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Characterization and surface-enhanced Raman spectral probing of silver hydrosols prepared by two-wavelength laser ablation and fragmentation

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Abstract

A four step Ag foil laser ablation-Ag nanoparticle fragmentation procedure in ultrapure water was carried out both under argon and in air. Pulses of a high power Nd/YAG laser were used for laser ablation (1064 nm) and for the three step Ag hydrosol treatment in the absence of Ag foil in the sequence 1064–532–1064 nm. Transmission electron microscopy (TEM) and surface plasmon (SP) extinction spectra provide evidence of Ag nanoparticle fragmentation in the second and third step of the procedure carried out under argon. While polydispersity of Ag hydrosol increases in the second step, both the polydispersity and the mean size of the nanoparticles are reduced in the third step. Qualitative and quantitative surface-enhanced Raman scattering (SERS)/surface-enhanced resonance Raman scattering (SERRS) spectral probing of systems with Ag hydrosols and the selected adsorbates at 514.5 nm excitation shows that Ag hydrosols obtained in the second step of the preparation procedure carried out in air are the most suitable substrates for SERS/SERRS experiments performed at this excitation wavelength.

Keywords: Surface-enhanced Raman spectroscopy; Silver hydrosols; Two-wavelength laser ablation

1. Introduction

Laser ablation of a metal target in liquid ambient was introduced by Henglein et al. [1] as a novel method of metal nanoparticle preparation. Along with the growing interest in nanosized materials, laser ablation has recently attracted attention of physicists and chemists as a versatile preparative method of both mono- and bi-metallic metal nanoparticles in the form of colloids (mostly hydrosols) [2–7]. Recent experimental effort on the field indicates that owing to its distinct

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advantages, such as opening of new preparative pathways and purity of the synthesis, laser ablation may, in future, well compete with traditional methods of metal hydrosol preparation, such as chemical reduction. On the other hand, the current knowledge of the mechanism of the ablation process and of the nanoparticle growths is only marginal. Exploration of the parameters of the procedure which affect the characteristics of the resulting metal hydrosols, such as their polydispersity, is mostly carried out on a trial and error basis and is often limited by the instrumental parameters of the laser equipment available.

Ag colloids prepared by laser ablation were invented as substrates for surface-enhanced Raman scattering (SERS) spectroscopy to alleviate the problem of contamination of Ag nanoparticle surface by residual ions which originate from the reductants employed in preparations of Ag colloids by chemical reduction procedures [2]. A comparative surface-enhanced resonance Raman scattering (SERRS) spectral testing of laser ablated and chemically prepared colloids with porphyrin species and other adsorbates confirmed these expectations [3,4]. Distinct differences in surface–adsorbate interactions were detected by comparison of the SERS and/or SERRS spectra of the same adsorbate in system with the laser-ablated and the chemically prepared colloids. For example, the comparative SERRS spectral evolution studies have shown a fast and complete metallation of a model porphyrin species upon its adsorption on the surface of laser ablated colloids [3], as well as modifications of the spacing effect of some thiol-derivatized compounds [5].

In this paper, we report the results of testing of a newly developed laser ablation-nanoparticle fragmentation procedure of Ag hydrosol preparation. The procedure consists of four steps: (1) ablation of a Ag foil in ultrapure water by 1064 nm pulses of a high power Nd/YAG laser; (2–4) a sequential treatment of the resulting Ag hydrosol by 1064–532–1064 nm Nd/YAG laser pulses in the absence of Ag foil. The treatment of the Ag hydrosol by laser pulses is targeted on reduction of the mean particle sizes as well as of the polydispersity of the hydrosol. While fragmentation of laser ablated Ag hydrosol by 1064 nm pulses was already reported in [3], the subsequent two steps are newly invented. The effect of the ambient is investigated by carrying out the procedure either under argon, or under ambient atmosphere (in air). Ag hydrosols collected from each step of the preparation procedure are characterized by surface plasmon (SP) extinction spectra of the resulting Ag hydrosol and by transmission electron microscopy (TEM) images of the deposited Ag nanoparticles. Furthermore, we report the results of testing of the Ag hydrosols obtained at each step of the preparation procedure as substrates for SERS/SERRS spectroscopy by both qualitative (spectral form of the adsorbate) and quantitative (normalized SERS/SERRS spectral intensities) evaluation of the

