way for future photonic device realization. Controlled injection of electrons and holes in addition to radiative recombination of the charge carriers is a requirement for electroluminescence and hence for the engineering of a carbon nanotube light emitting diode. A pn-junction is here created by electrostatically induced n-doped and p-doped segments of the carbon nanotube by means of local gates. Here we report photocurrent measurements on single semiconducting carbon nanotubes, grown to bridge a few micrometer wide trench in between two metal contacts. The nanotube is grown in the final step of the device fabrication, resulting in no post-growth processing and hence an ultra-clean system with potential to reach the single particle regime [4]. The doping of the system can be controlled by means of gate potential. Results from photocurrent imaging in combination with IV-measurements of a pn-junction in a suspended carbon nanotube will be presented. We show how the position of the pn-junction along the nanotube axis can be tuned as a function of gate potential as well as demonstrating a technique to image the transition from a pn- to a np-configuration of the local band bending in the carbon nanotube.

[1] P. Avouris, *Nature Photonics*, **2**, 341-350, (2008).
[2] J. Lefebvre, *Nano Letter*, **6**, 8, (2006).
[3] T. Mueller, *Nature Nanotechnology*, **5**, 27-31, (2009).
[4] G.A. Steele, *Nature Nanotechnology*, **4**, 363-367, (2009).

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In situ NEXAFS study of Initial Growth Process of Carbon Nanotube by Surface Decomposition of SiC

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Carbon nanotube (CNT) growth by thermal decomposition of SiC is a unique technique because CNTs grow only by heating SiC substrates above 1200 ºC in a vacuum. By this method, aligned zigzag-type CNTs with fairly uniform tube diameters can be produced without any catalysts. So far, it has been reported that nanosized cap structures (“carbon nanocap”) are initially formed and that these nanocaps determine the CNT structures. However, formation process of carbon nanocaps has never been clarified, although elucidation of growth mechanism would lead to control of structural parameters of CNTs. In this study, we carried out in situnear edge X-ray absorption fine structure (NEXAFS)spectroscopy measurement for the initial stage of CNT growth by surface decomposition of SiC. 6H-SiC single wafers with well-polished (000-1) carbon-face were used as samples. After HF treatments, the samples were transferred into a UHV chamber and heated up to an intended temperature under a H_2 ambient atmosphere. The sample temperature was monitored with a pyrometer. Above 1000 ºC, the heating rate was kept less than 1 º C/min to form carbon nanocaps. In situ C *K*NEXAFS measurements were carried out in the UHV chamber at BL-7A in the Photon Factory of KEK. The NEXAFS spectra were measured in Auger electron yield detection mode, keeping the sample at the heating temperature. Below 1000 ºC, the C *K* NEXAFS spectra were similar to those of 6H-SiC. At 1110 ºC, a weak C-C π^* resonance peak appeared at 285 eV in the spectrum, suggesting the beginning of decomposition of SiC surface. When the sample temperature was 1360 ºC, the NEXAFS spectrum was almost the same as that of graphite, indicting the carbon nanocap formation. Polarization dependence of the NEXAFS spectra indicated that direction of C-C bonds changed during the carbon nanocap formation. Based on these results, we propose a formation model for carbon nanocaps by surface decomposition of SiC.

[1] M. Kusunoki et al., *Appl. Phys. Lett.* **77** 531 (2000).
[2] T. Maruyama et al. *Chem. Phys. Lett.* **423** 317 (2006).

Tip Enhanced Raman Scattering & Multiprobe Scanned Probe Imaging & NanoLithography of Carbon Nanotubes & Graphene

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Research will be described that has focused on optimizing the essential components of instrumentation and probes for carbon nanotubes and Graphene functional imaging. One important such probe is for tip enhanced Raman scattering (TERS) and associated techniques based on full integration of scanned probe microscopy with microRaman spectroscopy. The results of this research effort have allowed for a general TERS solution that can be applied for both opaque and transparent samples and employing exciting developments of multiprobe scanned probe microscopy. It also permits for integration with all upright, inverted and dual 4 Pi microscope solutions. The probes that have worked best have been those that are based on single gold nanoparticles at the exposed tip of a low dielectric glass probe (see diagrammatic representation below). These probes were originally designed for use in tip enhanced non-linear optical microscopy (TEN) [1]. Such probes will be compared to other solutions in the literature especially those based on etched wires of gold or silver or coated silicon probes. The data indicate that single gold nanoparticle probes provide artifact free TERS results. As part of this research it has been necessary to define samples which have specific properties to demonstrate the nature of the TERS effect. This aspect of the research has identified the factors that maximize enhancement and minimize the optical interference that can be parasitic to the TERS signal.

In addition it will be shown that these TERS developments are compatible with exciting new directions in multiprobe scanned probe microscopy measurements (see above) with probes that include not only those for TERS but also those that can be applied to multiprobe electrical, thermal and Kelvin probe scanned probe microscopy. The results indicate that these developments together with their full integration with Raman spectroscopy are powerful techniques for such carbon based fundamental and applied developments.

[1] Barsegova et al, *Applied Physics Letters* **81**, 3461-63 (2002).

High-Resolution Photocurrent Microscopy of Carbon Nanotube Film Photodiodes

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Semiconducting carbon nanotubes (CNT) are a promising material for photovoltaic applications [1]. Within a photovoltaic element CNTs can take up various functionalities, e.g. as a light absorbing layer, conducting channel material or (transparent) electrode.

Here we present CNT thin film photodiodes in which CNTs act as the light absorbing layer and simultaneously promote the carrier separation and transport to the electrodes. The CNTs used in this study are highly separated (99%) semiconducting single-wall carbon nanotubes [2] that are self-assembled on a transparent substrate by an evaporation-driven process [3]. CNT thin film photodiodes are fabricated with two different contact metals, i.e. Palladium and Aluminum. The work function difference creates a built-in electric field in the device channel that transforms electron-hole pairs into free carriers at opposite contacts [4].

We use scanning oil-immersion laser microscopy in order to acquire short-circuit photocurrent and open-circuit photovoltage images of the CNT thin film photodiodes. A maximum optical resolution below 300nm is demonstrated by comparative measurements of the local potential landscape in the same device, with and without the use of immersion oil at different excitation wavelengths. The possibility to study the underside of the device contacts provides unique insight into the coupling mechanisms at the CNT-metal interface.

In Situ TEM Investigations Of Electronic And Mechanical Properties Of Nanotube Architectures

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Nanotubes have attracted great research interest due to their unique structure, novel properties and potential applications. However, it is important to have them connected via suitable interfaces for achieving specific functions and applications. While many studies have been conducted on the individual nanotube level, there are still only a few investigations on the complex architectures and the influence of interfaces on the device performance. In this contribution, we applied an *in situ* transmission electron microscopy (TEM) technique to investigate the electronic and mechanical properties of nanotube architectures. With the aid of atomically-resolved TEM imaging the interface structure and nanotube architecture properties were correlated. The first example is the electronic properties of fabricated carbon nanotube (CNT)-clamped metal atomic chains (MAC) [1]. This hybrid nanostructure was prepared by *in situ* machining a metal-filled CNT, which included peeling off carbon shells by a spatially positioned and energy selective electron beam and further elongating the exposed metal nanorod. First-principles calculations indicated that strong covalent bonds had been formed between the CNT and MAC. The electrical transport properties of the CNT-clamped MAC were experimentally measured, and quantized conductance was observed. The second example is the effects of a homogeneous interface on the mechanical properties of boron nitride (BN) nanobamboos, an assembly of short BN nanotubes [2]. By combining *in situ* TEM mechanical tests and molecular dynamics simulations, it was demonstrated that the interface geometry had an important influence on the mechanical properties. Under a geometry strengthening effect, the BN nanobamboos showed fracture strength and Young' modulus up to 8.0 GPa and 223 GPa, respectively.

[1] D.-M. Tang, L.-C. Yin, F. Li, C. Liu, W.-J. Yu, P.-X. Hou, B. Wu, Y.-H. Lee, X.-L. Ma, H.-M. Cheng, *Proceedings of the National Academy of Sciences* **107**, 9055 (2010).
[2] D.-M. Tang, C.-L. Ren, X. Wei, M.-S. Wang, C. Liu, Y. Bando, D. Golberg, submitted, (2011).

Quantification of the Metallic/Semiconducting Ratio of Bulk SWCNT Samples by Cobalt Porphyrin Probe EPR Spectroscopy

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A simple, quantitative, and self-calibrating spectroscopic technique for the determination of the ratio of metallic (M) to semiconducting (SC) single-wall carbon nanotubes (SWCNTs) in a bulk sample is presented. The technique is based on the measurement of the electron paramagnetic resonance (EPR) spectrum of the SWCNTs to which Cobalt(II) octaethylporphyrin (CoOEP) probe molecules have been added.[1] This yields signals from both CoOEP molecules on M and on SC tubes, which are easily distinguished and accurately characterized in this work. The EPR intensities can be directly related to the mass fraction of M and SC tubes respectively.[2] By applying this technique to a variety of SWCNT samples produced by different synthesis methods, it is shown that these EPR signals for porphyrins adsorbed on M and SC tubes are independent of other factors such as tube length, defect density, and diameter.[2] CoOEP adsorption is checked to be unbiased towards M or SC tubes.

[1] S. Cambré, W. Wenseleers, J. Čulin, S. Van Doorslaer, A. Fonseca, J. B.Nagy, E. Goovaerts, *ChemPhysChem* **9**, 1930 (2008).
[2] S. Cambré, W. Wenseleers, E. Goovaerts, D.E. Resasco, *ACS Nano*, **4**, 6717 (2010).

Micro-Dielectric Environment Effect on the Band Gaps of (n,m)Single-Walled Carbon Nanotubes

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The electronic states of carbon nanotubes are one of the most fundamental properties of the nanotubes. We report the finding that the band gaps of (*n,m*) SWNTs are strongly affected by the change in micro-dielectric environments around the isolated nanotubes [1]. In situ photoluminescence (PL) spectroelectrochemistry of the films containing fifteen isolated (*n,m*) single-walled carbon nanotubes (SWNTs) cast on ITO electrodes in organic solvents including DMSO, acetonitrile, DMF, THF and chloroform was completed and then the oxidation and reduction potentials, and band gaps ($\Delta E_{\mathrm{electr}}$) of the (*n,m*) SWNTs in the solvents were determined. We have discovered that the $\Delta E_{\mathrm{electr}}$ of the (*n,m*) SWNTs become greater as the solvent dielectric constants decreased, which is in sharp contrast to the optical band gaps (ΔE_{opt}) that show virtually no solvent dependence. Such a strong solvent dependence of the electrochemical band gaps is due to the difference in the solvation energy of the charged SWNTs produced during the electrochemical processes.

[1] Y. Hirana, Y. Tanaka, Y. Niidome, N. Nakashima, *J. Am. Chem. Soc.* **132**, 13072–13077 (2010).

Evaluation of Intrinsic Exciton Diffusion Length in Long Single-Walled Carbon Nanotubes

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Optical processes in single-walled carbon nanotubes (SWNTs) are mainly dominated by the dynamics of excitons which were confined in one dimension with large binding energy on the order of several hundred meV. It has established that excitons in SWNTs are mobile and, the exciton diffusion length that characterizes the average distance over which an exciton can diffuse within its lifetime is critical for SWNT photoluminescence (PL) efficiency. Previous experimental studies for evaluating the diffusion length of excitons in SWNT were mostly carried out with ensemble and surfactant or DNA wrapped SWNT samples, presenting an averaging and perturbed results. We here perform a direct measurement of the intrinsic diffusion length of excitons in a long individual-SWNT by using single-SWNT PL microscope. Long SWNT samples are prepared by gas flow-guided chemical vapor deposition on trench- patterned quartz substrates. The trenches with widths of 80-1000 nm were patterned periodically to get suspended SWNT with varying length. PL spectroscopy is performed to identify the chirality and the PL emission intensity of the individual long nanotubes. The performance of PL intensity depends on the length of the suspended SWNTs in air environment. The exciton diffusion length is extracted from the dependence of PL emission intensity on nanotube length from a single-SWNT. We show that the room temperature diffusion length in these clean and pristine SWNTs is on the order of 10^2 nanometers, which is significantly larger than those measured from surfactant [1, 2] or DNA [3] wrapped SWNT samples and on the same size scale for other suspended SWNT samples [4, 5].

[1] L. Cognet, et al., *Science* **316**, 1465-1468 (2007).
[2] L. Lüer, et al., *Nat. Phys.* **5**, 54-58 (2009).
[3] Y. Miyauchi, et al., *J. Phys. Chem. C* **114**, 12905-12908 (2010).
[4] K. Yoshikawa, et al., *J. Phys. Chem. C* **114**, 4353-4356 (2010).
[5] S. Moritsubo, et al., *Phys. Rev. Lett.* **104**, 247402-1-247402-4 (2010).

Solvents for Nanotubes and Graphene – Why the Difference?

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The effective dispersion of nanomaterials is universally acknowledged to be critical when one wishes to harness their full potential in devices or applications. Over the past number of years much work has been carried out on overcoming the inherent difficulties associated with producing high quality dispersions of both single walled carbon nanotubes (SWNTs) and graphene. Liquid-phase exfoliation of these intractable materials in organic solvents offers high quality dispersions from a relatively simple processing route. Whilst work by these authors has discovered and chararacterised families of new solvents for both SWNTs and graphene there remains outstanding questions as to why certain solvents work and others do not [1-2].

Herein, I shall present recent findings on the critical components necessary for solvents to debundle SWNTs and/or exfoliate graphite to produce graphene. Whilst these two materials have very similar surface energies (a critical component when considering suitable solvents for materials), the set of effect solvents for both are not identical. Reasons for this variation will be presented.

[1] Bergin, S.D., et al., *ACS Nano*, **3**(8): p. 2340-2350 (2009).
[2] Hernandez, Y., et al., *Langmuir*, **26**(5): p. 3208-3213 (2010).

How to Improve Interference Substrates for the Exploration of Graphene and Nanotubes

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Progress on single layer graphene can be attributed to making graphene visible using optical microscopes. Using interference colour changes on oxidized Si surfaces makes single layer graphene visible [1]. This can be explained using a Fresnel law based model. We use the transfer matrix method to calculate the local filed across the oxidized Si substrate showing that the maximum of optical surface standing waves fall at the surface of the substrate. This means that the interference substrate acts as a half cavity. We have calculated the broadening of the interference maximum due to the numerical aperture of the illumination optics. Adding a highly reflecting metal layer improves the performance of the half cavity and one can enlarge the amplitude of the surface standing wave increasing optical contrast. The fact that the maximum of the surface standing wave falls on the surface makes that the Raman signal is enhanced [2]. The maximum amplitude at the substrate surface corresponds to four times the amplitude in vacuum. We show how plasmon coupling combined with the enhanced field at the surface of the substrate contributes to the observed enhancement in graphene enhanced Raman spectroscopy [3].

Interfaces in Carbon Nanotube FETs Studied by Kelvin Probe Force Microscopy

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Carbon nanotubes are one of promising materials for CMOS devices because of their high carrier mobility. In the previous study, we have realized air-stable, high-performance, Si-process compatible, n-type carbon nanotube field-effect transistors (CNFETs) and CMOS inverters, utilizing fixed charges introduced in the gate insulator deposited by atomic layer deposition (ALD) [1, 2]. In this study, we studied interface dipole and charge distribution near the interfaces of the gate insulator layer by Kelvin probe force microscopy (KFM). First, we studied the interface between the contact electrode and the gate insulator. The HfO_2 dielectric films were deposited on an Au electrode by ALD technique, followed by post-deposition annealing at 300˚C in vacuum. The surface potential of the HfO_2 layer measured by KFM increased with the thickness of HfO_2,and saturated with a value of about 1 V at a thickness of about 10 nm, showing that positive charges distribute near the interface. The interface charge density was evaluated to be 4.5×10^{13} cm^{-2}. We also studied the interface between the HfO_2 gate insulator and a SiO_2 substrate. The interface charge density was evaluated to be 6.1×10^{13} cm^{-2}. In addition, we found that a monolayer deposition of HfO_2 caused an abrupt change in surface potential by 0.4 V. This suggests an existence of the interface dipole layer between the SiO_2 and the HfO_2. We discuss the effect of these interfaces on characteristics of CNFETs.

[1] N. Moriyama et al., *Nanotechnology*, **21**, 165201 (2010).
[2] N. Moriyama et al., *Appl. Phys. Exp.,* **3**, 105102 (2010).

Novel Testing Method Of Carbon Nanotube-Array Actuators

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Mats of randomly oriented carbon nanotubes, known as Bucky papers, show in contact with an ionic electrolyte an active strain based on the capacitor-like mode of operation [1]. The mats are manufactured by a filtration of an aqueous dispersion. The dispersion is made of commercially available CNT-powder. Various investigations show low reliability and reproducibility of powder-based structures because of the low powder-quality [2]. Furthermore the random orientation of the papers does not allow using the excellent properties of a single CNT. That is the reason why great efforts are made to align the free movable CNTs in the dispersion. Other aligned CNT-based structures like yarns or CNT-array-based papers suffer from low conductibility, low stiffness or bad alignment according to the manufacturing process. The mechanism of strain generation still remains undefined but there is a controversial discussion. Either it is a quantum-mechanical lengthening of C-bonds [3] or an electrostatic repulsion between charged CNTs [4]. Maybe it is a superposition of both mechanisms. The presented paper focuses on a method for measuring the free strain of as produced vertically aligned CNT-arrays. The advantage of this approach is the analysis of a highly oriented CNT-based structure. The analysed arrays are provided by the working group of Schulte (Polymer Composites, Technical University of Hamburg-Harburg, Germany). The tubes have an average diameter of 20nm therefore they can be identified as multi walled carbon nanotubes (MWCNTs). The average length depends on the CVD-processing time and differs between 500µm and 1300µm. The basic substrate is silicon. The cell of the set-up is designed for testing small volumes (15ml) of ionic electrolytes. The tested specimens are 10 x 10 mm in size. The specimen used as working electrode is fixed at the bottom of the cell by two PTFE-clamps. The clamps are electrical conductible because of inner Pt-electrodes. A CNT-mat or CNT-arrays positioned in the cell will be used as counter electrode. The calomel-reference electrode completes the three-cell set-up. A glass-cylinder, placed on the top of the CNTs transfers the deflection external of the electrolyte. The deflection of the glass-cylinder is measured by a confocal sensor. The tests show a similar quadratic correlation between activation voltage and free strain like it is found using CNT-mats within aqueous electrolytes. A maximum strain of 0.14% could be achieved. In comparison the cation-induced strain (negative charged electrode) has a dominant character. This presented test set-up, the way of analysis and the used specimen avoid on the one hand measuring secondary effects and allow on the other hand recording the reaction of one MWCNT standing in parallel as an array. Therefore the analysed effect must be dominated by a quantum-mechanical character.

[1] R. H. Baughman et al., *Science*, **284**, 1340-1344 (1999).
[2] N. Grobert,*Materials Today*, **9**, 64, (2006).
[3] S. Ghosh, et al., *Chem.Phys. Lett.,* **406**, 10-14, (2005).
[4] D. Suppiger, et al., *Phys. Chem.,* Vol. 11, 5180-5185, (2009).