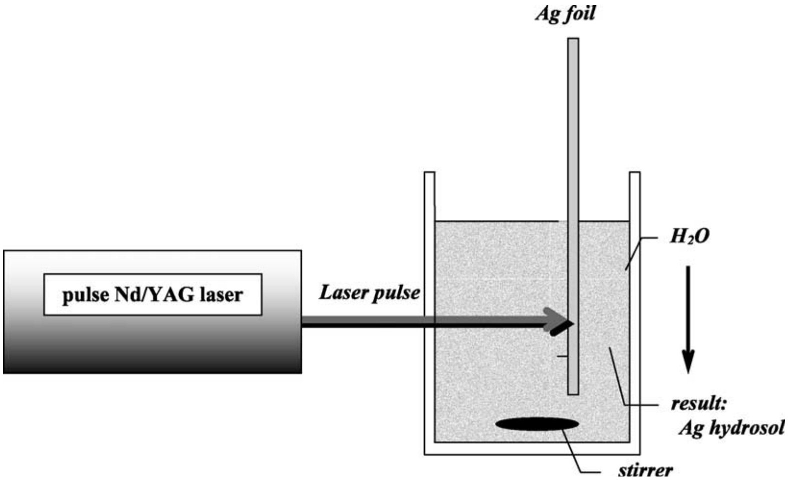

Fig. 1. Schematic depiction of laser ablation.

SERS and SERRS spectra of selected probe adsorbates. The SERS/SERRS spectral probing is targeted on optimization of the laser ablation/nanoparticle fragmentation procedure for preparation of Ag hydrosols as substrates for SERS and SERRS spectroscopy. Selection of adsorbates is based on the results of previous SERS/SERRS spectral studies. In particular, for 2,2′-bipyridine, two forms of Ag-bpy surface species (form I and form III) in systems with chemically prepared Ag hydrosols were described [8] and characterized [9,10]: form I as Ag^+-bpy, form III (tentatively) as Ag(0)-bpy. For 5,10,15,20-*tetrakis*(1-methyl-4-pyridyl) porphyrin (H_2TMPyP), three spectral forms H_2TMPyP of the porphyrin in systems with both laser-ablated and chemically prepared Ag hydrosols were identified [3,5,11,12]. The native form, i.e. H_2TMPyP, was identified on Ag nanoparticle surfaces modified by efficient spacers. Two different Ag-metallated species were tentatively attributed to metalation by Ag^+ and Ag [11].

2. Experimental

2.1. Materials

A Ag foil of 99.999% purity and deionized, doubly distilled water (the last distillation performed in a quarz apparatus) were employed for laser ablation procedure. All chemicals were of analytical grade quality.

2.2. Laser ablation

The active Q-switched Nd/YAG laser system Continuum Surlite I with repetition rate of 10 Hz, an effective diameter of pseudo-Gaussian spot of 5 mm and the pulsewidth (FWHM) of 6 ns was used for Ag hydrosol preparation. The output power was controlled by an optical power detector Gentec PSV-103. A four-step laser ablation and irradiation procedure was employed. The first (ablation) step was accomplished by treatment of a Ag foil immersed in ultrapure water in a quartz cell (30 ml) by pulses of 1064 nm wavelength with the energy of 310 mJ per pulse for 2–18 min. The laser beam was focused by a glass lens of 120-mm focal length. The subsequent steps were based on irradiation of Ag hydrosol by unfocused laser pulses of 1064 nm wavelength with energy 310 mJ per pulse for 20 min (the second and the fourth step) and by focused, frequency doubled pulses of the 532 nm wavelength with pulse energy of 170 mJ for 12 min (the third step) in the absence of the Ag foil. Prior to laser ablation, the Ag-foil and the ablation cell were purified in an ultrasonic bath. The solution was stirred during both the ablation and the irradiation steps. Preparations were carried out either in air, or under argon. A schematic depiction of the ablation procedure is shown in Fig. 1.

2.3. Preparation of samples for SERS and SERRS measurements

In each stage of the ablation-fragmentation procedure, 4.5 ml of Ag hydrosol were transferred for SERS/SERRS sample preparation. From each batch of the Ag hydrosol, the following samples were prepared: Ag hydrosol/bpy(10^{-4} M); Ag hydrosol/H_2TMPyP (3×10^{-7}M); Ag hydrosol/MESN(2×10^{-4} M)/H_2TMPyP (3×10^{-7} M). After acquisition of the SERS and/or SERRS spectra of the system, an appropriate amount of ethanol was added as internal intensity standard and the spectral acquisition was repeated.

2.4. Instrumentation

A JEOL-JEM 200 CX transmission electron microscope was employed for imaging of the Ag nanoparticles deposited on C-coated Cu grids. SERS and SERRS spectra of Ag colloid/adsorbate(s) systems were recorded with a modular multichannel Raman spectrometer described in ref. [12] using the 514.5 nm Ar ion laser excitation and 60 mW laser power at the sample. UV–vis (SP extinction) spectra of Ag hydrosols as well as of the samples for SERS and SERRS spectral measurements were acquired with Perkin–Elmer 340 and Lambda 5 UV–vis spectrometers.

2.5. Normalization of SERS and SERRS spectra

In each set of SERS and/or SERRS spectra, the intensities of selected SERS and/or SERRS spectral bands of the adsorbates expressed in terms of peak areas were normalized with respect to that of the most intense and well separated 881 cm^{-1} band of ethanol (internal intensity standard). Spectral bands of porphyrin species around 1500 cm^{-1} were also normalized with respect to the 1455 cm^{-1} of ethanol.

3. Results and discussion

3.1. Morphology of Ag nanoparticles

TEM images of Ag nanoparticles deposited from Ag hydrosols collected in each stage of the preparation procedure carried out under argon are shown in Fig. 2A–D. Ag hydrosol produced by the laser ablation (Fig. 2A) contains a large fraction of particles with sizes around 100 nm and only a small fraction of particles with sizes below 50 nm. Rod-shaped particles over 100 nm in length were also observed (not shown here). Particles obtained in the second step of the procedure, i.e. after the first treatment by 1064 nm pulses, have a broad distribution of particle sizes ranging from 10 to 100 nm (Fig. 2B). Ag nanoparticles obtained in the third step of the procedure, i.e. after the treatment by 532 nm laser pulses, contain a large fraction of particles with sizes around 30 nm and a small fraction of larger

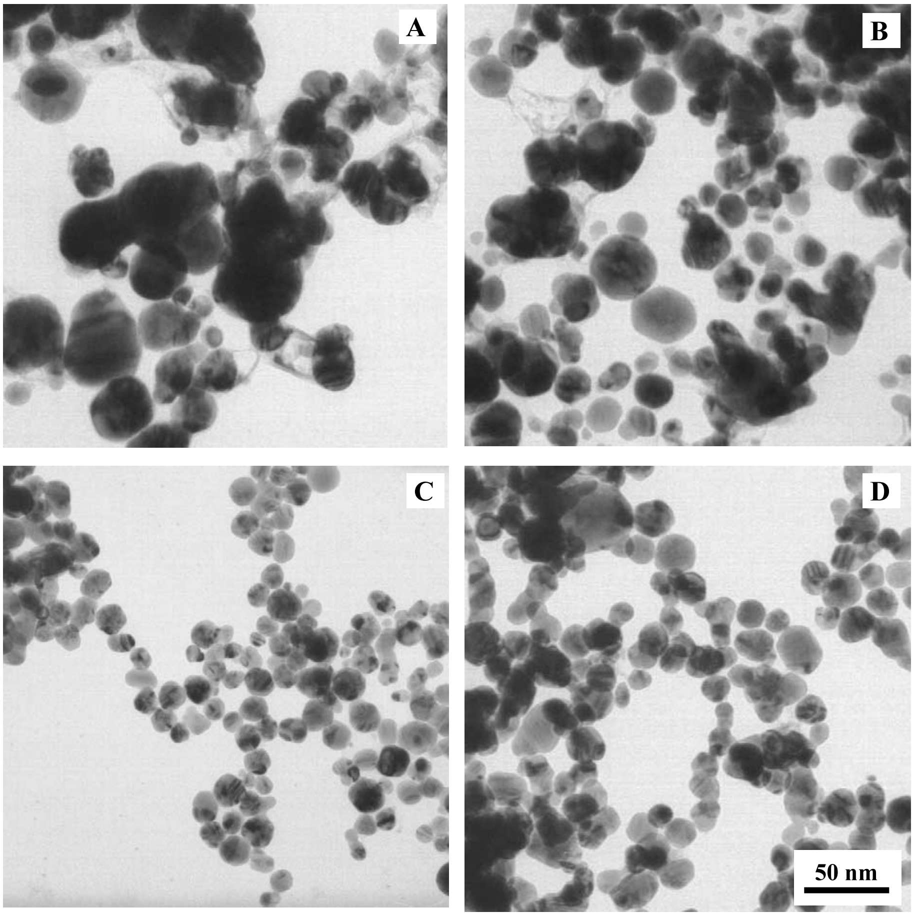

Fig. 2. TEM images of deposited Ag hydrosol nanoparticles collected from each of the four steps of the preparation: (A) after laser ablation by 1064 nm pulses; (B) after irradiation by 1064 nm pulses; (C) after irradiation by 532 nm pulses; (D) after the second irradiation by 1064 nm pulses.

and smaller particles (Fig. 2C). After the fourth step, i.e. another treatment by 1064 nm pulses, no significant further changes of particle sizes and their distribution are apparent (Fig. 2D).