Imaging & Tracking Single-Walled Carbon Nanotube Dynamics in Rock-Like Porous Media

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Single-Walled Carbon Nanotubes (SWNTs) have unique electronic and mechanical properties that have led to an increased interest for their use in a wide range of applications (i.e. composite materials, drug delivery, and electronics). Because of their extremely high aspect ratio and slenderness (~1 nm diameter), SWNTs can increase the electrical conductivity of fluids more effectively than other particles. Moreover, under appropriate conditions, SWNTs precipitate into highly conducting chains that can span macroscopic length scales.[1] Finally, because of their slenderness, SWNTs are expected to penetrate much tighter pores than isotropic particles of equivalent volume. Therefore, SWNTs can be useful in oil reservoirs as tools for sensing, targeting and as contrast agents. Recently, we have used direct imaging of SWNTs by tagging with fluorescent dyes [2] and semiconducting SWNTs by near-infrared (NIR) fluorescence [3,4] to directly measure bending dynamics and stiffness in aqueous media. We have also studied SWNT dynamics in agarose gels, a special case of porous media mimicking biological tissues and cells.[5] In this poster, we present current work studying the dynamics of single SWNTs within a rock-like porous media as a model for oil reservoirs. Rock-like porous media was produced by packing concentrated colloidal silica particles between clean glass coverslips where the thickness of the packed layer is equal to a few particle diameters thus allowing for optical imaging without index matching. Using an amphiphilic fluorescent molecule (PKH26, emission 567 nm) to tag surfactant stabilized SWNTs, we show that fluorescence at visible wavelengths can be used to directly image SWNT mobility within this porous media. Results are presented for SWNTs experiencing Brownian motion and under externally induced flow. In the no-flow case, reptation dynamics within the packed silica are measured and compared to that previously observed in agarose gels.[5] We find that, qualitatively, the lower porosity, large and fixed obstacles present in the silica pack versus that of agarose gels lead to slower and highly path dependent dynamics for SWNT motion. Silica particles have also been packed within microfluidic channels similar to column based electrophoresis techniques for fluorescent imaging and length separation of DNA and other macromolecules.[6] We show that, in similar devices, fluorescently tagged SWNTs can be imaged while flow is used to transport SWNTs through rock-like porous media with small pores (<1 micron) and low porosity. Ongoing work is focused on investigating the effects of SWNT surface functionalization toward forming conductive SWNT networks for signaling, as well as, specific targeting of oil-water interfaces within porous media.

[1] P.V. Kamat, K.G. Thomas, S. Barazzouk, G. Girishkumar, K. Vinodgopal, D. Meisel, *Journal of the American Chemical Society*, **126**, 10757-62, (2004).
[2] R. Duggal, M. Pasquali, *Physical Review Letters*, **96**, 246104-1-4, (2006).
[3] R.B. Weisman, S.M. Bachilo, D. Tsyboulski, *Applied Physics a-Materials Science & Processing*, **78**, 1111-6, (2004).
[4] N. Fakhri, D.A. Tsyboulski, L. Cognet, R.B. Weisman, M. Pasquali, *Proceedings of the*

National Academy of Sciences of the United States of America, **106**, 14219-23, (2009).
[5] N. Fakhri, F.C. MacKintosh, B. Lounis, L. Cognet, M. Pasquali, *Science*, **330**, 1804-7, (2010).
[6] Y. Zeng, D.J. Harrison, *Analytical Chemistry*, **79**, 2289-95, (2007).

Direct Measurements Of Bending Stiffness And Rippling Phenomena In Free-Standing Carbon Nanotubes

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Carbon nanotubes (CNTs) have a low mass and a high stiffness, which makes them suitable for future nano-electromechanical systems (NEMS), especially in high- frequency switching applications. In relays, the CNTs are bent during operation and a high bending stiffness is important throughout the bending sequence. Deformation modes will appear at large deflections, leading to a lower bending stiffness which in turn will influence the device performance. At relatively low bending curvatures there can be a wave-like rippling of the walls, while at higher bending curvatures there can additionally be a local collapse, buckling, of the walls. Buckling [1] and severe rippling [2] have both been observed using transmission electron microscopy (TEM). TEM imaging is not particularly useful though for detecting the very onset of the rippling, as there are only minute distortions of the CNT-walls [3]. Various theoretical modelling [3,4] have indicated at which strain levels the rippling would emerge, and how the bending stiffness would be affected. There has been very little experimental data to compare with though, thus far. Here we present direct measurements of the force response in freestanding carbon nanotubes. The measurements have been performed using a custom-built atomic force microscope (AFM) inside a scanning electron microscope (SEM). We have been able to detect the very onset of the rippling mode [5], which is manifested through an abrupt change in the bending stiffness of the CNTs. The stiffness drops by about a factor of two and the force response continues to be linear in the rippling phase. Critical strains for the rippling onset have been measured in nanotubes of 7-18 nm in diameter, and the obtained strain values compare well with theoretical modelling predictions. We have additionally found an indication that defects in the nanotubes will increase the critical strain value and give a reduction in Young's modulus. The present findings will have implications for the design of CNT-based NEMS, where exceeding the critical strain will influence the device performance.

[1] S. Ijima, C. Brabec, A. Maiti, and J. Bernholc, *J. Chem. Phys.* **104**, 2089 (1996)
[2] P. Poncharal, Z. L. Wang, D. Ugarte, and W. A. de Heer, *Science* **283**, 1513 (1999)
[3] M. Arroyo and I. Arias, *J. Mech. Phys. Sol.* **56**, 1224 (2008)
[4] I. Nikiforov, D.-B. Zhang, R. D. James, and T. Dumitrica, *Appl. Phys. Lett.* **96**, 123107 (2010)
[5] H. Jackman, P. Krakhmalev, and K. Svensson, Accepted for publication in *Appl. Phys. Lett.* (2011)

In Situ Raman Spectroscopy Of Carbon Nanotubes During Growth By A Local Heating Technique

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Most carbon nanotube synthesis methods require temperatures that are higher than what can be used for integration of nanotubes into electronics. In this study, a local heating technique is used to grow nanotubes in a CMOS-compatible process. High temperatures are generated locally on the sample by sending a current through a small molybdenum wire/heater which is deposited on the substrate. Nanotubes are grown from catalysts deposited on top of the heater whereas the temperature rapidly decreases to room temperature outside it. Since no furnace is required in this technique a small chamber that fits under a Raman microscope is used. This allows in situ Raman spectroscopy of the growing nanotubes. It is found that the heater is carbonised before any growth occurs and that the growth can be well described by the model used in refs. [1-3]. The kinetics show that the process is limited by mass transport of the carbon precursor. Fast growth rates are recorded despite the use of a cold carbon precursor, which has been shown to decrease the growth rate significantly [4]. We find that the molybdenum heater creates an additional pathway for the carbon cycle from gas to nanotube formation.

[1] E. Einarsson, et al., *Carbon*, **46**(6) 923-930 (2008).
[2] D.N. Futaba, et al., *Physical Review Letters*, **95**(5) 056104 (2005).
[3] M. Picher, et al., *Nano Letters*, **9**(2) 542-547 (2009).
[4] A.J. Hart, et al., *Small*, **3**(5) 772-777 (2007).

Abstract 355
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Effect of Laser Power on Raman Spectrum of Single-Walled Nanotubes

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Raman spectroscopy is now firmly established as a standard characterisation method for carbon nanotubes. While it is able to reveal many physical properties of the nanotubes, the most widespread application is to obtain a qualitative measure of the defect density of the nanotubes. This is measured by the relative intensity of the G- peak (~1580cm^{-1}) and the D-peak (~1350cm^{-1}), referred to as the G/D ratio. Although typically the wavelength of the laser used is reported, the power of the laser is rarely stated. In this work, we show briefly that the laser power can have a strong effect on the G/D ratio obtained from a nanotube sample. We discuss possible reasons for this, as well the effect this has on comparisons between samples tested under different conditions. We also recommend that the laser power be routinely quoted when reporting G/D ratios of carbon nanotubes.

Raman Metrology Of Uniaxially Strained Graphene

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The presented work summarizes various aspects of uniaxial deformation in single- and bilayer graphene studied by means of Raman spectroscopy. Graphene flakes were subjected to tension – compression uniaxial loading using the cantilever beam technique [1-4]. The evolution of the Raman single-resonance (G) and double-resonance (2D, G*) bands is monitored at strain levels < 1%. The position of all peaks redshifts under tension and blueshifts under compression. The G peak splitting into two sub-bands (G^- and G^+) which is caused by symmetry lowering, is observed in both strain directions. The sub-bands' intensities are used to calculate the crystal lattice orientation of the measured graphene flakes with respect to the strain axis [2,5]. The nature and splitting of the 2D band even in the unstrained flakes, when excited by the 785 nm (1.58 eV) laser line, is interpreted as the interplay between two distinct double resonance scattering processes [3].
Finally, it will be shown, that the flake geometry and the presence of residual strain strongly influence the deformation behavior of the individual flakes, which is then reflected in the Raman shift rates and slopes [2-4]. Most importantly, the observed differences between experiments using flakes firmly fixed in the substrate or simply laid on its surface are mainly due to slipping and non-uniform stress transfer at various stages of the loading cycles [4]. The stress transfer to graphene flakes from under- and/or overlying polymers as well as large-scale buckling [2] is monitored by detailed Raman mapping.

[1] O. Frank, G. Tsoukleri, I. Riaz, K. Papagelis, J. Parthenios, A.C. Ferrari, A.K. Geim, K.S. Novoselov, C. Galiotis, *Nature Communications* **2**, DOI: 10.1038/ncomms1247 (2011).
[2] O. Frank, G. Tsoukleri, J. Parthenios, K. Papagelis, I. Riaz, R. Jalil, K.S. Novoselov, C. Galiotis, *ACS Nano* **4**, 3131-3138 (2010).
[3] O. Frank, M. Mohr, J. Maultzsch, C. Thomsen, I. Riaz, R. Jalil, K.S. Novoselov, G. Tsoukleri, J. Parthenios, K. Papagelis, L. Kavan, C. Galiotis, *ACS Nano* **5**, 2231–2239 (2011).
[4] G. Tsoukleri, J. Parthenios, K. Papagelis, R. Jalil, A.C. Ferrari, A.K. Geim, K.S. Novoselov, C. Galiotis, *Small* **5**, 2397-2402 (2009).
[5] T.M.G. Mohiuddin, A. Lombardo, R.R. Nair, A. Bonetti, G. Savini, R. Jalil, N. Bonini, D.M. Basko, C. Galiotis, N. Marzari, K.S. Novoselov, A.K. Geim, A.C. Ferrari, *Physical Review B* **79**, 205433-8 (2009).

Doping Single-Walled Carbon Nanotubes With Nitrogen: A STM And STS Investigation

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Prior to the integration of carbon nanotubes (CNTs) into nanoelectronic and C-based devices, large batches of nanotubes with reproducible and controlled properties are necessary. Because of the strong dependency of the electronic structure of carbon nanotubes with respect to geometrical parameters such as the diameter and the helicity, many efforts have been directed towards controlling the chiral indices of the tubes during synthesis or towards sorting nanotubes according to theses chiral indices. Another method to tune the nanotubes' electronic structure is to use doping, which may lead to properties that are more controlled by the chemistry than by the structure of the tubes. One of the most promising candidates for doping carbon nanotubes is nitrogen, thanks to its suitable atomic radius. Nitrogen atoms can however adopt different local environments (graphitic-like, pyridinic-like) which can have various effects on the nanotube's electronic structure.

To investigate this impact, Scanning Tunnelling Microscopy(STM) and Spectroscopy (STS), appears as a unique tool since it can provide local information regarding both the structural and electronic properties of carbon nanotubes. For instance, this technique has given experimental evidence of the correlation between the chiral indices of single-walled CNTs and their electronic structure [1-2].

Here, we present the results of a STM/STS study of nitrogen doped single-walled carbon nanotubes, prepared by two different techniques: the vaporization with a continuous laser of a C:Ni/Y target under a nitrogen atmosphere [3]and a CVD floating catalyst reactor using a hot iron wire/CO/ammonia system [4]. These techniques lead to single-walled nanotubes with a nitrogen content ranging from 0.3 to 4%, as determined by EELS.

For both synthesis methods, the STM images of nitrogen-doped CNTs reveal the presence of defects which can be assigned to the presence of N atoms since they are not observed in pure single-walled CNTs prepared in a similar way. These defects appear as large protusions (1 to 3 nm wide) at the surface of the nitrogen-doped tubes. High resolution STM images of the defects display various patterns, associated with different configurations involving one or several N atoms. Another signature of the incorporation of nitrogen is the presence of interference patterns which can be extended up to a few nanometres away from a defect.

On the STSspectra, that measure the local density of states, we observe additional sharp peaks at the N-based defects, as compared to spectra recorded in defect-free area that only display contributions associated with the van-Hove singularities (vHs). These new peaks appear at energies that are different from those of the vHs and correspond to localized states. Based on a comparison between our STM/STS data, other experimental results and theoretical studies, we will discuss the nature of the defects induced by nitrogen doping of carbon nanotubes and their consequences on the tubes' structural and electronic properties.

[1] J.W.G. Wildöer et al., *Nature*, **391**; 59 (1998)
[2] T.W. Odom et al., *Nature*, **391**; 62 (1998)
[3] H. Lin et al*., J. Phys. Chem. C*, **113**, 9509 (2009)
[4] T. Susi et al*., Physica Status Solidi B*, **246**, 2507 (2009)

Anisotropic Optical Absorption Of Individual Carbon Nanotubes

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We first studied polarization-dependent Raman spectra of individual single- (SWNTs) and multi- walled nanotubes (MWNTs). Main goal was to investigate the Raman signal intensity and energy of G band as a function of the angle between the nanotube axis and the vector of the incident light (for two polarization configuration: VV and VH). We show that for the incident light polarized perpendicularly to nanotube axis the Raman peak intensity is fully diminished (to zero!). To our knowledge this has been never shown for individual multi-walled tubes. The interpretation of this behavior in case of MWNTs is based mainly on the depolarization effect and for SWNTs more significant are the availableoptical transition. Finally, we observed an extremely anomalous behavior: the dependence of energy of the G peak on the polarization direction of incoming light (not related with the symmetry of the G band). We propose that this behavior is related with anisotropy of the optical absorption of carbon tubes. The absorption anisotropy induced the change in local temperature of the tubes, what causes the shift of Raman peak.

Collection-Mode Near-Field Nanoscopy of Individual CNTs

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Applications of luminescent single-wall carbon nanotubes (CNTs) in nanosized optoelectronics and photonics devices envisioned for the next future [1] require suitable optical characterization methods addressing individual CNTs. Within this frame, the abilities exhibited by nonpropagating electromagnetic fields in overcoming the diffraction limits offer unique possibilities. For instance, photoluminescence (PL) from emitting CNTs adsorbed on transparent samples has been imaged and analyzed by tip-enhanced microscopy several years ago [2].

We are presently using a collection-mode, polarization-controlled scanning near-field optical microscope (SNOM) to analyze PL and scattering from individual CNTs. Collection is accomplished in near-field by an aperture-probe, whereas excitation is provided in far-field by an optical fiber-focuser. Since the focuser is placed on the same side of the sample where near-field collection takes place, the system can be adopted for both transparent and opaque substrates. Moreover, the polarization status of the excitation radiation can be reliably controlled by polarizing optics put in front of the optical fiber. Since the focuser holder is mounted on a piezoelectric translator driven independently from the sample scanner, the excitation spot can be freely adjusted on the sample surface with respect to the probe. Thus, effects of the optical interaction between the CNT and any neighboring nanostructures such as surface plasmon waveguides and concentrators can be easily analyzed.

Preliminary results indicate a spatial resolution in the few tens of nanometer range and sensitivity suitable to collect optical scattering from individual CNTs with a photon-counting detector.

[1] P. Avouris, M. Freitag, and V. Perebeinos, "Carbon-Nanotube Optoelectronics", in Carbon Nanotubes, *Topics Appl. Physics* **111**, 423-454 (2008); A. Jorio, G. Dressehlhaus, M.S. Dresselhaus,(Eds.), Springer-Verlag Berlin Heidelberg 2008.
[2] A. Hartschuh, H. Qian, A.J. Meixner, N. Anderson, and L. Novotny, *NanoLett*. **5**, 2310-2313 (2005).

Effect of Variations in Carbon-Carbon Bond Lengths on the Optical Absorption Properties of Different Carbon Nanotubes

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The electronic and optical properties of carbon nanotubes are known to be highly dependent on their diameters. For small-diameter nanotubes, the curvature of the nanotube sidewall has shown to significantly influence their electronic structures. One effect of this curvature is the change in the carbon-carbon bond length after geometry relaxation. In this theoretical work, we show the importance of geometry optimization in the prediction of the band structure and optical absorption spectra of nanotubes. We first study the effect of geometry relaxation on the carbon-carbon bond length along and perpendicular to the nanotube axis. For this purpose, we simulate three zigzag nanotubes with considerably different diameters ((4,0), (8,0) and (16,0) nanotubes with diameters of ~0.34, ~0.63, and ~1.27 nm, respectively) and calculate the bond length change resulting from the geometry optimization with different density functional theory (DFT) and hybrid methods. For example, after geometry optimization with the hybrid method of HSEH1PBE/6-31G,the carbon-carbon bond length along the nanotube circumference increases by about 4.37%, 0.92% and 0.27% from the original value of 1.42 nm in graphene for the (4,0), (8,0) and (16,0) nanotubes, respectively. In the next step, we show how this bond length change can affect the band structure and consequently the optical absorption spectra of carbon nanotubes. For instance, the first optical transition energy of the (4,0) nanotube decreases by %50 after geometry optimization (0.8 eV for a non- relaxed and 0.4 eV for a relaxed structure). For an (8,0) nanotube the first optical transition energy increases by 14% and for a (16,0) nanotube it decreases by 9%. We also perform a systematic study to separate the effects of the perpendicular bond length and the parallel bond length on the electronic bands and absorption spectra of nanotubes.

Functionalized Carbon Nanotubes: Comparative Study of Quantative Characterizatoin Methods

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The use of carbon nanotubes (CNTs) in different applications is now still limited due to nonreactive nature of nanotubes surface and due to their agglomeration into micron-size structures during the growth. To overcome these problems, a functionalization of CNTs by changing their surface composition via introduction or addition of other elements or groups of elements has proved to be efficient. The functionalization can improve solubility and processibility of CNTs, and, so, allows combining of the unique properties of nanotubes with those of other types of materials. An identification of the nature and the amount of functional groups introduced in CNTs is one of critical steps for the development of large scale application of functionalized nanotubes. This characterization is generally performed using Raman spectroscopy, X-ray photoelectron spectroscopy, electron microscopy combined with electron energy lost spectroscopy. These methods have high resolution, but they are costly for routine examination and their results sometimes are difficult to apply to the bulk material in general. Some of chemical methods such as titration and spectrophotometric methods are also applied in this field, but their using is often limited by physical adsorption of reagents by CNTs surface. In the present work the comparison of the results of several methods in quantitative determination of functional groups has been performed to investigate their advantages and limitations. Multi-walled CNTs functionalized with N- and/or O-containing groups were characterized with using both physical and chemical methods to find the correlation between the results of different techniques.

Optical Heterodyne Detection Visualizes the Spatial Resonance of Multilayer Graphene Cantilevers

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Graphene resonator is anticipated as ultrasensitive mass detectors and biosensors. To investigate the vibration of the graphene cantilever in various environments toward mass sensors of biological molecules, we developed the optical actuation and optical heterodyne detection based on the opto-mechanical heterodyne technique.[1]The graphene flakes were mechanically exfoliated over predefined 9µm-wide trenches on SiO_2 (300nm)/Si wafer to fabricate cantilevered graphene resonators. The length and width of the typical cantilevered graphene used in this study were 7µm and 7.5µm, respectively. For optical actuation of graphene resonators, we irradiated the graphene with a red laser (660nm, 300W) for thermal expansion by modulating the laser intensity, and with a blue laser (406nm, 1µW) to detect vibration amplitude by the optical detection technique. The modulation frequencies of two lasers were set with a small difference, Δf, resulting in the detection of the resonance at the frequency of Δf. First, to investigate the effects of gaseous dissipation of the graphene vibration, we measured the Q factors of the graphene vibration at the pressure of $1 \sim 10^4$ Pa. The Q factor at the pressure over 500 Pa was inversely proportional to the pressure, indicating that the graphene cantilever acts as in the free molecular flow. In contrast, the Q factor at the pressure below 500 Pa remained constant, implying that the energy loss induced by the collision of gas molecules was much smaller than the intrinsic energy loss of the graphene resonator. One of the advantages of our excitation/detection technique is that the vibration amplitude of the graphene can be spatially visualized over the surface of the graphene by changing the position of the laser that detects the vibration. This vibration mode analysis was examined using a combination of experiments and finite element method. In contrast, by changing the position of the laser that excites the vibration, thermal propagation of the graphene can also be estimated in order to determine where induces the vibration efficiently. This is crucial in the application using graphene-based nanoelectromechanical resonators in liquid.

[1] A. Yoshinaka et al*., Appl. Phys. Lett.* **98**, 133103 (2011).

The Use of Ga^+ Focused Ion Beam to Modify Graphene for Device Applications.

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Graphene, a two dimensional carbon structure, is a model system that comprises exciting possibilities for demonstrating new physics and novel electronic applications, [1-3] many of which can be appreciated only by making nanoscale modifications in its structure. [4,5] Therefore, the study of defects, impurities and nanoconfinement in a single layer graphene is of great importance to understand, predict and tune the behavior of such material. Normally, such structures are on the 5 to 100 nanometer scale up to micrometer scale and many applications are predicted and demonstrated, for instance: Ballistic room-temperature transistors, carbon-based spintronic devices and permeation membranes. Graphene nanostructures have already been fabricated by electron beam lithography followed by reactive ion etching, scanning tunneling microscopy lithography, and atomic force microscopy anodic oxidation, and by chemically derived techniques. In this study we demonstrate well controlled etching of single layer graphene by using a Ga^+ focused ion beam. Using this technique, we obtain different structures such as graphene nanoribbons and periodic array of scratches. Using charge injection and electrical force microscopy the ion fluence that cuts the graphene in two parts are obtained. By means of polarized Raman spectroscopy the quality of the graphene edges at the scratches are studied. The Raman spectroscopy studies show that the graphene is resilient under the etching conditions, indicating that commercial Ga^+ ion column is a powerful technique to produce graphene nanocircuits with defined graphene edges.

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science*, **306**, 666-669 (2004)
[2] A. K. Geim, K.S. Novoselov, *Nature Materials*, **6**, 183-191 (2007)
[3] R. V. Noorden, *Nature* **442**, 228–229 (2006)
[4] C. H. Park, L. Yang, Y. W. Son, M. L. Cohen, S. G. Louie, *Nature. Phys.* **4**, 213 (2008)
[5] I. Deretzis, A.Magna, G.Forte, R. Pucci, *Physical Review B*, **80**, 195413 (2009)

Direct Measurement of the Bending Stiffness of Individual Vertically Aligned Carbon Nanofibers (VACNFs)

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Vertically aligned carbon nanofibers (VACNFs) are synthesized in a plasma-enhanced chemical vapor deposition process (PECVD) in which the position, diameter, length, and alignment of individual nanofibers can be controlled accurately. This has provided an unprecedented opportunity to realize a new bottom-up-engineered material with excellent mechanical and electrical properties which could exploit the third dimension at a reasonable cost. VACNFs have been already employed in a number of applications including electron emitters [1], gene delivery arrays [2], and nanoelectromechanical systems [3, 4]. However, no direct measurement of the Young's modulus of VACNFs has been reported yet. Qi et al. have used nanoindentation method to measure the collective response of a forest of VACNFs with a distribution in length and diameter of the constituent nanofibers [5]. Kaul et al., have reported in situ uniaxial compression tests on individual VACNFs but they have not provided enough information to evaluate the accuracy of their measurements [6]. Indirect estimation of the VACNFs Young's modulus has also been reported by Eriksson et al. from measurements of the resonance frequency of a nanofiber deposited on top of an excitation electrode [7]. Here, we report on direct measurements of VACNFs Young's modulus using a piezoresistive atomic force microscope (AFM) cantilever implemented inside a scanning electron microscope (SEM). The VACNFs were grown from Ni catalyst seeds, patterned using electron-beam lithography on top of a stoichiometric TiN underlayer. The VACNFs were grown in a commercially available PECVD chamber (AIXTRON BlackMagic™). The nanofibers were approached from the side and pushed at the tip (resembling a cantilever beam) and force- deflection curves were obtained. By calibrating the AFM sensor the bending stiffness of the nanofiber could be determined. The Young's modulus was then estimated by taking the nanofibers dimensions into account. The sub-nano Newton force precision provided by the AFM force-sensor together with the fact the individual VACNFs could be observed in the SEM simultaneously during the measurements, has enabled us to measure the nanofibers Young's modulus with a high precision. Preliminary measurements indicate that VACNFs posses a Young's modulus between 40 to 100 GPa which is comparable to CVD grown carbon nanotubes of similar diameters [8].

[1] M.A. Guillorn, A.V. Melechko, V.I. Merkulov, E.D. Ellis, C.L. Britton, M.L. Simpson, D.H. Lowndes, L.R. Baylor, *Applied Physics Letters*, **79**, 3506 (2001).
[2] D.G.J. Mann, T.E. McKnight, A.V. Melechko, M.L. Simpson, G.S. Sayler, *Biotechnology and Bioengineering*, **97**, 680-688 (2007).
[3] J.E. Jang, S.N. Cha, Y. Choi, G.A.J. Amaratunga, D.J. Kang, D.G. Hasko, J.E. Jung, J.M. Kim, *Applied Physics Letters*, **87**, 163114-163111 (2005).
[4] J.E. Jang, S.N. Cha, Y.J. Choi, D.J. Kang, T.P. Butler, D.G. Hasko, J.E. Jung, J.M. Kim, G.A.J. Amaratunga, *Nature Nanotechnology*, **3**, 26-30 (2008).

[5] H.J. Qi, K.B.K. Teo, K.K.S. Lau, M.C. Boyce, W.I. Milne, J. Robertson, K.K. Gleason, *Journal of the Mechanics and Physics of Solids*, **51**, 2213-2237
[6] A.B. Kaul, K.G. Megerian, A.T. Jennings, J.R. Greer, *Nanotechnology*, **21**, - (2010).
[7] A. Eriksson, S. Lee, A.A. Sourab, A. Isacsson, R. Kaunisto, J.M. Kinaret, E.E.B. Campbell, *Nano Letters*, **8**, 1224-1228 (2008).
[8] K. Lee, B. Lukic, A. Magrez, J. W. Seo, G. A. D. Briggs, A. J. Kulik, and L. Forró, *Nano Letters*, **7**, 1598-1602 (2007)

Reconstruction of Graphene Layers under Electric Current: Sample Preparation and Preliminary Results

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Over the past few decades different carbon structures have been discovered including: Fullerenes, nanotubes, nanorribons and graphene single layer. For that reason, the Materials Metrology Division of the National Institute of Metrology of Brazil is making efforts in the study and development of carbon reference materials also including basic research in new carbon materials. The purpose here is to study a recent discovered carbon nanoribbon where we are building suspended devices in order to understand the reconstruction of graphene edges. The main motivation lies in the quest for perfect graphene edges, which have kept many scientists captivated since its first observations. Based on the results of Joule heating of graphitic nanoribbons inside a TEM, where sharp zigzag and armchair edges were visualized [1], we were motivated to construct a device to induce Joule heating of nanoribbons in a configuration such that the sample could be studied outside the electron transmission microscope. Such device allows us the metrology of the material pre- and post- experiment. In this work we will expose our different approaches to build such device and the results of the electric transport experiments will be presented.

[1] X. Jia, et al. *Science,* **323**, 1701, (2009)

Controlled Stacked Graphene Bilayer Structures: An Experimental Method

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It has been recently shown that the superposition of two graphene sheets should result in a superlattice pattern which structure depends on the rotation angle between each layer [1]. It appears that the Moiré patterns that correspond to the mismatch between the atoms from the top and bottom layers induce some new Raman signature. The properties of this Raman peak will depend essentially on the angle of rotation between graphene layers [2].
One of the problems to overcome in order to study graphene superlattices is the control of the angle of rotation between graphene layers. In this work we show that the use of an Atomic Force Microscopy is an extremely useful tool to manipulate graphene sheets. A focused Ion beam milling was used to induce the main folding direction and as a consequence control the superlattice structure. All the synthesized materials were further studied by Raman spectroscopy and the results are compared to theoretical predictions.
Our results are in agreement with the prediction Gupta et al [3]. Indeed, it appears that the mismatch rotation angle between graphene layers induces a static potential. It seems that this potential is able to transfer momentum equals to photo-excited electrons. On the other hand we propose a method to determine of the symmetry of graphene superlattices via Raman spectroscopy.

[1] Mele, E. J., *Phys.Rev.B*, **81**, R161405-161409 (2010).
[2] Carozo, V; Almeida,C.M.; Ferreira ,H.E; Cançado, L.G.; Achete, C.A; Jorio, A.; submitted (2011).
[3] Gupta, A. K.; Tang, Y.; Crespi, V. H.; Eklund, P. C.; *Phys. Rev. B* , **82**, R241406-R241409 (2011).

Optical Microscopy and Micro-Manipulation Methods to Build Carbon Nanotube Electrical Nano-devices

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The observation of graphene on silica/silicon substrate was one of the greatest advances in terms of graphene technology [1]. Indeed, it has permitted to localize, and then easily analyze a one atom thick material. It has been shown that a 300 nm silica layer on top of a bulk silicon wafer allows by constructive interferences to improve the contrast of graphene due the absorption of light by this same material [2]. Based on this work we developed a method that allows us to directly observe carbon nanotube, multiwalled (MWNT) as well as single walled (SWNT), using optical microscopy. Based on our experimental result, we build a model that shows how light interference as well as the presence of the silica layer permits to tune the broadness of the nano-object shadow observed in optical microscopy. The model takes into account the light wave length, the silica layer thickness and the polarity of the light.
After characterizing the nanotube by Raman imaging we were able to easily manipulate them with an Atomic Force Microscope (AFM) tip. The AFM used in contact mode allows us to precisely push a given nanotube over an electric device designed by photo-lithography. The characterization of a unique carbon nanotube conductivity is also exposed in here. This work shows that it is now possible to build Nano Electro Mechanical Systems (NEM´s) by using simple tools which are actually micro and macro scale devices.

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang,Y. Zhang, S. V. Dubonos,I. V. Grigorieva, A. A. Firsov *Science*, **306**, 666-669 (2004)
[2] Libo Gao, Wencai Ren, Feng Li and Hui-Ming Cheng *ACS Nano*, **2**(8) 1625-1633 (2008)

Wall-Selective Probing Of Double-Walled Carbon Nanotubes Using Covalent Functionalization

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Double-walled carbon nanotubes (DWNTs) present an original coaxial geometry in which the inner wall is isolated by the outer wall, while the latter is in direct interaction with the environment. Covalent functionalization, performed using an aryldiazonium salt, is presented here as an efficient tool to investigate DWNT devices. Optical and electrical properties of DWNTs are measured in pristine, functionalized and defunctionalized states. Absorption and resonant Raman spectroscopy measurements, on individual DWNTs and networks, show that the functionalization is reversible upon thermal annealing and occurs strictly at the surface of the outer wall, leaving the inner wall essentially unaltered by the chemical bonding. Individual DWNT field-effect transistors are operated in functionalized state with current flowing mainly through the inner wall, with a current intensity comparable to a pristine single-walled carbon nanotube device. Electrical transfer characteristics are demonstrated to provide unambiguous identification of the metallic or semiconducting character of both walls. Current saturation at high bias is also measured in the inner wall of functionalized DWNT, leading to novel insight on the current saturation mechanism. Finally, opportunities enabled by the wall-selectivity of the functionalization are discussed: fundamental experiments about wall to wall interactions in DWNTs are made possible, but also the design of novel environment-sensitive electronic devices in which the inner wall is used for electrical transport while the outer wall chemically interacts with external stimuli.

Challenging in Characterizing Modified SWCNT

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A great effort has been directed in recent years towards the chemistry of single-walled carbon nanotubes (SWCNT); that is, the control of exfoliating and adding diverse chemical addends to their sidewalls. This field has matured rapidly and has reached the point where a vast array of functional moieties can be linked to SWCNT through both covalent and non-covalent interactions. Being able to "tune" the type, quantity, and location of functional groups on the SWCNT is an extremely valuable tool, particularly for applications in composite materials. Despite its obvious importance, the ability to characterize the types and quantities of functional groups attached to SWCNT has proven to be a difficult task. Here we will present our work in the characterization of functionalized SWCNT and the different tools used to identify functionalities and determine the functionalization degree.

Carbon Nanoubes as substrates for Surface Enhanced Raman Spectroscopy

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The surface enhanced Raman spectroscopy (SERS) has attracted great attention in the last 30 years. It can increase the Raman signal of molecules by several orders of magnitude facilitating the detection of even trace molecules. In SERS effect, the substrates play a key role, being the responsible for the intensification of the Raman signal. The substrates are obtained by conventional deposition or immobilization of metal nanoparticles on a surface. The current challenge is the gain in performance with the fabrication of nanostructured SERS substrates. Recently, it was shown that if this surface is composed by carbon nanotubes, the effect can be dramatically increased. Also very recently, single or few layers of graphene were seen to work as SERS substrate without even the presence of metallic particles. In this work we investigate the Raman spectra of Raman spectra of octadecilamine molecules bonded to the surface of single- wall carbon nanotubes. Laser excitation energy is changed from 1.92 to 3.81 eV and the dependence of the Raman signal with excitation energy is observed. We note that under special conditions of resonance, the Raman signal of octadecilamine interacting with carbon nanotubes is strongly increased, becoming even stronger than the resonant Raman signal of the carbon nanotubes.

Combining Independent Measurements on Individual Carbon Nanotubes

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We have studied the individual properties of freely suspended carbon nanotubes (CNTs) using three different measurement techniques: electronic transport measurements, Raman spectroscopy and electron diffraction measurements in a transmission electron microscope. The two latter techniques give two independent methods to determine the chirality of the nanotube [1,2]. CNTs with determined chiral indices are then studied, allowing us to tie the optical and electronic response to a known lattice structure. We have e.g. recently performed the first time-resolved (femtosecond) four-wave-mixing (FWM) measurements on individual (8,4), (24,14) and (28,14) CNTs [3], directly probing both exitonic and vibrational dynamics. We will present those measurement, as well as transport and Raman measurements of known individual CNTs down to cryogenic temperatures.

[1] J. Rintala et al., *J. Phys. Chem. C*, **113**, 15398, (2009)
[2] H. Jiang et al., *Carbon*, **45**, 662, (2007)
[3] P. Myllyperkiö, et al., *ACS Nano*, **4**, 6780, (2010)

Isolated and shape defined graphene layers in a single litographic step

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Graphene layers produced by micromechanical cleavage are always surrounded by thicker, unwanted graphitic material that could interfere with the fabrication of electronic devices as it results in shorts or compromises lithography. Also, they are randomly shaped, while shape control is required for application.

Here we present a technique that allows, in a single and quick lithographic step, the production of fully isolated graphene samples of defined shape. Graphene flakes are first obtained by micro-mechanical exfoliation on a Si + SiO_2 substrates and characterized by optical microscopy and Raman spectroscopy. PMMA is spin-coated onto them and patterned via e-beam lithography in order to define on the graphene sample the contour of the desired shape. After resist development, oxygen plasma is used to etch the uncovered part of the graphene. This results in an island (graphene covered in PMMA) of desired shape isolated from the rest of the polymer film. The latter is then removed by immersion in de-ionized water, while the lithographically defined island remains on the substrate. All the graphitic material is removed from the substrate together with the polymer film. PMMA is eventually dissolved leaving a completely isolated and shaped graphene sample. The frame width is few microns wide and requires only seconds to be e-beam written. The plasma is very mild, as just part of the monolayer has to be etched, and does not affect the polymer-covered part of the flake. Raman spectroscopy shows the process does not induce any structural defects in the resulting shape-defined flakes.

STM Images of Carbon-Nanotube Quantum Dots:Seeing a Wigner Molecule of Correlated Electrons

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The paradigm of few-electron complexes in quantum dots (QDs) relies on the idea that the lowest- energy quantized levels are filled according to Pauli's exclusion principle. If Coulomb repulsion is sufficiently strong to overcome the kinetic energy cost of localization, a different scenario is predicted: a “Wigner” molecule (WM) forms, made of electrons frozen in space according to a geometrical pattern. Despite considerable experimental effort, evidence of the WM in semiconductor QDs has been elusive so far. Here we demonstrate theoretically that WMs occur in gate-defined QDs embedded in typical semiconducting carbon nanotubes (CNTs). The unambiguous signatures of the WM state must be searched in the scanning tunneling microscopy (STM) images of the electrons. Through exact diagonalisation (ED) calculations, we unveil the inherent features of the electron molecular states. We show that, like nuclei in a usual molecule, electrons have localized wave functions and hence negligible exchange interactions [1, 2]. ED results for single and double QDs provide a simple interpretation for transport experiments in ultraclean CNTs [3, 4].

[1] A. Secchi and M. Rontani, *Phys. Rev. B* **80**, 041404(R) (2009).
[2] A. Secchi and M. Rontani, *Phys. Rev. B* **82**, 035417 (2010).
[3] V. V. Deshpande and M. Bockrath, *Nature Phys.* **4**, 314 (2008).
[4] F. Kuemmeth et al., *Nature* **452**, 448 (2008).

Abstract 703
MSIGN11

Measuring Chirality Distribution of NIST RM 8281 Long Fraction Carbon Nanotubes by Raman Spectroscopy

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Carbon nanotubes are available today for commercial use everywhere and the control of its properties and quality is an issue of major relevance [1]. Single-wall Carbon Nanotubes are grown by different methods and with different characteristics which determine their physical properties. Separation methods try to isolate the tubes by their properties such as electrical behavior, size, etc. One of the challenges is to find a suitable way to address the chirality distribution of the tubes in a sample and that could be used to control the production and separation of the tubes. Here we present a methodology and the results of an intensity analysis of the Resonance Raman RBM signal of the single-wall carbon nanotube sample RM 8281 produced by NIST in order to determine its diameter and chirality distribution. The method consists of correcting the obtained RBM signal by the Resonance Raman cross-section, as calibrated by the "super-growth" water assisted CVD sample[1]. We show a comparison between our results and the ones obtained by transmission electron microscopy and photoluminescence.

[1] A. Jorio; E. Kauppinen, A. Hassanien. *Carbon Nanotube Metrology*. In: Ado Jorio; Mildred S. Dresselhaus; Gene Dresselhaus. (Org.). *Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications*. (Springer-Verlag GmbH, Heidelberg, 2008), v. 111, p.61- 90
[2] P. B. C. Pesce, P. T. Araujo, P. Nikolaev, S. K. Doorn, K. Hata, R. Saito, M. S. Dresselhaus, and A. Jorio. *Appl. Phys. Lett.* **96**, 051910, 201

Abstract #
CNT-NET

Polymers and Advanced Polymer Matrix Composites Reinforced with Aligned Carbon Nanotubes: Focus on Mechanical Properties

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No abstract received

Carbon Nanotube Organisation in Polymer Nanocomposites

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We use optical and electron microscopy as well as spectroscopic Raman imaging to explore the carbon nanotubes dispersion and organization in thermoplastic polymers. Depending on the type of nanotubes used such as single, double or multiwall wall tubes, we find considerable differences in dispersion behavior. Raman G band imaging with tube filling as low as 0.16wt% is used to map the tube distribution and to distinguish between regions with agglomerated and dispersed tubes. Analyzing the G band line shape, we find that size and the presence of other forms of carbon influence in an important way the dispersion of the tubes. We show how flow and polymer wetting influences the dispersion and anisotropy and compare the tube distribution at different length scales. We find that substantial parts of the tubes remain agglomerated in larger bundles at percolation (0.3 wt% for double wall tubes) showing there is a considerable potential in improving the conductivity in CNT networks at low filling.