3.2. SP extinction spectra of Ag hydrosols

SP extinction spectra of the Ag hydrosols measured after each step of the procedure for two different preparations carried out under argon and in ambient atmosphere are shown in Fig. 3A–D. The spectra of Ag hydrosols collected from each step of the procedure carried out under argon (Fig. 3C) show an evolution consistent with particle size changes demonstrated by the corresponding TEM images (Fig. 2). In particular, reduction of the fraction of the large particles (around 100 nm) after the treatment of the ablated hydrosol by 1064 nm pulses (second step) manifests itself by decrease of the SP extinction at wavelengths above 500 nm. Production of a large fraction of nanoparticles with sizes around 30 nm after the treatment by 532 nm pulses manifests itself by an apparent decrease of the halfwidth of the extinction band, and the reduction of the fraction of large particles (around 100 nm) by a further decrease of extinction at wavelengths above 500 nm. In accord with the TEM images,

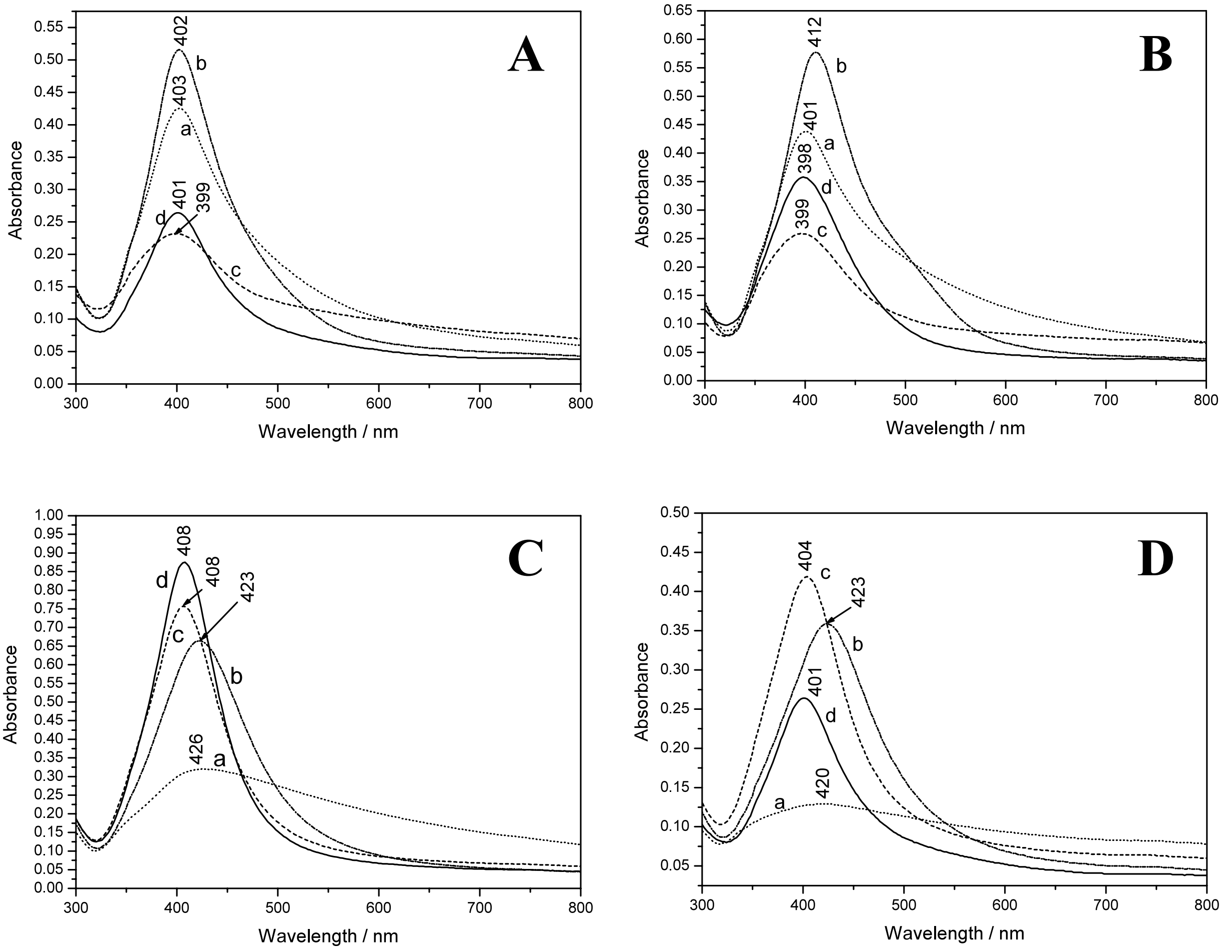

Fig. 3. SP extinction spectra of Ag hydrosols collected from each of the four steps of two different preparations carried out in air (A and B) and under argon (C and D): curve a, after laser ablation by 1064 nm pulses; curve b, after irradiation by 1064 nm pulses; curve c, after irradiation by 532 nm pulses; curve d, after the second irradiation by 1064 nm pulses.

no significant changes in the SP extinction curves are observed after the fourth step, i.e. another treatment by 1064 nm pulses.