Structure and Properties of Composites of Carbon Nanotube Fibres

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One of the most promising routes to exploit the axial properties of CNTs is to assemble them into a macroscopic fibre, with the tubes aligned parallel with the fibre axis; a strategy similar to that proposed eight decades ago for the development of high-performance polymer fibres [1]. Carbon nanotube fibres can be produced by drawing from an array of vertically aligned CNTs [2]; by wet-spinning from a liquid crystalline suspension of CNTs [3]; or they can be spun directly from the reactor by drawing them out of the hot-zone during CNT growth by chemical vapour deposition (CVD) [4], the process used in this work.

Considerable attention has been devoted to optimising the structure of CNT fibres at the different stages of their production: controlling the synthesis of specific nanotubes [5], the assembly of CNTs into a fully dense fibre [6, 7] and using post-spin treatments to obtain specific properties [8]. However, the integration of CNT fibres into composites and the properties of these composites have received comparatively less attention, in spite of these aspects being fundamental for many potential applications of this new high-performance fibre. The CNT fibres have yarn-like open structure [9], with a surface area of around 200 m^2/g which is readily accessible to polymer molecules; indeed polymer infiltration occurs without applying pressure and is simply driven by capillary forces. The ingress of polymer gives rise to a hierarchical architecture when the fibres are integrated in composites. We present measurements of electrical conductivity, thermal conductivity and coefficient of thermal expansion (CTE) for CNT fibre/composites and discuss the effects of capillary-driven adhesion between CNT fibre and matrix. The degree of infiltration and the identity of the basic reinforcing element is analysed by scanning electron microscopy and synchrotron X-ray diffraction. These results are compared with those from more traditional carbon fibre (CF) composite specimens manufactured in exactly the same way.

[1] W.H. Carothers, & J.W. Hill, J. *Appl. Chem. Soc*., **54**, 1579-1587 (1932).
[2] M. Zhang, K.R. Atkinson, & R.H. Baughman, *Science*, **306**, 1356-1361 (2004).
[3] L.M. Ericson et al., *Science*, **305**, 1447-1450 (2004).
[4] Y.L. Li, I.A. Kinloch, & A.H. Windle, *Science*, **304** (5668), 276-278 (2004).
[5] M. Motta, et al., *Physica E*, **37**, 40-43 (2007).
[6] K.K. Koziol, et al., *Science*, **318**, 1892-1895 (2007).
[7] S. Fang, M. Zhang, A. Zakhidov, & R.H. Baughman, *J. Phys. Condens. Matter*, **22**, 24221 (2010)
[8] C. Fang et al., *App. Phys. Lett*., **97**, 181906 (2010).
[9] J.J. Vilatela & A.H, Windle, *Adv. Mater*., **22**, 4959-4963 (2010).

Abstract 51
CNT-NET

Dispersion and Composite Processing Of Polymer Coated Graphene

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Liquid phase exfoliation and dispersion of graphene, i.e. single layer graphite, is a critical challenge for bulk processing of graphene into advanced materials and devices. We demonstrate a suite of techniques for dispersing pristine graphene using polymer coatings for the purpose of liquid-phase nanocomposite processing. First, we illustrate a unique in situ polymerization technique to develop localized polymer coatings on the surface of dispersed pristine graphene sheets in solution. These polymer coatings do not disrupt the pristine structure or superior properties of the graphene sheets; instead, these coatings allow for stable, aggregation resistant graphene dispersions, as characterized through rheology, SEM, and AFM. We also demonstrate that certain polymers naturally wrap and stabilize pristine graphene in various organic solvents. We prepare epoxy/graphene nanocomposites with the wrapped graphene. We also make polymer-wrapped graphene and PVA nanocomposites by solution casting and doctor blading. In both the nanocomposites graphene enhances the mechanical properties.

Abstract 405
CNT-NET

Highly Conductive, Long-Range SWNT Network Structure Made by Wet Shear Dispersion

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Carbon nanotubes (CNT) have been studied as fillers in diverse multifunctional composites due to a wide range of the excellent properties. Dispersion technology of CNTs is challenging to realize commercial products such as coatings, heat sink, and structural members. Much efforts have been focused on dispersing CNTs individually into matrices, however, deterioration in CNT quality by damaging the surface and shortening was an inevitable problem [1].

Here we present long-range SWNT network structures comprised of long (hundreds of microns), flexible nanotubes, which can reach the electrical, thermal conductivity and mechanical robustness throughout matrices like polymers and metals. The SWNT network structures were made by dispersing as-grown SWNT forests in solvent through a shear from wet-jet mill, where mostly keeping the SWNT quality. The SWNT forests were synthesized by water-assisted CVD method 'Super Growth'. First, the SWNT forest was suspended in solvent showing the configuration like trunks of a tree. To control the SWNT network structure, we applied different shears at 20-120 MPa on the wet dispersion. By the shear dispersion with vortex flow, the trunks (big nanotube bundles) were transformed into fine meshes. To observe the structure, the SWNT ensembles were discretely laid on a flat substrate. An SEM observation revealed that nanotubes spread continuously in each ensemble, which differs from a network through contacts of individually-dispersed nanotubes. The trunks from the starting SWNT forest were unravelled widely with the increased jet pressure, resulting in more SWNT ensembles as well as a reduction in the ensemble size. The SWNT ensembles ranged tens of microns to 1 mm in size. A digital microscope enabled the 3D analysis of SWNT ensemble in solution, which is indicative of a randomly spreading network structure. Entanglement of these SWNT ensembles in solution caused a high apparent solution viscosity depending on the structure. A wide variety of solvents is applicable to fabricate the SWNT ensembles on the wet process, such as organic solvents of methyl isobutyl ketone, ethanol, DMF, and even water without surfactants. These SWNT suspensions from many solvents are stable for several months without precipitation at the concentration any higher than 0.3 mg/mL, where the SWNT ensembles intertwine.

Buckypapers made from these SWNT ensembles showed a high electrical conductivity of 60- 90 S/cm. In contrast to the long-range SWNT network structure, Buckypapers from ultrasonication-processed, shortened SWNTs gave a low conductivity of ~50 S/cm.

In this study, we propose a novel SWNT network structure, which stretches hundreds of micron long to deliver the excellent properties in matrices. The SWNT ensembles were recently utilized for SWNT rubber wire [2] and SWNT Buckygel actuator [3], yet, the detail was unclear.

[1] P. M. Ajayan, J. M. Tour, *Nature*, **447**, 1066-1068 (2007).

[2] T. Sekitani, H. Nakajima, H. Maeda, T. Fukushima, T. Aida, K. Hata, T. Someya, *Nature Mater.*, **8**(6), 494-499 (2009).
[3] K. Mukai, K. Asaka, T. Sugino, K. Kiyohara, I. Takeuchi, N. Terasawa, D. N. Futaba, K. Hata, T. Fukushima, T. Aida, *Adv. Mater.*, **21**, 1582-1585 (2009).

Carbon Fiber – Carbon Nanotube Hybrid

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Since long back, carbon fibers (CF) have been used as a reinforcement material in various polymer matrices. Carbon fibers effectively increase the mechanical strength of polymer composites. However, due to wide gaps between two fibers in the matrix, the electrical conductivity of those composite materials does not improve significantly. Since the mass production of carbon nanotubes (CNT) became possible, CNTs are being used as filler into various CF-polymer composites. The conventional method is to mix 0.5 to 5% CNTs in resin-based composite materials to enhance their electrical conductivity.

In this work, however, instead of mixing CNTs into fiber-resin matrix, we preferred to grow CNTs directly on CFs. This proved to be easier and more effective in improving the mechanical strength as well as electrical conductivity of the composite, simultaneously. Commercially available carbon fibers were loaded with iron and cobalt catalysts and chemical vapour deposition was carried out at 600 °C using camphor as the carbon source. CNTs of different densities were grown on CFs with different camphor feed weights. Controlled mixing of as-grown CF-CNT hybrid to commercial polypropylene (PP) was found to enhance the tensile strength, flexural strength, electrical conductivity and thermal conductivity significantly. This approach offers a convenient way of improving mechanical strength and electrical conductivity of composites at more affordable prices.

High Shear Fluid Processor Assisted Dispersion of MWCNTs within Epoxy and the Properties of the Resulting Composites

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Homogeneous dispersion of CNTs within polymer matrix is the key to accomplishing the desired mechanical, thermal and electrical properties in the resulting composites. In this study, as a novel approach, a specially designed high shear fluid processor that exposes uniformly the liquid suspensions to very high stresses was successfully conducted to disperse pristine and acid treated MWCNTs within epoxy resin. TEM investigation showed that the high shear fluid processor makes possible the control of length reduction of MWCNTs based on the processing conditions. Thermal and mechanical properties of the resulting composites were measured, conducting Dynamic Scanning Calorimetry (DSC) and Dynamic Mechanical Analyzer (DMA), respectively. Electrical conductivity of the samples was also measured. It was determined that the samples processed with the processor exhibited much better properties than the samples processed with traditional methods, such as high shear mechanical stirrer or sonicator.

A Simulation Study on the Effects of Shear Flow and Nanotube Shape on the Microstructure and Electrical Properties of Carbon Nanotube/Polymer Composites

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Particle-level simulations are used to simulate carbon nanotube (CNT)/polymer composites in simple shear flow. A resistor network algorithm is used to determine the electrical conductivities. Effects of different parameters such as nanotube flexibility, aspect ratio, shape and tunneling length and flow fields on the electrical conductivities of the composites can be studied with this method. Results show that using curved nanotubes with high aspect ratio and imposing shear flow reduces the electrical percolation threshold by facilitating the formation of a conductive network. We proved that nanotube agglomeration is beneficial for the electrical conductivity in CNT/polymer composites. In agreement with previous research, we show that the rate of imposed shear flow influences the conductivities of the composites as well as aggregation and orientation of the nanotubes. Flow induced orientation is studied by measuring the anisotropy in the flow-gradient and flow-vorticity planes. The degree of anisotropy is quantified by anisotropy factor and orientation angle measurements. Our simulations show that at high shear rates CNT aggregates are broken down because of the high hydrodynamic forces. Therefore a conductive network cannot be established and conductivity of the composite decreases. Broken aggregates create smaller aggregates or individual nanotubes which then align in the flow direction. Hence the individual cluster number and the anisotropy factor increases. At low shear rates the motion of the nanotubes causes build-up of agglomerates and decrease in orientation factor. Hence when the shear rate is decreased a conductive network can be formed increasing the conductivity of the composites.

Abstract 688
CNT-NET

Interfaces in Nanotube- and Graphene-Based Nanocomposites

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Efficient interfacial stress transfer in nanocarbon-based nanocomposites, such as those reinforced by nanotubes or graphene, is essential for the nanomaterials to realize their potential as high-performance composites. The types of interface that are important in such nanocomposites are:

- The interface between the polymer matrix and the nano-reinforcement.
- Internal interfaces between individual walls in multi-walled carbon nanotubes.
- Internal interfaces between the atomic carbon layers in multi-layer graphene.

Carbon nanotubes and graphene both have strong, well-defined Raman spectra and it is well established that the Raman bands shift when these nanomaterials are subjected to stress [1-4]. The presentation will review the use of Raman spectroscopy to follow stress transfer in nanocomposites reinforced with both nanotubes and graphene. It will be demonstrated that the technique has the ability to distinguish between stress transfer between the polymer matrix and outer interface of the reinforcement and stress transfer between the constituent layers of multi-layer nanostructures. It will be shown that failure of interfacial stress transfer can be observed and the efficiency of stress transfer may be evaluated at each interface. The findings of these investigations will have important implications for the future design of nanocarbon-based nanocomposites materials.

[1] S. Cui, I.A. Kinloch, R.J. Young, L. Noe, M. Monthioux, *Advanced Materials*, **21,** 3591-3595 (2009).
[2] L. Gong, I.A.Kinloch, R.J. Young, I. Riaz, R. Jalil, K.S. Novoselov, *Advanced Materials*, **22,** 2694-2697 (2010).
[3] L.B. Deng, S.J. Eichhorn, C.C. Kao, R.J. Young, *ACS Applied Materials & Interfaces*, **3,** 433-440 (2011).
[4] R.J. Young, L. Gong, I.A. Kinloch, I. Riaz, R. Jalil, and K.S. Novoselov, *ACS Nano*, **5,** 3079-3084 (2011).

Abstract 390
CNT-NET

Role of Nanotube-Nanotube Contacts in Modeling the Reinforcement Efficiency of Carbon Nanotubes in Polymer Matrices.

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In the recent years, great effort has been devoted to study the effectiveness of carbon nanotubes in mechanical reinforcing of polymer matrices. However, despite the enormous amount of experimental data available in literature, a theory correlating the physical properties of the fillers with the final nanocomposite behavior is still missing. Experimental measurements of both mechanical moduli and electrical conductivity of nanocomposites [1-2] have highlighted the relevance of nanotubes networking in determining the effective macroscopic behavior of such nanocomposite systems. In particular, the reinforcement capability of carbon nanotubes in a polymeric matrix certainly depends by both their length and amount but, undoubtedly, their arrangement and contacting [3] within the hosting medium plays a fundamental role in the load transfer mechanism. In addition, experimental findings support the evidence that the clustering of the nanotubes implies a sensible decrease of the effective mechanical efficiency of the carbon nanotubes in the polymer matrices reinforcement.

Only recently [4] a mechanical properties model has been proposed that explicitly accounts for the reduction of the stress transfer efficiency between reinforcing nanotubes and hosting matrix via a reduction of the effective filler length with the increasing nanotubes content. The modeling approach takes origin by the Philipse's Random Contact model [5] which relates the excluded volume of a particle to the average number of contacts between an ensemble of such shaped particles. The shear lag micromechanics of short fibers has been then modified to address the reduction of the effective aspect ratio of the nanotubes resulting from nanotube-nanotube contacts. Moreover the waviness of the nanotubes within the polymer matrix is also accounted for by the deviation of the excluded volume evaluated for curved nanotubes from the straight rod assumption. The aspect ratio of the reinforcing carbon nanotubes represents indeed, the controlling parameter for the determination of the mechanical properties of the nanocomposite system.

Model is here compared with a large amount of experimental data for carbon nanotubes polymer matrix composites showing a very good agreement.

[1] J.N. Coleman, U. Khan, W.J. Blau, Y.K. Gun'ko, *Carbon*, **44**, 1624-1652 (2006)
[2] W. Bauhofer and J.Z. Kovacs, *Composites Science and Technology*, **69**, 1489-1498 (2009)
[3] A. Martone, C. Formicola, M. Giordano, M. Zarrelli, *Composites Science and Technology*, **70**(7), 1154-1160 (2010).
[4] A. Martone, G. Faiella, V. Antonucci, M. Giordano, M. Zarrelli, *Composites Science and Technology*, in press (2011).
[5] A.P. Philipse, Langmuir, **12**(5), 1127-1133 (1996).

Impressive Fatigue Life and Fracture Toughness Improvements in Graphene- Based Epoxy Composites

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We report enhancements of 28-111% in mode I fracture toughness and up to 1580% in uniaxial tensile fatigue life through the addition of small amounts (≤1 wt.%) of graphene oxide to a DGEBA/F epoxide resin. Graphene oxide was synthesized in our laboratory by intercalation with a reaction of sulfuric acid and potassium permanganate followed by ultrasonic exfoliation of helical-ribbon carbon nanofibers (CNFs). TEM evidence revealed a unique mechanism of unraveling and splaying open of the nanofibers yielding large, high-quality, mostly mono- and few-layer graphene oxide sheets. Epoxy dispersions containing these sheets were subsequently prepared by three-roll calendar milling and individually cast into suitable test coupons. Composites containing the parent CNFs and a control group (0 wt.% reinforcing phase) were similarly prepared and tested for comparison.

Results indicate substantial toughening imparted by the inclusion of the nanocarbon phases. Compared to the control group, CNFs slightly outperformed graphene oxide at equivalent weight fractions. At 1 wt.%, fracture resistance was improved by 78% with CNFs versus a 63% improvement through graphene oxide addition. Fracture surface inspection by SEM revealed much rougher crack propagation zones suggesting significant defection of propagating crack fronts. Graphene oxide composites, while also exhibiting deviations from the mirror-like fracture surface of the virgin polymer, displayed bowlines normally indicative of the pinning of cracks between inclusions. Typically, nanomaterials cannot account for crack pinning due to their small size relative to crack tip opening distances. The large 2D dimensions of the graphene oxide sheets however can justify the observance of pinning.

Fatigue trends displayed a different behavior. While improvements from CNF addition were substantial, they were limited to low applied stress levels. The addition of only 0.5 wt.% CNF yielded a mean fatigue life enhancement of 180% at 20 MPa applied stress. A slight reduction in performance was observed at the highest applied loads, -15% at 40 MPa. This distortion in response led to a 'flatter' *S-N* curve, a desirable phenomenon indicative of superior fatigue properties and one typical of fibrous composites. More impressive gains over the full range of applied stress amplitudes were observed in the 0.5 wt.% graphene oxide composites. The flatter appearing *S-N* curve previously evident by the CNF composites was preserved but shifted to much longer lives. At 25 MPa applied loading, mean fatigue life was 1580% that of the control. At the highest comparable stress level (40 MPa), where CNFs failed to provide additional robustness, mean life was extended by 420%. Gains in toughness and the fatigue superiority of the graphene oxide composites in this study are indicative of the exciting prospects for this remarkable new material in the composites field.

Abstract 517
CNT-NET

Unidirectional MWCNT sheet/epoxy composites

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Since the discovery of carbon nanotube (CNT), high mechanical properties of CNTs are intensively researched. So far, CNTs has been regarded as short fibers with the length of several tens micro-meters, and so it has been commonly used as filler to reinforce matrices for light-weight structural components [1]. Recently, we established a chemical vapor deposition growth method of ultra-long and highly spinnable multi-walled carbon nanotube (MWCNT) arrays [2]. From the highly spinnable arrays, unidirectionally aligned MWCNT paper sheets were formed [3]. The aligned MWCNT sheet is suitable to reinforce composite materials. In this study, we fabricated unidirectional MWCNT sheet/epoxy composites and investigated mechanical properties.

MWCNT arrays were grown by chloride assisted chemical vapor deposition. $FeCl_2$ is used as precursor of Fe catalyst. MWCNTs grow with a high growth rate over 0.1 mm/min up to 2 mm and the array is highly spinnable. By pinching and pulling out the edge of the MWCNT array, a MWCNT web, which is a two dimensional MWCNT network, is drawn. Then a unidirectionally aligned MWCNT sheet paper was fabricated by winding MWCNT webs on a drum, and the rolled MWCNTs structure was cut opened. MWCNTs are connected by van der Waals and no binder material is used. Since MWCNTs are aligned in the drawn direction in the web, the alignment is maintained in the web and thus MWCNTs are highly aligned in the sheet. The MWCNT sheet shows highly anisotropic features in electrical and thermal conductivity and mechanical properties [3].

Unidirectionally aligned MWCNT/epoxy composites were fabricated by a hand lay-up method. Epoxy was well impregnated into the MWCNT sheet. MWCNTs are well aligned in the composite. By this procedure, highly aligned MWCNT composites are formed very easily in a short time. MWCNT volume fraction was 14 %. Tensile tests of unidirectional MWCNT/epoxy composites were carried in the aligned direction. Young's modulus increased from 3GPa for pure epoxy to 31GPa for composite, and tensile strength increased from 81MPa to 137MPa.The present large reinforcement was surely due to a high degree of alignment and ultra-long MWCNTs.

[1] D. Qianet al., *Appl. Phys. Lett.*, **76**, 15 (2000).
[2] Y. Inoue et al., *Appl. Phys. Lett.*, **92**, 213113 (2008).
[3] Y. Inoue et al. *Carbon* **49**, 2437 (2011).

Manufacturing and Properties of High Weight-Fraction Aligned Polymer Nanocomposites (APNCs)

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Exploitation of prominent, distinct axial CNTs properties are proposed to enable high electrical and mechanical properties of so called functional aligned polymer nanocomposites (APNCs). The use as highly electrical and thermal conductive polymer composites promise potential in electronics or use as sensitive load-sensors, demand high quality CNTs and new approaches of manufacturing. Due to the nearly 1-dimensional orientation and high length of CNTs a clear morphology or state of distribution/orientation is given: Besides the intermediate goal to provide a pure carbon based pathway which can challenge metallic conductors, the electrical and mechanical characterisation of this idealized CNT morphology will contribute to the understanding and modelling of low-volume content, dispersed CNT/epoxy composites. Only a comprehensive view on mutual dependency of (i) components, (ii) manufacturing steps (iii) and the resulting APNC properties can enable this. Therefore aspects of CNT-synthesis, resulting structural quality, geometric like aspect ratios, internal entanglement and orientation, must be taken in consideration as additional influence of different experimental approaches for alignment, densification and epoxy impregnation to increase performance of APNCs.
We manufactured APNCs consisting of up to 16 layers of highly packed in-plane oriented CNT-carpets or selective thin films of up to 96mm length. Individual layers of aligned CNTs are based on high quality MWCNT arrays with an extremely low D/G-Band ratio and lengths up to 1.7mm and were infiltrated by an epoxy system. The basic studies on this composite class are dealing with the influence of different layer build-ups (like bridging non coherent carpet areas, via alternative stacking of different amounts of horizontal aligned CNT-films) on electrical conductivity and its temperature and mechanical load dependence. We discuss on aspects of manufacturing which raise slight variations in properties of produced APNCs.
To sum up: We provide insight into progressing studies on high-performance APNCs which can now reproducibly be manufactured in a broad structural variation: reaching from extreme long films for sensing application of area up to 90x29mm² with an electrical conductivity of 50 S/m up to 16-layered samples of 30x30mm² and typical thicknesses of ≈300µm with outstanding axial electrical conductivity of $>2\cdot10^4$S/m.

Abstract 43
CNT-NET

Network Structure and Electrical Conduction In Carbon Nanotube Modified Polymers

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Carbon nanotube (CNT) addition to polymers allows for the design of electro-conductive polymer nanocomposites [1]. With the formation of an electrically conducting network throughout the electrically non-conducting polymer matrix, the CNTs enable electric current flow through the material. Due to their outstanding electrical properties and high aspect ratio, small quantities of CNTs induce a significant improvement in electrical conductivity of the host polymer. In addition, the ability of CNT/polymer nanocomposites to couple electrical properties with mechanical deformation enables their use as a multifunctional material in sensing and actuating applications [2]. With regard to such applications the topic of this research is focused on the network structure and the electrical conduction mechanism in CNT/polymer nanocomposites.

It has recently been shown that information about the network structure and electrical conduction mechanism in CNT/polymer nanocomposites can be obtained from the piezoresistive response of such materials [3]. In this research changes in the CNT network are real-time traced by monitoring the electrical resistance of CNT/polymer nanocomposites subjected to tensile and compressive stresses. For samples under tensile stress a non-linear positive dependence of the sample resistance on the tensile strain is found. Further, it is shown that the increase in resistance cannot be explained by the changes in geometry of the sample under tension, hence, indicating a change in the material electrical resistivity due to changes in the CNT network. For CNT concentrations above the percolation threshold, the increase in electrical resistivity with tensile strain is explained by a combination of two distinct mechanisms: (i) decrease in the number of conducting paths throughout the sample, and (ii) increase in the resistance of the conducting paths due to an increased tunnelling resistance between neighbouring CNTs. Based on this, it is proposed that the electrical resistivity, ρ, depends on the tensile strain, ε, is follows:

$$\rho \ \alpha \begin{cases} \varepsilon^{(1/a)} \\ e^{(b\,\varepsilon)} \end{cases}$$

a and *b* are constants, both depending on the material properties of the system at hand. The respective magnitude of the two mechanisms was found to depend on CNT concentration, with mechanism (i) and (ii) being more pronounced for high and low CNT concentrations, respectively. In addition, the potential to sense mechanical deformation was found to increase with decreasing CNT concentration.

Network structure and electrical conduction mechanism in CNT/polymer nanocomposites are further investigated by compression testing. The above qualitative model is extended to include compressive strain, and the respective magnitude of the two mechanisms behind electrical resistivity changes is examined as a function of filler concentration and compressive strain.

[1] J. N. Coleman, S. Curran, A. B. Dalton, A. P. Davey, B. McCarthy, W. Blau, and R. C. Barklie, *Phys. Rev. B*, **58**, R7492-R7495, (1998).
[2] C. Li, E. T. Thostenson, and T. W. Chou, *Compos. Sci. Technol.*, **68**, 1227-1249, (2008).
[3] M. H. G. Wichmann, S. T. Buschhorn, J. Gehrmann, and K. Schulte, *Phys. Rev. B*, **80**, 245437, (2009).

Abstract 594
CNT-NET

Nanocarbon Composites for SHM

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This contribution takes a detailed look at composite materials based strain and damage measurement. Structural health monitoring (SHM) generally relies on some form of deformation measurement. This has been done with superior performance composite sensors based on carbon nanoparticles in a polymeric matrix. A multiscale approach transfers their capabilities into micro-fiber reinforced plastic material as it is in widespread use. Such composite structures are an excellent example for the urgency, as well as the feasibility, of vastly improved SHM capabilities. Carbon nanoparticles allow modification of a broad range of materials with only minimal amounts of particles needed to achieve conductivity. However imparting conductivity and some form of piezoresistive property is only the first step to improved SHM. It is critical to understand the principles and consequent limitations to formulate a powerful SHM concept. This contribution will take a detailed look at the mechanisms and highlight critical issues for applications e.g. influence of moisture.

Multifunctional Free-Standing Single-Walled Carbon Nanotube Films

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The unique properties of single-walled carbon nanotube (SWNT) films, such as high porosity and specific surface area, low density, high ratio of optical transmittance to sheet resistance, high thermal conductivity and chemical sensitivity, and tunable metallic and semiconducting properties, open up a new avenue for a wide range of applications. Free-standing films offer a unique form factor for novel applications. We report here a simple and rapid method to prepare multifunctional free-standing SWNT films with thicknesses from a sub-monolayer to a few micrometres having outstanding properties for a broad range of exceptionally performing devices.

We have fabricated state-of-the-art key components for nanoparticle filtration with a figure of merit of 147 Pa^{-1}, transparent and conductive electrodes with a sheet resistance of 84 Ω/□ and a transmittance of 90%, electrochemical sensors with extremely low detection limits below 100nM, and polymer-free saturable absorbers for ultrafast femtosecond lasers. Furthermore, the films performed as the main components in gas flowmeters, gas heaters and thermoacoustic loudspeakers.

Nasibulin et al. *ACS Nano*, Publication date (Web): March 1, 2011.DOI: 10.1021/nn200338r

Abstract 694
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Translation of CNT in the Processing of Conductive Nanocomposites

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Carbon nanotubes are ideal fillers to achieve electrical conductivity in polymer composites. Conventional polymer shaping and processing technologies include extrusion, molding, drawing and fiber spinning for example. All these processes involve polymer flow, and in particular shear and extensional flow fields with velocity gradients respectively perpendicular or parallel to the flow direction. Flow yields most often an increase in resistivity which is ascribed to the rotation and flow induced alignment of the particles. Indeed alignment lowers the inter-particle contact probability and thereby the conductivity of the material. The effect of laminar shear has been the topic of several studies over the last years. However, the contribution of extensional flow remains vague in spite of its ubiquity in polymer processing. We present an experimental study in which the contribution of extensional flow is isolated. It is found that the resistivity of extruded composites displays a quadratic increase as a function of the draw ratio. A simple statistical model that considers the relative translation of the particles accounts for this behavior and reveals that translation has much more dramatic consequences than rotation on the conductivity and percolation of nanocomposites. We hope that the present results can provide a new guidance to optimize the processing of polymers filled with conductive particles.

Carbon Nanofiber Bucky Paper Interleaves for Improved Interlaminar Fracture Resistance of CFRP Composites

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Carbon fiber reinforced plastic (CFRP) composites have been extensively used in the aerospace, military, automotive and sporting goods industries owing to their high specific strength and stiffness. However, these laminated composites can experience premature failure because of interlaminar stresses caused by cracks present between layers of different orientations especially under impact loading. The delamination process represents a fundamental weakness of all laminated composite materials. Several techniques have been successfully devised to improve the delamination resistance, namely designing 3D fabric architecture, transverse stitching or pinning the fabric, fiber hybridization, toughening the matrix resin, and placing an interleaf, typically of thermoplastic material, in the interplay regions of the laminate. These methods enhanced the interlaminar properties but at the cost of in-plane mechanical properties. Thus, it is ideal to find an effective technique to improve the through-thickness properties without compromising the basic in-plane properties.

Carbon nanotubes (CNTs) or nanofibers (CNFs) in a sheet form or bucky paper offers a platform to eliminate the above issue in fabricating composites with high concentration nanotubes/ nanofibers. Bucky papers show a great promise for many potential applications, such as supercapacitors, electrodes, actuators, sensors, field emitters and hydrogen storage materials. In this work, partially cured CNF-epoxy bucky papers are interleaved in CFRP composites and their effects on the interlaminar shear properties, such as the mode-II fracture toughness and interlaminar shear strength, are specifically evaluated. CNF bucky papers were fabricated by vacuum filtration of functionalized CNF-acetone dispersion. Three different techniques were used to impregnate the bucky papers with epoxy resin, including simple soaking, hot compression and vacuum infiltration. The results, both in terms of young's modulus measurements and SEM observations, showed that the best quality of nanotube wetting was achieved through vacuum infiltration. Thus, partially cured CNF- bucky papers were placed in the mid-plane of the laminate made from CFRP prepregs and co-cured to produce CFRP hybrid composites with bucky paper interleaves. Several interlaminar fracture properties were characterized, including the mode-II interlaminar fracture toughness and shear strength. Remarkable 104% and 31% improvements, respectively, were obtained due to interleaving of CFRP composites with CNF bucky papers. Microscopic examination of the fracture surfaces indicates synergic toughening and strengthening mechanisms arising from the CNF interleaves. The CNFs acted as supplementary reinforcement to the matrix rich interface and promoted bonding between the neighbouring plies. Damage initiation and propagation were discouraged by the CNF bridging and pull-out mechanisms offered extensive fiber pull out mechanism, giving rise to much improved fracture energy required for interlaminar crack propagation.

Processing and Properties of Multiscale Carbon Fibre Reinforced Composite for Aerospace Application

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Carbon Fibre Reinforced Polymers (CFRPs) are increasingly used in aircraft as they combine lightness and good mechanical properties. However some, mainly matrix-dominated, drawbacks are encountered. The present study aims for increasing the damage tolerance of these composite materials. One approach to increase the mechanical properties of the matrix is its modification using nanomaterials, particularly carbon nanotubes.

In this work the attention is focused on materials dedicated to aerospace applications and on commercially available carbon nanotubes. Their influence on the properties and processability of an aerospace grade epoxy resin (RTM6) has been first studied. A good dispersion of the CNTs in the resin could be achieved resulting in the increase of the viscosity, which does not allow the production of multiscale CFRPs using vacuum assisted infusion processing. A route towards the manufacture of multiscale CFRPs which overcome some of the processing difficulties will be presented in this work. The CNTs are introduced in the dry preform between the NCF layers. The whole assembly is then infused using vacuum assisted infusion. In this way laminates presenting a high fibre volume content (~60 vol.-%) have been successfully infiltrated. Results in terms of fracture toughness, impact resistance and fatigue properties of these multiscale CFRP will be presented.

Abstract 708
CNT-NET

Localisation of Carbon Nanotubes in Melt Mixed Thermoplastic Polymer Blends

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The combination of blend systems with conductive nanoscaled fillers by melt mixing processes offers compared to single-polymer-composites much higher potential for the development of conductive composites with significantly lower filler concentrations. Aiming at tailoring new blend nanocomposite systems, a comprehensive understanding of the mechanisms responsible for the localization of conductive fillers like carbon nanotubes (CNT) or carbon black (CB) is required.

Recent results indicate that multiwalled carbon nanotubes (MWCNTs) tend to be selectively localized in one of the blend phases after melt mixing.

Different concepts are described in literature to explain the localization of solid nanofillers in polymer blends. Some authors attributed the observed particle arrangements to melt viscosity effects, but most frequently nanofiller localization is explained by the system's tendency to minimize its free energy. One possibility to express this generally valid principle is the wetting coefficient ω_a. Examples can be found for blends with nanosilica, carbon black and MWCNTs. Nevertheless, the predictions with the wetting coefficient significantly suffer from the difficulties to accurately measure the interfacial tension γ between nanoparticles and liquids. The measurement problems arise from the macro-, micro-, and nanostructure of the agglomerated nanoscaled surfaces of the filler. Thus, all standard measurement methods that are based on the contact angle or capillary effects are significantly disturbed by the surface structure and the obtained values can strongly deviate from the real surface properties of an individual nanoparticle.

The present study tries to access the interfacial interactions in between CNTs and polymer matrices by analyzing the localization of MWCNTs in different dual phase polymer blend systems made of polar polymers. The blends were produced using 5 min of melt mixing in a small-scale co-rotating microcompounder. MWCNT-polymer interactions are discussed by means of nanotube localization, nanotube aspect ratio, wetting coefficients and characteristic features like the molecular architecture of the blend partners.

Furthermore, the kinetics of the MWCNT-transfer from one blend phase to the other during melt mixing is discussed. The complete transfer of MWCNTs from a poly (styrene acrylonitrile) (SAN) precompound into an initially unfilled polycarbonate (PC) phase during 5 minutes of discontinuous melt mixing in a microcompounder has been observed recently [1].

However, the typical time scale of the occurring transfer and the responsible transport mechanisms are presently unknown. The kinetics of the CNT transfer mechanism was investigated for very short mixing times. The CNT transfer turned out to be fast and effective and strongly coupled to the development of the interfacial area of the blend.

The efficiency of CNT transfer appears to be generally higher as that of other fillers with differing geometrical shapes such as silica or carbon black. This can be attributed to the much higher aspect ratio of the nanotubes [2]. The suggested shape dependence of nanofiller localization can be evaluated by investigating the simultaneous transfer of MWCNTs and carbon black (CB) from SAN precompound into a thermodynamically preferred and initially unfilled polycarbonate (PC) phase during melt mixing.

[1] A. Göldel, G. Kasaliwal, P. Pötschke, *Macromolecular Rapid Communications* **30** 6, 423-429 (2009).
[2] A. Göldel, A. Marmur, G. R. Kasaliwal, P. Pötschke, G. Heinrich, *Macromolecules*, doi: 10.1021/ma200793a.

Manufacturing Of Hybrid Epoxy/Glass Fibre/CNT Composites Under Electric Field

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This study investigates the effect of application of an intermediate frequency electric field during the infusion and cure of glass fibre preforms using a high temperature aerospace epoxy system loaded with non-fuctionalised MWNTs. Conventional infusion was modified to accommodate the addition of CNTs and the application of field, whilst on-line resistivity monitoring was carried out at different levels of field. The influence of field on the anisotropic conductivity and the delamination toughness of the hybrid composites was established.

A process was developed for the efficient dispersion of carbon nanotubes in the epoxy. This involves the production of a masterbatch using ultrasonication of a solvent-CNT suspension, mixing with the epoxy and evaporation of the solvent followed by high shear mixing and dilution. The final suspension has a uniform state of dispersion with maximum aggregate size that does not exceed 5 μm. The good state of dispersion translates to high quality infusions involving only marginal adaptation of the conventional process. The nanotubes are distributed uniformly within the fibrous composite with CNTs infiltrating microchannels between individual fibres. An 1 kHz field was applied in the thickness direction by incorporating layers of bronze mesh electrodes in the infusion assembly. Significant reduction of the resistivity of the uncured hybrid composite was observed, from a value that exceeds 1500 Ωm to a value in the 500-750 Ωm range. The reduction in resistivity follows an exponential decay with relaxation times in the 3-4 min range. The final resistivity of the uncured material as well as the relaxation time decrease with increasing field.

The conductivity of the cured composite material correlates well with the on-line monitoring results. The application of the electric field increases the final conductivity of the hybrid composite in the thickness direction. This increase, which is higher for higher fields, reaches up to one order of magnitude. The in-plane conductivity remains unaffected by the field. These results, which are indicative of the preferential alignment/aggregation of CNTs in the field direction, are supported by SEM observations. The effect of nanotube addition and of field application on Mode I delamination toughness was investigated. The scatter of the results, which is inherent to the architecture of infusion fabrics, hinders the manifestation of unequivocal effects. There is a tendency for increasing toughness with the addition of nanotubes (10% higher compared to an epoxy/glass fibre control) and with electric field application (20% for the highest field compared to the control). Microscopy of delamination fracture surfaces is indicative of CNT pull out which can be related with an increase in toughness.

The results of this investigation demonstrate the feasibility of CNT modification and electric field application in composites manufacture. The application of field results in greater flexibility in manipulating the conductive behaviour of structural fibrous composites in terms of both anisotropy and local enhancement. Extension of the concept to carbon fibre composites is envisaged in the future.

An Alternative Method for Obtaining Good Dispersions and Orientation of MWCNTs in an Aerospace Epoxy Resin

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The use of multi-walled carbon nanotubes (MWCNTs) as nanofillers in epoxy resins, able to enhance the mechanical and electrical properties of the composites, has been widely studied [1]. The resulting properties of these nanocomposites strongly depend on the quality of the nanotube dispersion. Moreover, the surface treatment employed to functionalize MWCNTs appear to play a key role for establishing good interactions between the matrix and the filler.
MWCNTs are advantageous in the fabrication of robust and conducting composites because they could be oriented within the matrix and they could also exhibit extremely high aspect ratios. In this study we followed the method of Lee et al. [2] in order to obtain good orientation of the treated MWCNTs within the epoxy resin.
In particular, we used a novel type of nanotubes termed “oxygen-doped MWCNTs”,as nanofillers. In order to enhance the degree of dispersability of the tubes within the matrix, MWCNTs were functionalized with carboxylic groups [3]. Subsequently, the tubes were dispersed in isobutanol and stabilized in a basic medium. The dispersions were then filtered with a Teflon membrane (0.45 µm average pore size) so as to obtain dispersed and perpendicularly orientated MWCNTs [2]. This MWCNT network was then transferred to the resin RTM6 by the peeling method, in order to form a well defined “comb” consisting of MWCNTs. The resin was then cured and their mechanical and electrical properties were successfully measured.

[1] a) W. Bauhofer et al., *Comp. Sci. Tech.*, **69,** 1486 (2009); b) Skakalova V et al, *Synth. Met.,* **152**(1-3), 349 (2005).
[2] Lim C., Min D.-H., Lee S.-B., *Applied Physics Letters* **91**, 24317 (2007).
[3] O. Martin, A. Maroto, M- Terrones, J. Baselga (in preparation).