The shapes of SP extinction curves of Ag hydrosols collected from the four steps of two different preparations carried out in air (Fig. 3A, B) show a fairly good match. In contrast to preparations under argon (Fig. 3C and D), preparations in air results into a partial aggregation of Ag hydrosol after the third preparation step, i.e. treatment of the hydrosol by 532 nm pulses, as witnessed by the shapes of the SP extinction curves (Fig. 3A, B, curves c). In the fourth step, the aggregates appear to be partially fragmented (Fig. 3A, B, curves d).

3.3. SERS/SERRS spectral probing of Ag hydrosols

All samples of Ag hydrosols (collected from each step of preparations carried out both in air and under argon) were SERS/SERRS active at 514.5 nm excitation for all there types of systems. Form I of Ag-bpy surface species was identified as a single spectral component in Ag hydrosol/bpy (10^{-4} M) systems. H_2TMPyP as the major spectral component and Ag-TMPyP (form III) as the trace spectral component were recognized in the Ag hydrosol/MESN(2×10^{-4} M)/H_2TMPyP (3×10^{-7} M) systems. Two types of Ag hydrosol/H_2TMPyP (3×10^{-7}M) systems were identified. Type I systems yielded SERRS spectra of the metalated form of the porphyrin, AgTMPyP (form II). Type II systems yielded SERRS spectra in which marker bands of both the metalated porphyrin, AgTMPyP (form II) and of the native, free-base form of the porphyrin, i.e. H_2TMPyP were observed. For systems prepared from Ag hydrosols synthesized in air (Fig. 4A and B), contribution of H_2TMPyP signal to AgTMPyP signal was repeatedly observed for hydrosols collected after the first and the second step of the procedure. Both for systems prepared from the hydrosols synthesized in air and under argon, observation of the H_2TMPyP appears to correlate with a good stability of the hydrosols with respect to aggregation. Observation of SERRS spectral bands of H_2TMPyP in system without a purposefully introduced spacer indicates that a part of the porphyrin molecules was attracted to the surface via ionic interaction of the cationic side-groups to the outer part of the electric bilayer enveloping and stabilizing the Ag nanoparticles in the hydrosol. No incorporation of Ag^+ into the center of the porphyrin macrocycle occurred and the porphyrin thus remained unperturbed. By contrast, a fraction of porphyrin molecules which interacted with Ag^+ ions on the bare surface was converted into AgTMPyP (form II), in parallel with the results reported in [3]. An instantaneous adsorption of the unperturbed cationic porphyrin indicates that the outer part of the electric bilayer enveloping the laser ablated and fragmented nanoparticles is most probably negatively charged. An important condition for observation of H_2TMPyP signal appears to be preservation of this bilayer during Ag hydrosol preparation and transport. For samples of Ag hydrosols for which the electric bilayer was perturbed already during their preparation and/or transport, as witnessed by the spontaneous aggregation, almost no signal of the unperturbed H_2TMPyP was observed.

Furthermore, normalized relative intensities of selected spectral bands of the particular adsorbate were plotted as a function of the preparation step from which the Ag hydrosol was collected. The results obtained for Ag hydrosol/bpy and Ag hydrosol/MESN/H_2TMPyP system using Ag hydrosols collected from the steps of preparations in air and under argon are shown in Figs. 5 and 6, respectively. The variations of the relative intensities are found to be within one order of magnitude. For preparation procedures carried out in air, evolution of relative intensities as a function of the step of the preparation procedure shows similar trends for all adsorbates and from preparation to preparation (Fig. 5). In particular, the normalized relative intensities of adsorbate bands in systems prepared from Ag hydrosols collected after the first and the second step are repeatedly approximately two times higher than in those prepared from the hydrosols after the third and fourth step. The decrease of the SERS-activity of the hydrosols after the third step of preparation is probably related to the spontaneous aggregation of the hydrosol during preparation, i.e. prior to the SERS-active system preparation.

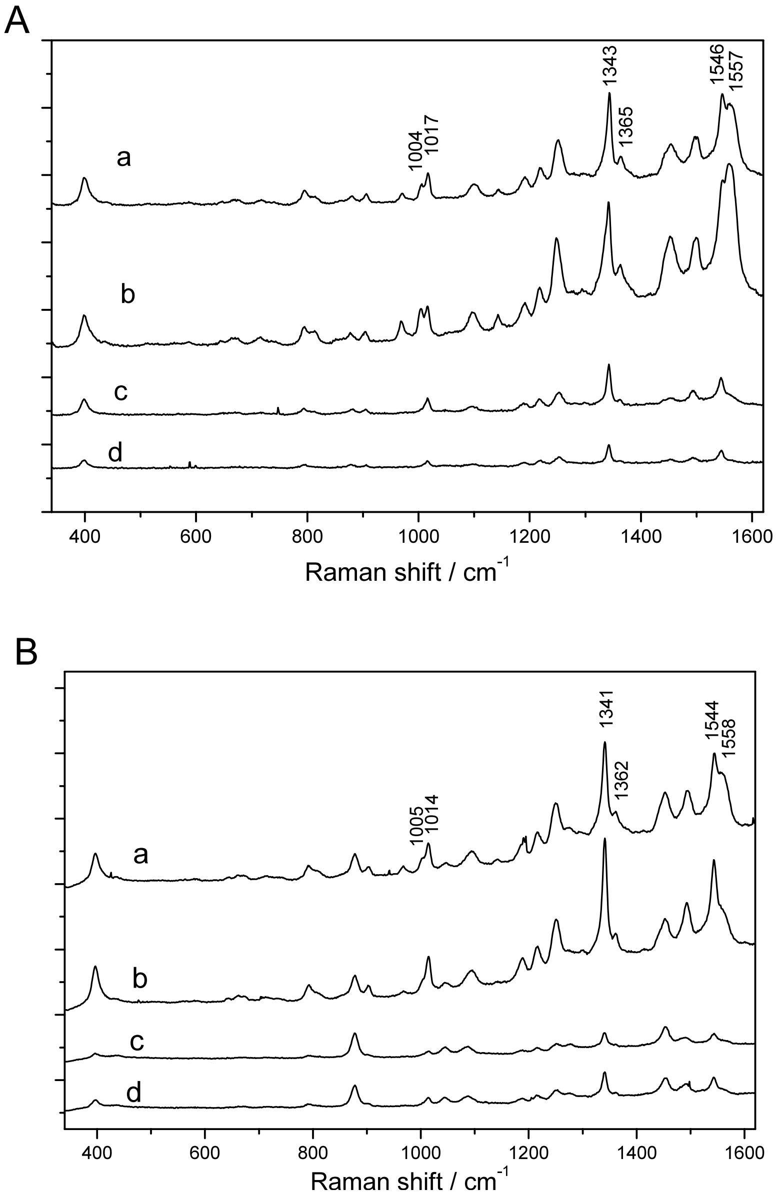

Fig. 4. SERRS spectra of Ag hydrosol/H_2TMPyP (3×10^{-7} M) systems. Ag hydrosols were collected from each of the four steps of two different preparations (A and B), both carried out in air: spectrum a, after laser ablation by 1064 nm pulses; spectrum b, after irradiation by 1064 nm pulses; spectrum c, after irradiation by 532 nm pulses; spectrum d, after the second irradiation by 1064 nm pulses.

By contrast, for preparations carried out under argon, mutually non-correlating variations of relative intensities of the adsorbate bands as a function of the preparation step of the Ag hydrosol occur both among the individual adsorbates, and from preparation to preparation (Fig. 6). The observed irreproducibility of SERS/SERRS experiments in this case may be related to oxidative processes initiated by exposure of Ag hydrosol prepared and stored under argon to air during SERS/SERRS sample preparation.