Mapping Local Microstructure and Mechanical Performance Around Carbon Nanotube Grafted Silica Fibres: Methodologies for Hierarchical Composites

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The introduction of carbon nanotubes (CNTs) modifies bulk polymer properties, depending on intrinsic quality, dispersion, alignment, interfacial chemistry and mechanical properties of the nanofiller. These effects can be exploited to enhance the matrices of conventional microscale fibre-reinforced polymer composites, by using primary reinforcing fibres grafted with CNTs [1]. This work developed a methodology that combines atomic force microscopy, polarised Raman spectroscopy and nanoindentation techniques, to study the distribution, alignment and orientation of CNTs in the vicinity of epoxy-embedded micrometre-sized silica fibres, as well as, the resulting local mechanical properties of the matrix. Raman maps of key features in the CNT spectra clearly show the CNT distribution and orientation, including a ‘parted’ morphology associated with long grafted CNTs. The hardness and elastic modulus of the epoxy matrix were improved by 28% and 24%, respectively, due to the reinforcing effects of CNTs. Moreover, a slower stress relaxation was observed in the epoxy region containing CNTs, which may be due to restricted molecular mobility of the matrix. The proposed methodology is likely to be relevant to further studies of nanocomposites and hierarchical composites.

[1] H. Qian, E. S. Greenhalgh, M. S. P. Shaffer, A. Bismarck, *J. Mater. Chem.*, **20**, 4751-4762, (2010).

Thermal, Electrical and Morphological Characterization of High Density Polyethylene/Carbon Black/Multiwalled Carbon Nanotube Hybrid Composites

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Conductive filler filled polymer composites deserve interest in wide range of applications. Conductive polymer composites possess the merits of light weight, ease of excellent formability, moldability, and chemical resistance. A composite consisting of conductive filler and an insulating polymer becomes electrically conductive as the filler content exceeds a certain critical value, which is generally attributed to percolation phenomenon. From the practical point of view, a low percolation threshold offers possibility that the composite processability and mechanical properties are less deteriorated. This can be achieved by employing immiscible polymer blends instead of single polymer systems. Carbon black (CB) and Multiwall Carbon Nanotube (MWCNT) filled polymer composites can be used in a variety of industrial applications where high conductivity is an important physical parameter.
The electric behaviour of filled high density polyethylene/carbon black (HDPE/CB, 75/25) composites filled with varying amounts of MWCNT viz., 0.25, 0.50, 0.75, 1.0 and 1.5 by wt% have been investigated. The electric properties such as surface resistivity, volume resistivity, dielectric constant and dissipation factor (tan δ) have been measured with reference to the filler content (wt %) and frequency. Surface resistance and conductivity of these composites depends on weight percentage of MWCNT loading. The thermal behaviour of the composites has been studied by differential scanning calorimeter (DSC).The two phase morphological behaviour is studied using scanning electron microscope (SEM).

[1] C. Zhang, C.-A. Ma, P. Wang and M. Sumita, *Carbon*, **43**, 2544-2553 (2005).
[2] M.O. Lisunova, Y.P. Mamunya, N.I. Lebovka and A.V. Melezhyk, *European Polymer Journal*, **43**, 949-958 (2007).

Influence of Manufacturing on Electrical Performances of Graphite Nanoplatelet Filled Polystyrene

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Manufacturing strategy is important for the appropriate incorporation of filler into a polymeric matrix, and this in particular refers to nanofilers. Direct-graphite nanoplatelets (GNP) were used as filler in polystyrene (PS). The as-received GNP material contained microscopic size agglomerates formed by nanoscopic size graphite nanoplatelets. Refining of the microagglomerates (break-up) and production of graphene layers (exfoliation) desirably needs to take place during manufacturing. Herein, several melt processing methods used to prepare GNP/PS are in focus. The manufacturing methods used include both, melt and solvent routes, and include elongational flow mixing (EFM), high shear energy micro compounding, roll-milling/calendering, and Brabender mixing chamber, as well as sonication and surfactant assisted solvent processing using N-methyl-pyrrolidone (NMP). We analyze particle break-up and exfoliation, and the effects on electrical conductivity and surface smoothness of the composite, both of importance in high-voltage applications. The composite is characterized by melt rheology, Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM) with MeX surface topography software, optical microscopy with image analysis, X-ray Diffraction (XRD), and electrical resistivity measurements.

We find that manufacturing processes influence the material´s morphology and properties in different ways. As could be expected, sonication and surfactant assisted solvent processing yielded both good deagglomeration and production of thin graphene stacks/layers. Elongational flow dispersive mixing, studied here using a recently developed mixer (RMX, Scamex, France), efficiently refines the GNP microagglomerates, and the particle break-up is closely comparable to that in solvent processing. Both the processes yield composites having smoother surfaces compared to the ones from other processing methods. Solvent processing and micro-compounding are more efficient than the other processes in the production of exfoliated thin graphene stacks/ layers. Thin graphene stacks/layers, particularly, provide electrical conductivity, at lower amount of filler content.

The Effect of Solvent on Mechanical and Electrical Properties of Highly Conductive Multiwalled Carbon Nanotube/Silicone Rubber Composites

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Three-roll milling (TRM) process is solvent-free and scalable to mass production. However, it has a difficulty in dealing with high loading of CNTs (carbon nanotubes) as it is not easy for them to be fully wetted through a pre-mixing process, such as a simple stirrer or a planetary mixer. This means that CNTs could be scattered into air during TRM, causing serious health or environmental problems and poor dispersion state. In this situation, a solvent can be introduced to solve above-mentioned problems by lowering viscosity of composites, enhancing the wettability and preventing the particle scattering. The objective of this study is to investigate the effect of the addition of solvent on mechanical and electrical properties of multi-walled carbon nanotube (MWCNT)/silicone rubber composites and to develop the highly conductive composite with the enhance properties. The influence of the solvent was evaluated in terms of viscosity, electrical conductivity, and tensile properties. The rubber composite containing 8 phr MWCNTs was successfully fabricated in the form of a plane heater, whose heating uniformity was observed to be excellent in heating uniformity.

Double-Walled Carbon Nanotube – Copper Nanocomposites with a Very Low Friction Coefficient

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Double-walled carbon nanotubes (DWCNTs) were prepared by CCVD. A copper powder was prepared by the oxalate decomposition and H2 reduction route. DWCNT-Cu composite powders (carbon content Cn = 0.5, 1, 2, 3, 4, 5, 10 and 16 vol.%) were prepared by a rapid route without oxidative acidic treatment or ball-milling to avoid damaging the DWCNTs. They were consolidated by spark plasma sintering (700°C, 100 MPa).

The specimens were studied using specific surface area measurements, field-emission-gun scanning electron microscopy (FESEM), scanning white-light interferometry optical microscopy, Vickers microhardness and friction experiments performed using a pin-on-disc reciprocating flat geometry. The dispersion of the DWCNTs in the powder is satisfactory up to C_n = 5 vol.%., leading to sintered specimens with a relative density over ca. 92%.

Wear appears very low and the average friction coefficient against a steel or an alumina ball markedly decreases upon the increase in carbon content up to 5 vol%. This is accompanied by a doubling of the Vickers microhardness and a decrease of the Cu grain size. Maximum Hertzian contact pressure data could indicate that the surface DWCNTs and bundles are deformed and broken, possibly resulting in the formation of a graphitized lubricating tribofilm in the contact.

Abstract 484
CNT-NET

Micro-scale 'Air-gap' Circuitry with Conducting Carbon Nanotube - Copper Composite

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Single wall carbon nanotubes have long been envisaged as ideal materials for microelectronic applications. The interest in carbon nanotubes arises from a combination of their exceptional thermal conductivity and ability to withstand high current densities. However, their poor electrical conductivity and inability to precisely manipulate and process them have been major obstacles in realising CNT based microelectronic devices. Here, we achieved the synthesis of CNT-copper composite (conductivity, $\sigma=10^5$ Scm^{-1}) showing 1000 times higher conductivity than pristine CNT ($\sigma=10^1$-10^2 Scm^{-1}). The composite, synthesised from super-growth CNT [1], through a novel organic phase electrodeposition route also lends itself to standard lithographic processes and is therefore integrate-able into a variety of micro-structures and microelectronic circuits. A combination of X-ray diffraction, thermo- gravimetric and specific surface area analysis reveal high, uniform filling of Cu in the aligned CNT matrix explaining the high conductivity observed for the composite.

To explore the possibility of microelectronic applications of CNT-Cu composite, micro-scale, three-dimensional engineering of CNT-Cu composite has been demonstrated. Relying on the mechanical stability of CNT beams, spatially suspended CNT-Cu lines have been fabricated. As the next step, we have achieved fabricating of micro-scale, multi-tier circuits, with CNT-Cu lines exhibiting complete electrical isolation from each other. The adjacent CNT-Cu lines in a given tier and across multiple tiers are engineered without any dielectric medium bridging them. The absence of a dielectric material between the CNT-Cu lines in these circuits renders them as 'air-gap' circuits. This realization of dielectric-less, air-gap circuits paves the way for fabrication of faster and efficient microelectronic devices.

Further, the CNT-Cu composite shows lower (2.2 times) coefficient of thermal expansion compared to pure copper. The conductivity of CNT-Cu composite also exhibits a higher degree of temperature stability compared to pure copper. The combination of high temperature stability and low thermal expansion coefficient, along with micro-level pattern- ability is thought to be very important in reducing thermal failure of CNT-Cu lines thereby paving the way for practical and reliable CNT based microelectronic circuits and devices.

[1] K. Hata, D. N. Futaba, K. Mizuno, T. Namai, M. Yumura, S. Iijima, *Science*, **306**, 1362-1365 (2004).

Polymer/Carbon Nanotube Composites for Liquid Sensing: Processing, Properties and Physical Model

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Electrically conductive polymer composites (CPC) based on carbon nanotubes (CNTs) are suitable candidates for sensing applications. Especially the detection of liquids is of great interest. The sensory capacity of CPC is based on the interaction between polymer matrix and the liquid in terms of a swelling kinetic resulting in changes of the electrically conductive filler network. The decreasing network density results in a electrical resistance increase, which is commonly expressed as relative resistance change R_{rel} considering the initial resistance R_i and the resistance R(t) at time t.

For this study, polycarbonate (PC)/multi-walled carbon nanotube (MWNT) composites were melt-mixed based on the masterbatch technique using a co-rotating twin-screw extruder. A screw profile having a length to diameter ration of 48 containing mixing elements, a rotation speed of 500min^{-1}, a throughput of 5kg/h, and a temperature of 260 °C were used for both mixing steps to produce composites containing 0.125 to 4.0 wt.% MWNT. These processing conditions were used according to a previous optimisation study [1].

Composites were compression-moulded to plates and U-shaped samples were punched out. These samples were immersed in solvents (methylene dichloride, tetrahydrofuran, acetone, and ethyl acetate) in order to investigate the time depending relative resistance change. As these four solvents exhibit differences in the diffusion kinetics controlling their penetration into the PC matrix, different R_{rel} curves were observed.

Light microscopy revealed that the diffusion of solvents can be monitored in terms of a pronounced diffusion front. This diffusion front separates a swollen skin from a dry core having the initial resistivity of the composite. Based on this observed skin-core morphology, a physical model based on the parallel connection of two time depending resistances was designed using several parameters like, diffusion parameters, composite characteristics, and geometrical values. Simulated R_{rel} curves based on the physical model were compared to experimental data, which were obtained on the CPC and very good agreements were observed. Using this model the influence of CNT content and kind of solvent could be described exactly [2].

Finally, the selectivity of the presented CPC will be discussed in context with the Hansen Solubility concept. The interaction between CPC and solvents was found to depend on the solvent's molecule size and solubility similarity, which can be expressed using the distance in Hansen Space, R_a. Using this method, a solvent mapping was performed, enabling the interaction prediction of the CPC for any specific solvent [3].

[1] T.Villmow, B. Kretzschmar, and P. Pötschke, *Composites Science and Technology*, **70**, 2045-2055, (2010).

[2] T. Villmow, S. Pegel, P.Pötschke, and G. Heinrich, *Polymer*,10.1016/j.polymer.2011.03.029, (2011).
[3] T. Villmow, A. John, P. Pötschke, and G. Heinrich, *to be submitted*, (2011).

Abstract 25
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Photoelectric, Nonlinear optical (NLO) and Photorefractive (PR) Properties of CNT/Polymer Composites

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Photoelectric and photorefractive (PR) properties at 1064 nm and 1550 nm, nonlinear optical (NLO) and electron-transport behaviour was investigated for high T_g polymers (polyvinylcarbazole, PVK, and aromatic polyimide, API) containing carbon nanotubes (CNT). It was found that a composite containing 0.26 wt.% single-wall carbon nanotubes (SWNT) shows very high third-order susceptibility ($1.85 \pm 0.35 \times 10^{-10}$ esu). [1] This enables the use of stable unplasticized polymers in photorefractive cells. Consequently, CNT polymer composites possess the ability towards stable photoelectric and photorefractive performance in near IR region, at above mentioned wavelengths.

[1] A.V. Vannikov, A.D. Grishina, R.W. Rychwalski, *Carbon*, **49**, 311-319 (2011)

A Novel Approach For Nanocarbon Composite Preparation

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Carbon nanotubes (CNTs) and nanofibers (CNFs) are promising components for the next generation high performance structural and multi-functional composite materials. One of the largest obstacles to create strong, electrically or thermally conductive CNT/CNF composites is the difficulty of getting a good dispersion of the carbon nanomaterials in a matrix. Typically, time-consuming steps of the carbon nanomaterial purification and functionalization are required. We propose a new approach to grow CNTs/CNFs directly on the surface of matrix and matrix precursor particles. As the precursor matrix we utilized cement, the most important construction material, and copper powder. Carbon nanofibers were successfully grown on the surface of cement particles and copper powder without additional catalyst. We synthesised novel hybrid materials, wherein carbon nanomaterials are attached to the matrix particles.Investigations of the physical properties of the cement hardened paste made of this material revealed as high as 2 times increase in the compressive strength and 40 times increase in the electrical conductivity after 28 days curing in water. The new synthesized material has been proven to increase 3 times the compressive strength of mortar. The composites based on copper and CNFs prepared by vacuum hot pressing showed the increase in hardness from 35 to 60 kg/mm^2 almost retaining pure copper electrical properties.

Nasibulin et al., *New Journal of Physics*, **11**, 023013 (2009).
Nasibulina et al., *Carbon*, **48**, 4556-4577 (2010).

Tailoring the Electrical Properties of Carbon Nanotube–Polymer Composites

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Advances in functionality and reliability of nanocomposite materials require careful formulation of processing methods to ultimately realize the desired properties. An extensive study of how the variation in fabrication process would affect the mechanism of conductivity and thus the final electrical properties of the carbon nanotube–polymer composite is presented. Some of the most widely implemented procedures are addressed, such as ultrasonication, melt shear mixing, and addition of surfactants. It is hoped that this study could provide a systematic guide to selecting and designing the downstream processing of carbon nanocomposites. Finally, this guide is used to demonstrate the fabrication and performance of a stretchable (pliable) conductor that can reversibly undergo uniaxial strain of over 100%, and other key applications are discussed.

Y. Y. Huang and E. M. Terentjev, *Adv. Funct. Mater.*, **20**, 4062 (2010)

Microwave Assisted Surface Modification of MWCNT:In/SnO$_2$ Composite Prepared by Soft Chemistry Route.

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Nanocrystalline tin oxide thin films doped with indium are coated on multiwall carbon nanotubes by simple soft chemical route. The as prepared composite and the composite with microwave treated were put under various spectroscopic characterisations for the complete surface modification of MWCNT. The structural studies reveals that the in doped SnO$_2$ formed the tetragonal structure on CNTs surface with (11 1), (1 0 1) and (2 1 1) strongest peak orientations. The calculated lattice constant (a=4.7, c=3.1) shows that there is no strain induced defect between the CNTs surface and coated layer. The FE-SEM images shows that the modified surface of CNTs and is confirm by the increase in diameter of the CNTs from its original size. The Photoluminescence analysis shows the blue and green emission band with the excitation wavelength of 350 nm. The hybridization nature between the CNTs and coated layer was observed by Laser Raman spectroscopic studies.

[1]. Q. Kuang, S.-F. Li, Z.-X. Xie, S.-C. Lin, X.-H. Zhang, S.-Y. Xie, R.-B. Hung, L.-S. Zheng, *Carbon*, **44**, 1166-1172 (2006).
[2]. J. Gong, Q. Chen, *NSTI-Nanotech*, **3**, 232-235 (2004)

Abstract 227
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Controlled Growth of Vertically Aligned Carbon Nanotube Arrays and Their Application in Photovoltaic Cells

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Catalyst aggregation affects the growth of vertically aligned carbon nanotube (CNT) arrays, in particular in the aspects of structures, waviness, entanglement, lengths, and areal density. CNT arrays varying from multi-walled to single-walled and from tangled to well-aligned are synthesized by tuning the catalyst aggregation. It is shown that the catalyst aggregation is closely associated with the Fe thickness, buffer layer, and annealing environment. Well aligned CNT arrays are synthesized by tuning the catalyst aggregation and CNT sheets can be drawn continuously, which are further used as templates to deposit TiO_2 composite films by CVD of titanium isopropoxide. Such composite film exhibits a good interface between CNT and TiO_2 as Ti-C and C-O bonds are observed. The CNT@TiO_2 composite film is conducting and can be directly used as the photoanode in photovoltaic cells with an incident photon-to-current conversion efficiency up to 32%. Moreover, the CNT@TiO_2 photoanode is flexible and the photocurrent can be maintained by 80% after bending to a radius of 8 mm for 100 times. Our results reveal that the well-bonded interface between CNTs and TiO_2 promotes the photoinduced electrons transferring smoothly from TiO_2 to CNTs and therefore helps prohibit the charge recombination.

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Influence Of Ball Milling On The Properties Of Multiwalled Carbon Nanotubes And Their Polycarbonate Composites

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Dry grinding of carbon nanotubes (CNTs) using ball mills is a common way to produce tailored CNTs material for composite applications. In order to assess the influence of the ball milling procedure on the properties of Nanocyl™ NC7000 nanotube material, the length distribution before and after milling for 5 and 10 hours was quantified using transmission electron microscopy (TEM).In addition, the agglomerate size of the nanotubes powders, the dispersability in aqueous surfactant dispersions using centrifugal separation analysis, and the nanotubes structure using RAMAN and XPS were investigated. With increasing ball milling time a significant nanotube shortening, a decrease of agglomerate size, and an increase of packing density took place and a worse dispersability was observed. In the XPS study a higher [O]:[C] ratio was found for the ball milled nanotubes indicating the formation of oxygen groups on the nanotubes surface. It was found that the D/G ratio using RAMAN investigations was not significantly changed. In melt mixed CNT polycarbonate (PC) composites, the electrical properties, the nanotubes length distribution after processing, the nanodispersion of nanotubes and the macrodispersion of residual CNT agglomerates using TEM or light microscopy were studied. The changed properties of the ball milled nanotubes are reflected in the properties of the PC composites. The electrical behaviour of the melt mixed PC composites indicated that the electrical percolation threshold increased slightly with ball milling treatment time of the nanotubes. The formation of a conductive network in the composites depends on the properties of the nanotubes, e.g. aspect ratio and dispersability, and on the processing conditions (here masterbatch dilution). The investigation of the CNT powders showed that with ball milling treatment time the nanotubes length, and thus the aspect ratio, as well as the dispersability was decreased. For the CNTs extracted from the PC composites an additional decrease of the nanotubes length to 31-66% was found caused by the melt mixing process. However, even after melt processing NC7000 had higher nanotubes lengths than NC7000-5h and NC7000- 10h. These findings are an explanation for the slightly lower electrical percolation threshold of the melt mixed composites with NC7000 in comparison to the ball milled nanotubes.