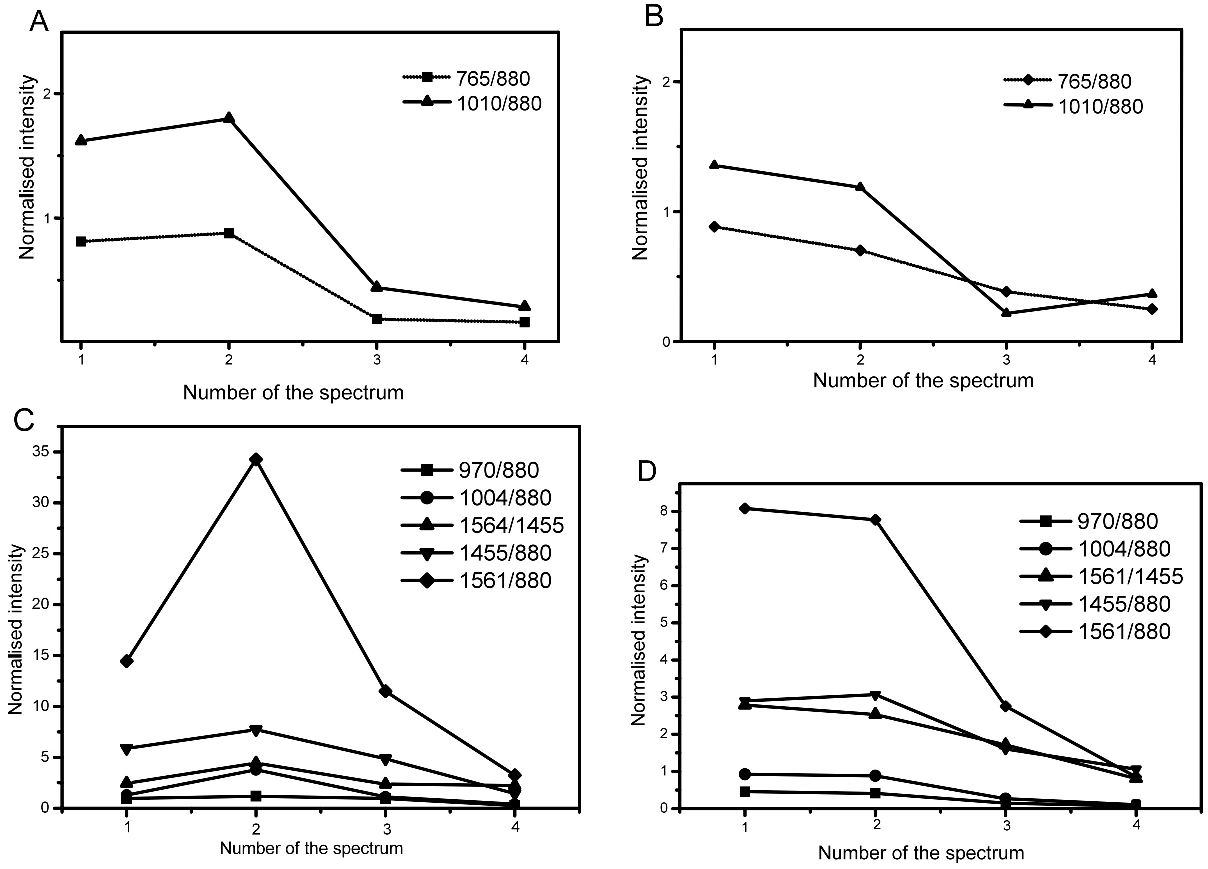

Fig. 5. Relative intensities of spectral bands of form I of Ag-bpy in SERS of Ag hydrosol/bpy(10^{-4} M) system (A and B) and of H_2TMPyP in SERRS of Ag hydrosol/MESN(2×10^{-4} M)/H_2TMPyP (3×10^{-7}M) (C and D) plotted as a function of the preparation step from which Ag hydrosol was collected. Samples of the Ag hydrosols were collected from two different preparations carried out in air.

4. Conclusions

1) Laser-ablated Ag hydrosol nanoparticles are fragmented in the second (first irradiation of Ag hydrosol by 1064 nm laser pulses) and third (irradiation of Ag hydrosol by 532 nm pulses) step of the preparation procedure carried out under argon. Fragmentation of large particles in the second step increases polydispersity of the Ag hydrosol, while fragmentation in the third step decreases polydispersity and further reduces the mean size of Ag nanoparticles.
2) Qualitative and quantitative SERS/SERRS spectral probing of systems with Ag hydrosols and the selected adsorbates at 514.5 nm excitation as well as testing of the stability of the hydrosols against a spontaneous aggregation and of the reproducibility of the SERS/SERRS experiment shows that Ag hydrosols obtained in the second step of the preparation procedure carried out in air, i.e. after fragmentation of the laser-ablated hydrosol by 1064 nm pulses, represent the most suitable SERS-active substrates. Such SERS-active hydrosols can thus be prepared in a single-wavelength experiment carried out in ambient atmosphere.

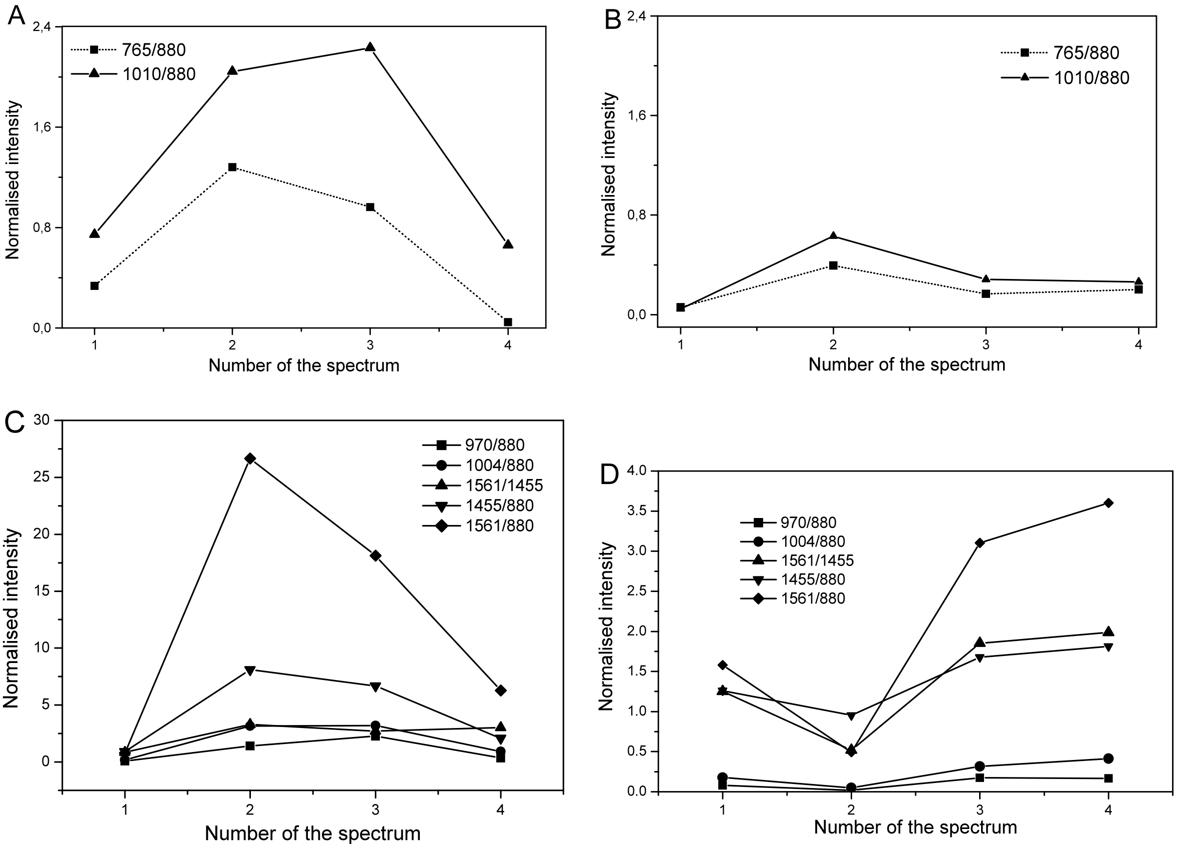

Fig. 6. Relative intensities of spectral bands of form I of Ag-bpy in SERS of Ag hydrosol/bpy(10^{-4} M) system (A and B) and of H_2TMPyP in SERRS of Ag hydrosol/MESN (2×10^{-4} M)/H_2TMPyP (3×10^{-7}M) (C and D) plotted as a function of the preparation step from which Ag hydrosol was collected. Samples of the Ag hydrosols were collected from two different preparations carried out under argon.

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References

[1] A. Fojtík, A. Henglein, Ber. Buns. Gesellsch.-Phys. Chem. Chem. Phys. 97 (1993) 252.

[2] J. Neddersen, J. Chumanov, T.M. Cotton, Appl. Spectrosc. 47 (1993) 1959.

[3] M. Procházka, P. Mojzeš, J. Štepánek, B. Vlćková, P.Y. Turpin, Anal. Chem. 69 (1997) 5103.

[4] I. Srnová, M. Procházka, B. Vlćková, J. Štěpánek, P. Malý, Langmuir 14 (1998) 4666.

[5] B. Vlćková, P. Šmejkal, M. Michl, M. Procházka, P. Mojzeš, F. Lednický, J. Pfleger, J. Inorg. Biochem. 79 (2000) 295.

[6] T. Tsuji, K. Iryo, Y. Nishimura, M. Tsuji, J. Photochem. Photobiol. A: Chem. 145 (2001) 201.

[7] I. Lee, S.W. Han, K. Kim, Chem. Commun. (2001) 1782.

[8] M. Kim, K. Itoh, J. Phys. Chem. 91 (1987) 126.

[9] I. Srnová-Šloufová, B. Vlćková, T.L. Snoeck, D.J. Stufkens, P. Matéjka, Inorg. Chem. 39 (2000) 3551.

[10] I. Srnová, B. Vlćková, I. Némec, M. Šlouf, J. Štépánek, J. Mol. Struct. 482/483 (1999) 213.

[11] M. Procházka, P.-Y. Turpin, J. Štěpánek, B. Vlčková, J. Raman Spectrosc. 33 (2002) 758.

[12] P. Šmejkal, B. Vlćková, M. Procházka, P. Mojzeš, J. Pfleger, Vibr. Spectrosc. 19 (1999) 243.