Localisation Of Carbon Nanotubes In Polyamide Blends With Non-Reactive And Reactive Rubber

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Blending of two immiscible polymer matrices can be an effective way to combine favourable properties of both blend partners. The additional incorporation of multiwalled carbon nanotubes (MWCNTs) in such thermoplastic blends may further enhance the blend properties and especially generate electrical conductivity. In the present study, 20 wt% of non-reactive rubber AFFINITYTM EG8200G and maleic anhydride functionalized rubber EXXELOR VA1803 were melt blended with polyamide 6 (PA6, ULTRAMID® B27E).It was observed that the blend morphology was finer in case of the reactive rubber. When using non-reactive rubber big rubber domains were found in the continuous polyamide phase. Furthermore, 3 wt% MWCNTs (NC7000, Nanocyl S.A.) were added to the blend using different incorporation strategies:

- The MWCNTs were added in the molten blend.
- The MWCNTs and both polymers were dry premixed and melt mixed together.
- A PA6-MWCNT-masterbatch was diluted with polyamide and rubber.
- A rubber-MWCNT-masterbatch was diluted with PA6.

Interestingly, the different strategies resulted in case of the reactive rubber in different localisation behaviours of the MWCNTs. Next to differences in the wettability of MWCNTs by the two polymers, a chemical reaction or adsorption between the maleic anhydride groups of the functionalized rubber and functional groups of the MWCNTs can influence the localisation of MWCNTs. Even if these nanotubes are as produced non-functionalised tubes, in XPS measurements small amounts of oxygen could be detected concluding that hydroxyl- or carboxyl-groups are located on the surface of NC7000. It was found that in blends containing non-reactive rubber the MWCNTs were always localised selectively in the polyamide phase as shown by transmission electron microscopy (TEM) images. This seems to be the thermodynamically preferred phase. Independent of the mixing strategy the blends were electrically conductive. If the reactive rubber was used for the preparation of the blends, the incorporation strategy influenced significantly the localisation of the nanotubes and the electrical volume conductivity of the blend. Only if a polyamide-MWCNT-masterbatch was used for the blend manufacturing, a conductive blend with electrical volume conductivity of 3E-7 S/cm could be obtained. In all other cases the blends were non-conductive. It may be assumed that nanotubes with functional groups first coming in contact with the reactive rubber, either by incorporating them in a rubber-masterbatch or the molten blend or as the rubber melts first during mixing all components together, may be trapped in that phase. TEM images indicate that the localisation of MWCNTs was not selectively; the MWCNTs were localized in both blend phases. These findings demonstrate the significant influence of maleic anhydride groups of the rubber

component on the localisation of MWCNTs in the different blend phases which results in different values of electrical volume conductivity of the blends.

Freestanding, robust CNT papers and their composites for Supercapacitors

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Supercapacitors (SCs), also named electrochemical capacitors, have been receiving much attention due to their high power capability, modest energy density, excellent reversibility and long cycle life. Withtheincreasingdemandforpowersystemsdeliveringenergyinthehigh-powerform, SCs are widely used in communications, military equipments, home appliances, transportation, and so on. The performance of electrode materials plays an important role in SCs, though various factors are involved. Recently, light and flexible electronic products have pioneered the fashion trend in market, which has put forward new requirements for electrode materials. Here, light, freestanding and robust carbon nanotube papers, also known as buckypaper, are presented as high-performance electrode materials for SCs. Firstly, large size freestanding buckypapers were prepared by a vacuum filtration method, whose porosity and microstructure could be fine tuned by the CNTs' structure, such as aspect ratio, diameter and their assembly. Then, the Faradaic active material (such as MnO_2 or PANi) was uniformly coated on the surface of CNT sketch in the buckypaper by an electro deposition strategy. This buckypaper composite combined the high capacitance with excellent electro conductivity together based on the CNT skeleton, and showed good electrochemical capacitive performances. Additionally, the flexible and electro conductive characteristic enable the buckypaper composite to be directly used as both electrode material and collector, constructing a structure/function integrating composite. Consequently, a flexible all-solid asymmetric SC was assembled as a demo, using the buckypaper composite electrode and colloid electrolyte. The presented research work is expected to propel the CNT macro materials toward possible applications in energy storage.

Twin-Screw Extrusion of PP-MWCNT composites: Influence of feeding position

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Different types of commercial multiwalled carbon nanotubes (MWCNT) vary in their characteristics such as e.g. length, diameter, purity, agglomerate density and strength, and surface functionalization. Based on these characteristics, it appears to be necessary to perform individual optimization of extrusion melt mixing conditions for different nanotube materials in order to get excellent states of MWCNT dispersion in the polymer matrix. This the adaption of processing conditions such as screw configuration, mixing speed, temperature profile, throughput, and the way of filler feeding to the respective type of MWCNT. In our investigations, the influence of feeding conditions of MWCNT, namely Baytubes® C150P and Nanocyl^{TM} NC7000, into polypropylene (PP) wasinvestigated with respect to achieve high electrical conductivity and suitable nanotube dispersion. Both MWCNT types were fed at selected concentrations either in the hopper of the twin-screw extruder or using a side feeder at otherwise constant extrusion conditions (rotation speed, throughput, temperature profile) using a Berstorff ZE25 twin-screw extruder. Afterwards, injection moulding was performed under constant conditions. The results indicate that Baytubes® C150P should be preferably added into the hopper as electrical resistivity measured on compression and injection moulded samples is lower, elastic modulus, yield strength and impact strength are higher, and dispersion as assessed by light microscopy is better as compared to side feeding. On the other hand, for Nanocyl^{TM} NC7000 addition the use of side feeding is preferable as it leads to better electrical resistivity, dispersion, and mechanical properties.

Dispersability Of MWNTs In Polymer Solutions And Its Effect On The Electrical Conductivity Of Thin Films

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For the development of thin films of electrical conductive CNT-polymer nanocomposites with high transparency a sufficient quality of CNT dispersion in the polymer solution is essential. In our study we investigate the dispersion of commercial multiwalled carbon nanotubes (MWNTs, Nanocyl™ NC7000) in different polymer solutions by variation of the polymer concentration, the CNT content and the ultrasonic treatment time. The sedimentation behaviour of the dispersions was studied under centrifugal forces using a separation analyser (CSA, LUMiSizer® 6100-29). The space and time resolved extinction profiles as a measure of the stability of the dispersion and the particle size distribution were evaluated. A related study on different commercially available CNTs in aqueous surfactant dispersions is reported by Krause et al. [1]. MWNTs were dispersed in polycarbonate-chloroform solutions with the polymer concentration in the chloroform varying between 0.25 and 1 wt.%. The MWNT content was fixed to 1 wt.% referred to the added polymer, i.e. the CNT amount in the solution was increasing from 0.037 g/l to 0.148 g/l with increasing polymer concentration. Ultrasonic treatment was applied for 0.5, 1, 2, 5 and 10 min to disperse the nanotubes in the polymer solution. As reference, equal MWNT amounts were dispersed in pure chloroform under the same conditions. During the CSA measurements, the initial slope of the integral transmission as a function of centrifugation time is a measure of the sedimentation rate of the CNTs. In polymer solutions the sedimentation rate was found to be significantly lower than in pure chloroform, indicating a higher stability of the MWNT dispersions caused by the addition of the polymer. As expected increasing ultrasonic treatment time leads to a distinct decrease of the sedimentation rate and to smaller particle sizes of remaining CNT agglomerates in the dispersions. In polymer solutions with a CNT concentration of 0.037 g/l and 0.074 g/l the mean particle size (d_{50}) after 10 min ultrasonic treatment was much lower and the size distribution narrowed as compared to a CNT concentration of about 0.148 g/l, indicating the existence of a critical CNT concentration for sufficient dispersability. In pure chloroform the CNTs show a very broad particle size distribution for all CNT concentrations and only a minor influence of the ultrasonic treatment on the particle sizes. Electrical conductivity measurements on PC-CNT-solution cast films indicate distinct influences first of the polymer concentration in the solution and second of the ultrasonic treatment time on the surface resistivity. With only 1 wt.% MWNTs the surface resistivity could be reduced to about 10^4 Ω/sq compared to the pure PC having a resistivity of 10^{16} Ω/sq. Further investigations concentrated on the dispersability of CNTs in other polymer solutions like polymethylmethacrylate-chloroform-solutions and polyvinylidenfluoride- dimethylformamide-solutions, followed by a defined adjustment of the CNT concentration in the solutions for achieving optimum dispersability and high electrical conductivity in composite films.

[1] B. Krause, M. Mende, P. Pötschke, G. Petzold, *Carbon*, **48**, 2746-2754, (2010).

The Role Of Matrix Viscosity On MWCNT Dispersion And Electrical Properties In Thermoplastic Composites

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Melt mixing is a highly convenient method to produce thermoplastic composites containing multiwalled carbon nanotubes (MWCNTs). In order to benefit from the outstanding intrinsic properties of carbon nanotubes, a high degree of dispersion within the thermoplastic matrix is needed. The mechanisms of MWCNT dispersion in thermoplastic matrices and the correlation to the electrical percolation behaviour are still not well understood. The molecular weight of the matrix polymer and, thus, its melt viscosity strongly influence the dispersion of primary nanotube agglomerates, as it was recently shown for polycarbonate based composites [1]. The aim of this investigation is to gain deeper understanding and to find general tendencies concerning the influence of melt viscosity on MWCNT dispersion and electrical properties of MWCNT/polymer composites where different classes of thermoplastic polymers (polar and non polar, amorphous and crystalline) are concerned. Five different polymers, low density polyethylene (PE), polyetheretherketone (PEEK), polybutylene terephthalate (PBT), polycarbonate (PC) and polyamide 12 (PA12), each with three different melt viscosity levels (low, medium and high viscosity), were melt mixed with Baytubes® C150P using a DACA microcompounder. As constant mixing temperatures were used within the same polymer type, huge differences in melt viscosity resulting in applied shear stress during melt mixing were obtained. With increasing melt viscosity, better dispersion of primary MWCNT agglomerates was visualized using light microscopy. For the electrical percolation thresholds, a significant increase with melt viscosity was obtained for all five polymers. For the formation of a conductive network, not only an effective MWCNT dispersion and distribution are needed, but also electrical contacts between the individualized nanotubes have to be established. The formation of such networks consisting of single MWCNTs and secondary agglomerates was shown using TEM investigation especially for samples with low viscous matrices. In the composites based on high viscous matrices the well dispersed MWCNTs did not form such networks at low contents. The mobility of the nanotubes to form secondary agglomerates is obviously reduced at higher melt viscosity. Another aspect influencing the electrical percolation threshold is the shortening of the nanotubes during the melt mixing process. As an example, PC based composites were used to quantify this effect by dissolving the processed nanotubes from the PC [2]. A significant decrease of the aspect ratio after melt mixing was found. Despite better dispersion, the shortening was more pronounced in the high viscous polycarbonate matrix, explaining the higher percolation thresholds. In summary, at higher matrix melt viscosity, better MWCNT dispersion, more pronounced nanotube shortening, and higher electrical percolation thresholds were found for all investigated polymers.

[1] G. R. Kasaliwal, A. Göldel, P. Pötschke, G. Heinrich, Polymer, **52**, 1027-1036 (2011).

[2] B. Krause, R. Boldt, P. Pötschke, Carbon, **49**, 1243-1247 (2011).

Raman Spectroscopy Studies Of Graphene Nanocomposites

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Graphene is known as the strongest materials human being have found which was first isolated by the micromechenical cleavage from graphite in 2004 by the newest Manchester Nobel Prize winners Professor Geim and Novoselov. Since the excellent performance mechanical properties, graphene is an ideal candidate for a reinforcement in composites. It has been demonstrated in this study that Raman spectroscopy is a powerful technique to monitor the polymer-graphene interfacial properties that stress transfer takes place from the polymer matrix to monolayer graphene, proving graphene acts as a reinforcing phase. Shear-lag theory has been modelled in the analysing of reinforcement mechanism. In addition, below the interface failure strain, according to the mappling line alone the strain axis, the stress is distributed uniformly in the centre of the monolayer and falls to a low level at the edges. However, above the failure strain (0.6%), it becomes highly non uniform. The change in the strain distributions has been shown to be due to a fragmentation process due to the development of cracks, most likely in the polymer coating layers, with the graphene remaining intact. The strain distributions in the graphene between the cracks are approximately triangular in shape, and the interfacial shear stress in the fragments is only about 0.25 MPa, which is an order of magnitude lower than the interfacial shear stress before fragmentation. This relatively poor level of adhesion between the graphene and polymer layers has important implications for the use of graphene in nanocomposites, and methods of strengthening the graphene-polymer interface are discussed.

[1] L. Gong, I.A. Kinloch, R.J. Young, I. Riaz, R. Jalil, K.S. Novoselov., Interfacial Stress Transfer in a Graphene Monolayer Nanocomposite, *Advanced Materials,* **22**(24), 2694-2697 (2010).
[2] R.J. Young, L. Gong, I.A. Kinloch, I. Riaz, R. Jalil, K.S. Novoselov., Strain Mapping in a Graphene Monolayer Nanocomposite, *ACS Nano*, published online: doi/abs/10.1021/nn2002079.

Abstract 307
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Development of Joining Method for Aluminum and CFRTP by CNT Reinforced Nano Anchors

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Recently, application of CFRP is expanding from sports equipment to aerospace products. Especially, carbon fiber reinforced thermo plastic (CFRTP) is a remarkable material because of its possibility to reduce production time and cost. And necessity to assemble CFRP parts and metallic parts is increasing to redeem disadvantages of CFRP about heat resistance, wear resistance and workability with metallic parts. But its adhesion performance is less than conventional CFRP. Therefore low cost, high cycle joining and high strength joining method is necessary. In this study, we proposed a novel joining method for CFRTP and aluminum. The process of novel joining method we proposed is as following; first, alumite film is prepared on an aluminum specimen, and a piece of CNT reinforced thermoplastic film is fabricated. Then the composite film is sandwiched with a CFRTP specimen and the aluminum specimen. Finally, these stacked materials are welded by a heating tool. The alumite film is prepared to cast the CNT reinforced film into the nano scale holes of alumite film. We prospected the casted CNT reinforced film works like anchors to create strong mechanical joints. Moreover, CNTs would increase the toughness of small anchors. In the experiment, we applied ultrasonic vibrations in addition to the normal electrical heater as the heat source for the heating tool. Difference of the casting quality to create anchors, density of CNTs, orientation of CNTs and joint strength due to the size of nano holes, the diameter and length of CNTs and the effect of ultrasonic assist were investigated.

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Polyurethane-Carbon Nanotube Composite As Anticorrosion Coating Materials

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Polyurethane-carbon nanotube (PU-CNTs) composite coating materials were developed. The coating materials were applied on mild steel panels. The effect of CNTs on corrosion properties, mechanical properties as well as on morphology was investigated. The CNTs were prepared by floating Catalyst Chemical Vapor Deposition (FC-CVD) method using toluene as a source of hydrocarbon, and hydrogen as reacting gas at a flow of 300 ml/min, and temperature at 900°C. Corrosion tests were performed in aqueous solution (3.5 wt%) of NaCl using impedance spectroscopy technique as electrochemical analysis technique. The impedance was very high close to 10^7 ohm.cm^2 after 30 min immersion in 3.5 wt % NaCl as compared to 10^5 ohm.cm^2 for Blank PU coating materials. These results showed improvement in corrosion resistance. Mechanical properties such as impact resistance and adhesion were also improved after incorporation of CNTs. Higher impact resistance test was observed for PU-CNT composite as compared to pure PU composite materials. Higher adhesion value was observed in cross-cut tap test for PU-CNT composite as compared to pure composite materials. The effect on morphological properties is also will be discussed.

Hybrid CNT/Silver Flakes - Epoxy Adhesives for Space Applications

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The domain of electrically and thermally conductive adhesives for the assembly of electronic devices (from digital to microwave applications) on various substrates (metallic packages, multichip modules, printed circuit boards) very likely makes use of silver particles as conductive filler. They are mostly shaped as micrometric flakes. Two main drawbacks however exist: very high filler loadings are needed to obtain sufficiently high electrical and thermal conductivities and, because of these high loadings, the mechanical properties of the adhesives are fairly poor. When compared to silver flakes, carbon nanotubes (CNTs) are known to have very low percolation thresholds and intrinsic longitudinal electrical and thermal conductivities comparable to those of metals. Thus, CNTs could be useful as filler because lower loadings would be required. In recent years, patents, commercial or scientific surveys have shown the development of high performances thermally and electrically conductive adhesives using a combination of micro- and nanoparticles. Double-walled carbon nanotubes (DWCNTs) or multi-walled carbon nanotubes (MWCNTs) have been dispersed with micrometric silver flakes in an epoxy matrix. Thermal and electrical conductivities of resulting composites have been measured. An electrical hybrid percolation has been observed as well as conductivity levels up to 10^3 S/m. Scanning and transmission electron microscope provided images of the microstructure. Standard reliability testing (thermal shocks) for space applications on silver flakes filled commercial adhesives and hybrid CNTs + silver flakes showed significantly higher shear strength of hybrid composites. In this work, hybrid CNTs + silver flakes composites showed a good dispersion, high electrical conductivity and complied with reliability tests for space applications.

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Carbon Nanotube-Alumina Nanocomposites: Preparation, Densification and Properties

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Alumina is one of the most commonly used ceramics for mechanical or thermomechanical applications. Over the years there has been much effort to increase its toughness and fracture strength through the incorporation of carbon nanotubes (CNTs). A recent study [1] reporting the doubling of the toughness of double-walled CNT - MgO composites, compare to MgO, pointed out the need to obtain a unique microstructure, including a low content of long double-walled CNT and nanometric matrix grains. One of the main difficulties regarding the preparation of the nanocomposites is to obtain a powder with a homogenous dispersion of the CNTs. This work aims at investigating several preparation techniques and also at comparing the influence of CNTs with different number of walls. In the first part of this study, two commercial alumina powders (γ-Al_2O_3, average grain size 10 nm and α-Al_2O_3, average grain size 100 nm) were impregnated with small quantities of iron and molybdenum precursors (nFe/nAl = 0.005, 0.01, 0.02 and nFe/nMo = 4 or 5) by the method of the emergent liquid. The impregnated-powders were calcined in air and submitted to a Catalytic Chemical Vapor Deposition (CCVD) treatment in order to in-situ form the CNTs (mainly single- or double-walled). The CCVD parameters (Ar/H_2-C_2H_4 or H_2-CH_4, maximum temperature) have been studied. In the second part, nanocomposite powders were prepared by wet-mixing pre-existing CNT and α- Al_2O_3 under ultrasonic agitation, leading to stable suspensions which were freeze- dryed. Double-walled CNTs (lab-made) and commercial multi-walled CNTs (8 and 20 walls in average) were used. In the third part, selected powders were submitted to Spark Plasma Sintering (1350°C, 150 MPa, 6 min) or Hot-Pressing (1450°C, 43 MPa, 15 min) to obtain dense nanocomposites, which were characterized by XRD, FESEM and Raman spectroscopy. The electrical and mechanical properties will be presented and discussed in correlation with the CNT characteristics and the microstructure.

[1] A. Peigney, F. Legorreta Garcia, C. Estournès, A. Weibel, Ch. Laurent, Carbon, **48**, 1952-1960 (2010).

Influence Of Thermo-Rheological History On Filler Network And Properties Of Polymer Composites: Carbon black, Carbon Nanotubes And Combinations

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It is generally accepted, that the morphology of the ‘network’ formed by conductive (nano) fillers determines the resulting electrical and mechanical properties. The ‘superstructure’ formed by carbon nanotubes is known to be strongly dependent on the thermo-rheological history (e.g. transient or steady shear deformation, annealing in the quiescent melt) [1-7]. Similar effects have been found for carbon black (CB) in epoxies and thermosets [8,9]. This paper compares shear induced destruction and build-up of CNT, CB and their combined filler networks in polymer melts. For this purpose combined conductivity and rheological measurements were performed in the composite melts. The composites with polycarbonate as matrix materials containing multi-walled carbon nanotubes (MWCNT) and/or carbon black (CB) were prepared by melt mixing using a micro compounder. Both, MWCNT/CB ratio and total filler concentration were varied. The shear induced formation/destruction of the filler networks formed by MWCNT, CB and their combinations were analysed and discussed in terms of filler agglomeration / de-agglomeration [6,7]. The models developed for CNT agglomeration [7] were extended to CB and the combined CNT/CB networks.

[1] Sandler, J. K. W., Windle A. H., Martin, C. A., Schwarz, M. L., Bauhofer, W., Schulte E. K. Shaffer M. S. P., *Continuous Nanophase and Nanostructured Materials*, **788**, 221-226 (2004).
[2] Alig I., Skipa T., Engel M., Lellinger D., Pegel S., Pötschke, *Physica Status Solidi B*, **244,** 4223-4226 (2007).
[3] Alig I., Skipa T., Engel M., Lellinger D., Pegel S., Pötschke, *Polymer*, **49,** 1902-1909 (2008).
[4] Alig I., Skipa T., Lellinger D., Birdel, M., Meyer H., *Physica Status Solidi B*, **245**, 2264-2267 (2008).
[5] Alig I., Skipa T., Lellinger D., Pegel S., Pötschke, *Polymer*, **49**, 3524-3532, (2008).
[6] T. Skipa, D. Lellinger, M. Saphiannikova, I. Alig, *Physica Status Solidi B*, **246**, 2453–2456 (2009).
[7] T. Skipa, D. Lellinger, M. Saphiannikova, I. Alig, *Polymer*, **51**, 201-210 (2010).
[8] Schueler R. Peterman J., Schulte K. Wentzel H., *Macromolecular Symposia*, **104**, 261-268 (1996).
[9] Schueler R. Peterman J., Schulte K. Wentzel H.P., *Journal of Applied Polymer Science*, **63**, 1741-1746, (1997).

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Epoxy / Nanocarbons composites as Smart materials

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One of the most significant current discussions in nanocarbons is their usage in various sensing devices. It has been promised that carbon nanotubes can be used as strain sensors to evaluate composite interfaces in a non-destructive manner. As well as high- performance nanocoatings based on epoxy resins currently in development for aircraft skins for sensing mechanical damage. The aim of this paper is to predict the level of reinforcement of nanotubes (CNTs) in Epoxy composites from the rate of shift of the G`-Raman bands with strain when the composite is deformed. An excitation frequency of 633 nm (1.96 eV) HeNe laser and a back-scattering geometry were used to collect the Raman spectra. Epoxy composite samples with 0.1 wt% CNT were subjected to deformation using four-point bending tests over a strain up to 0.6%.

Effect of CNT Quality on Properties of Polymer Matrix CNT Composites

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CNT has excellent properties such as high electrical conductivity, thermal conductivity and high Young's modulus and high tensile strength; hence they are used as filler for polymer matrix composite. When CNTs are synthesized by CVD method, the qualities of them are generally not high. So the purpose in this study is to clarify the effect of CNT quality on the properties of polymer based CNT composite and to develop polymer matrix CNT composite which have excellent properties. First, about 600 μm long CNT were synthesized by rf plasma CVD method. Then the CNT were annealed at 1500, 1800 and 2000°C to improve the quality. The quality of CNTs was evaluated by I_D/I_G ratio of Raman spectroscopy. Before annealing, in-house CNT's I_D/I_G ratio was 0.99. Then applying the annealing of 5 minutes at 2000°C the ratio changed to 0.09. Second, CNT/Polycarbonate composite were fabricated using both as synthesized CNTs and annealed CNTs. Then resistivity and tensile strength test of the composite were measured. As a result, the composite with higher quality CNTs showed lower resistivity and one tenth resistivity of the composite with as synthesized CNT. The range of surface resistivity is from 10^2 to 10^3 Ω/sq. Meanwhile, the composite with high quality CNT (annealed CNT) showed lower Young's modulus and tensile strength than the composite with as synthesized CNT. The reason is that the surface of high quality CNT is less active and the adhesion strength between polymer and CNT's surface is weak. A lot of CNTs were pulled out in the fracture of the specimen with annealed CNT. High quality CNT does not always work well for the properties of polymer matrix CNT composite. It is important to apply surface modification technique to improve the mechanical properties of polymer matrix CNT composites.

Polyaniline Nanocomposites With Graphene And Carbon Nanotubes For Bionical Applications

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Bending actuators of polyaniline (PAni) nanocomposites with graphene oxide (GO) were produced by means of interfacial in situ polymerization. HCl 1M and toluene were the aqueous and organic solutions, respectively, and ammonium persulfate was used as oxidant agent. The GO, produced from helical-ribbon type carbon nanofibers, was previously ultrasonicated for its complete exfoliation and dispersion in aqueous solution, before the reaction started. The resulting nanocomposites were dedoped with NaOH for making it soluble in N-methyl-pyrrolidone (NMP). After producing films of these nanocomposites were subsequently redoped with HCl 1 M for its conversion in a conductive structure. For comparison purposes, PAni nanocomposites with multiwall carbon nanotubes (MWCNT), nitrogen doped multiwall carbon nanotube (CN_x), and carbon nanofibers (CNF) were also produced. Nanocomposites were produced at 1.1 and 3.3 wt-% of carbon nanofiller.

The chemical structural analysis of nanocomposites was carried out by means of Raman spectroscopy. The dispersion was monitored by the superficial texture of films and by transmission electronic microscopy (TEM). The electrical resistivity was measured through the four points probe method. The bending actuation was measured in an electrochemical cell with HCl 1 M as electrolyte. The actuators immersed in electrolyte were used alternately as electrode work and contraelectrode with voltages of 1.5, 3 and 5 V, where bending, speed response, and work cycles were measured.

The nanocomposites that had the better charge dispersion were (in descending order): PAni-CNF, PAni- GO, PAni-MWCNT and PAni-CN_x. The highest electrical conductivity of 8 S/cm occurred in PAni-GO composites that showed a synergy between PAni and GO, both of them showed lower electrical conductivities of 4 S/cm and 10^{-3} S/cm, respectively. It is very possible that GO doped PAni polymeric chains as Cl^- anion does. The rest of the charges did not improve significantly the pure PAni electrical conductivity. In actuation response, the better actuators were PAni-MWCNT and PAni-GO which worked at a relatively low time response with a voltage of 3 V, unlike the others composites and pure PAni that needed 5 V; and the bending of these actuators was higher than the rest. Therefore, the composites of PAni with MWCNT and GO resulted more adequate for the development of actuators and artificial muscles.

Electrical Resistivity of Nano-graphite Reinforced High density polyethylene/Carbon Black Nanocomposites

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Electrically conductive composites, including polymers filled with conductive particles, display a broad spectrum of properties [1]. One of the most attractive features of conductive polymer composites is the positive temperature coefficient (PTC) effect, which indicates a sharp increase in their resistivity near their melting region. These PTC effects are sometimes followed by a negative temperature coefficient (NTC) effect, namely, a decrease in the resistivity. PTC composite materials have a wide range of industrial applications and can be used as self-regulating heaters, current limiters, over-current protectors, microswitches, sensors, etc., with the advantages of excellent formability, moldability, light weight, and flexibility. Thus, the ideal performance characteristics of a PTC composite material include a low room temperature resistivity, high PTC intensity, low NTC intensity, with high reproducibility, a quick response rate, low cost, together with a low conductive filler content [2,3]. In this paper, nano-graphite (NG) and carbon black (CB) filled high density polyethylene (HDPE) hybrid composites were fabricated by melt mixing method. The effects of CB and NG contents at room temperature resistivity and positive temperature coefficient (PTC) behavior of the nanocomposites were studied. As NG content increased, a significant reduction in room temperature resistivity of the composites was observed. The incorporation of small amount of NG content into HDPE/CB composites significantly improves the PTC intensity and repeatability of the hybrid nanocomposites. The maximal PTC effect, whose intensity was about six orders of magnitude, was presented in the HDPE/CB/ NG (80/20/0.25) nanocomposite with a relatively low room temperature resistivity. This is due to incorporation of NG, minimizes the migration of the conducting particles and the deformation of shape of the PTC material.

[1] Z.M. Dang, C.W. Nan, D. Xie, Y.H. Zhang, S.C. Tjong, *Appl. Phys. Lett.*, **85**, 97 (2004).
[2] J.H. Lee, S.K. Kim, N.H. Kim, *Scripta Materialia,* **55**, 1119–22 (2006).
[3] H. Bar, M. Narkis, G. Boiteux, *Polymer Composites*, **12**, (2005).

Ultra-broadband Pulse Generation In Fiber Lasers With Double Wall Carbon Nanotube Saturable Absorbers

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Mode-locked and Q-switched lasers can generate short pulses using saturable absorbers [1]. Currently, the dominant technology is based on semiconductor saturable absorber mirrors (SESAMs). However, narrow tuning range, complex fabrication and packaging limit their application [2]. Nanotubes and graphene offer simpler and cost-effective alternatives [1,3-5]. Broadband operation can be achieved by using a distribution of tube diameters [1,6], or by using graphene [1,3-5,7,8], due to the gapless linear dispersion of Dirac electrons [5,9]. Here, we produce Double Wall Nanotube (DWNT)-polymer composites to be used as saturable absorbers for pulse generation in Yb-, Er- and Tm-doped fiber lasers. We use tubes produced by Catalytic Chemical Vapour Deposition (CCVD) of methane [10], with >90% DWNTs, having ~1.1 nm inner and ~1.8 nm outer diameters, as determined by Raman and High-resolution transmission electron microscopy. The DWNTs are dispersed in water in presence of surfactants by ultrasonication, producing homogeneous and stable dispersions. After ultracentrifugation, the top fraction is decanted and mixed with a polymer, to give a~50μm DWNT-polymer composite. A $2mm^2$ piece of this composite is then sandwiched between a fiber pigtailed FC/PC connector and combined with Yb-, Er- and Tm- doped fibers. We get mode-locked pulses at 1066, 1559 and 1883 nm with 0.284, 6.5 and 3.2 nm spectral width and pulse duration of 4.85, 532 and 1.6 ps. In addition, a Q-switched laser generating 1μs and 60 nJ pulses at 1890 nm is also demonstrated.

[1] T. Hasan et al., *Adv. Mater.*, **21**, 3874 (2009)
[2] U. Keller, *Nature* **424**, 831 (2003)
[3] Z. Sun et al., *ACS Nano*, **4**, 803 (2010)
[4] Z. Sun et al., *Nano Res.*, **3**, 653 (2010)
[5] F. Bonaccorso et al. *Nat Photon.*, **4**, 611 (2010).
[6] F. Wang et al., *Nat. Nanotech.*, **3**, 738 (2008)
[7] T. Hasan et al., *Physica Status Solidi (b)*, **247**, 2953 (2010).
[8] D. Popa et al., *App. Phys. Lett.*, **97**, 203106 (2010).
[9] A. K. Geim, and K. S. Novoselov, *Nat. Mater.*, **6**, 183 (2007).
[10] E. Flahaut, et al., *Chem. Commun.* 1442 (2003).

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Strain Sensing Using Multiwall Carbon Nanotube / Epoxy Nanocomposite

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Electrically conductive nanoparticles can be used in polymer matrices to create a conductive network. The electrical resistance of these nanocomposites is sensitive to applied mechanical load. Recent investigations have shown that the electromechanical response can be used for stress/strain sensing and damage detection. Conducting nanoparticle modified matrix systems therefore are a promising self-sensing material and have a great potential in fibre reinforced composite structures for health-monitoring applications. In this work, electrically conductive nanocomposite films based on epoxy and multiwall carbon nanotubes were investigated regarding their potential for strain sensing applications with electrical conductivity methods. The direct current electromechanical response of the films subjected to mechanical load was measured. For this purpose the films were directly bonded on a substrate. Different conductive network structures were investigated concerning the linearity and sensitivity of the film sensors. Two different manufacturing routes were used to produce nanocomposite films. In the first route multiwall carbon nanotubes are dispersed in an epoxy resin via a high shear mixing process first and subsequently thin films are prepared. This process leads to a statistical like network structure of the particles inside the film. Therefore it is expected that the films have isotropic electromechanical properties. The second route uses highly in-plane oriented carbon nanotube carpets, which were infiltrated by an epoxy system. The resulting network structure of these nanocomposite films is highly anisotropic and direction dependent electromechanical properties are supposed. For the electromechanical measurements a glass fibre reinforced laminate with a lay-up which allows high strains (up to 20%) was chosen as a substrate for the films. It was found that the nanocomposite films exhibit distinct resistance vs. strain behaviour. For both types of films an almost linear increase in resistance vs. strain is observed within small strains, while for higher strains the isotropic films show exceptional nonlinearity with a resistance decrease below the initial resistance value. In case of the anisotropic films a further increase of the resistance is observed for higher strains. A direction dependent electromechanical sensitivity of the anisotropic films is also found. Thus it can be concluded that the carbon nanotube network structure plays an important role in electromechanical nanocomposite film sensors.

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High Shear Dispersion In Thermoset And Thermoplastic Matrices

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In case of industrial scale or bulk nanocomposites reliable quantification of the dispersion state is a key issue. This contribution is based on a recent paper dealing with visualization of carbon nanotubes with a scanning electron microscope. Voltage contrast imaging is a way to image dispersions of conducting particles in insulating matrices. The work covers an illustration of practical aspects which are critical to evaluating the dispersion state for a wide variety of composites. Additionally a discussion of approaches to assess the dispersion state and dispersion processes is to be presented. Due to intensive research in matters of dispersion technology and associated rheological aspects a significant amount of experience was gained with commercial and experimental products, be it multiwall carbon nanotubes, single wall carbon nanotubes, or other high specific surface area particles including few layer graphene. In order to exploit the particles potential, be it mechanical, electrical or thermal - specific dispersion states have to be attained and stabilized throughout processing. This contribution aims to sensitizing especially the industry oriented community to the problem and establishing steps to a best practice for this issue.

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Imaging Of Carbon Nanotubes In Non-Conductive Matrices

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In case of industrial scale or bulk nanocomposites reliable quantification of the dispersion state is a key issue. This contribution is based on a recent paper dealing with visualization of carbon nanotubes with a scanning electron microscope. Voltage contrast imaging is a way to image dispersions of conducting particles in insulating matrices. The work covers an illustration of practical aspects which are critical to evaluating the dispersion state for a wide variety of composites. Additionally a discussion of approaches to assess the dispersion state and dispersion processes is to be presented. Due to intensive research in matters of dispersion technology and associated rheological aspects a significant amount of experience was gained with commercial and experimental products, be it multiwall carbon nanotubes, single wall carbon nanotubes, or other high specific surface area particles including few layer graphene. In order to exploit the particles potential, be it mechanical, electrical or thermal - specific dispersion states have to be attained and stabilized throughout processing. This contribution aims to sensitizing especially the industry oriented community to the problem and establishing steps to a best practice for this issue.

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Preparation and Characterization of MWCNT Modified Thermoplastic Starch Composites

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This study aims to investigate tensile mechanical and electrical properties of corn starch-based thermoplastic (TPS) composites containing various contents (0.1, 0.5 and 1 wt. %) of multi walled carbon nanotubes (MWCNTs). Corn starch was plasticized with a proper combination of glycerol and stearic acid. TPS composites with MWCNT were prepared via melt extrusion followed by injection molding. TPS containing 1 wt. % of MWCNTs exhibited markedly higher tensile strength and elastic modulus than TPS. However, incorporation of MWCNTs did not mirror the same profound effect at relatively low loading rates (0.1 and 0.5 wt. %) on TPS tensile mechanical properties, although highly beneficial to TPS toughness enhancement regardless of weight content. TPS electrical conductivity was revealed to increase with increasing MWCNT contents.XRD measurements implied that incorporation of MWCNTs increased the TPS degree of crystallinity. Scanning and Transmission Electron Microscopy (SEM and TEM) were furthermore conducted to examine tensile sample fracture surfaces and to visualize dispersion state of MWCNTs within TPS matrix, respectively. SEM examination revealed that MWCNT altered significantly TPS fracture surface morphology. TEM investigation showed that, within TPS, tiny MWCNT clusters were in the majority relative to individual MWCNT, which was favorable to TPS electrical conductivity.

Molecular Dynamics Simulations of Thermal Boundary Conductance in Nanotube-polymer Composites

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Polymer nanocomposites are one of the most promising applications of carbon nanotubes (CNTs). For thermal transport, thermal boundary conductance (TBC) between CNT and polymer governs the overall effective thermal conductivity, particularly with absence of percolation effect due to the low inter-tube thermal conductance. In this study, to gain fundamental understanding in the mechanism of TBC between CNT and polymer, we have investigated the influence of their dynamical properties on TBC by using molecular simulations. The polymer (polyethylene) matrix was first prepared using a coarse-grained lattice model to fully relax the chain conformation near the nanotube-polymer interface, followed by reverse-mapping of an atomistic model. Thermal boundary conductance was then calculated by non-stationary molecular dynamics simulations based on lumped heat capacity method. By performing the molecular dynamics simulations for various interatomic force constants (IFCs) and temperatures, we confirmed the general mechanism of TBC, that is, elastic thermal energy transport with increasing contribution of inelastic transport with temperature. In addition, the TBC increases with the anharmonic IFCs of CNT, indicating that the rate of phonon relaxation in CNT also influences TBC. We further discuss the dependence of these characteristics on polymer structure and phase.

Interfacial Stress Transfer in Graphene Composites

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Graphene is one of the stiffest and strongest known materials with a Young's modulus of the order of 1TPa and a fracture stress ~ 130 GPa. These properties make graphene an ideal candidate for use as a reinforcement in high-performance composites. We have previously prepared model composites consisting of single graphene flakes (monolayer and thicker) sandwiched between thin polymer films and employed Raman spectroscopy to monitor stress transfer from the polymer matrix to the graphene during deformation [1]. These studies showed that a reinforcement of 1 TPa is achievable from a graphene flake. However, the studies did highlight the poor interface between the graphene and the surrounding polymer matrix, with an interfacial strengths as low as 0.2 MPa being recorded [2]. As a result, flakes larger than 30 microns are required ideally for the full stress transfer efficiency. Herein, we have studied the polymer-graphene interface in more detail, using both a range of polymer matrices and a selection of different fillers (graphene, few layer graphene, graphene oxide and nanoplatelet fillers). Raman spectroscopy was used to elucidate the degree of stress transfer that occurred across the interface. The effective reinforcement of the graphene filler materials was also found to depend on the strain history of the sample. Therefore, graphene- epoxy composites were subjected to a cyclic stress loading and the subsequent failure and healing of the van der Waal interface between the graphene and epoxy studied.

[1] L. Gong, I. A. Kinloch, R.J. Young, I. Riaz, R. Jalil, K.S. Novoselov, *Advanced Materials*, **24**, 2694-2697 (2010).
[2] R.J. Young, L. Gong, I.A. Kinloch, I. Riaz, R. Jalil, K.S. Novoselov, *ACS Nano*, **5**., 3079–3084 (2011)