

Role of silver nanoparticle growth in formation of silver-2,2'-bipyridine surface species exhibiting photoinduced charge transfer

Karolína Šišková¹, Ivana Šloufová-Srnová^{1,2}, Blanka Vlčková¹, Peter Mojžeš³

¹Department of Physical and Macromolecular Chemistry, Charles University, Hlavova 2030, 12840 Prague 2, Czech Republic

²Institute of Macromolecular Chemistry, AVCR, Prague, Czech Republic

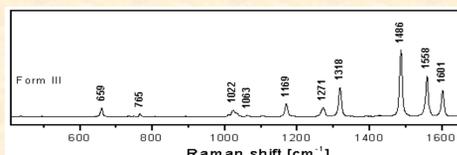
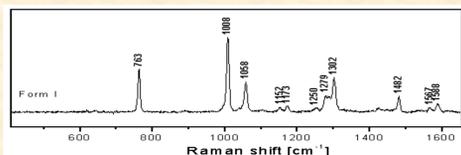
³Institute of Physics, Charles University Prague, Czech Republic

E-mail: siskova@natur.cuni.cz

Introduction

Surface-enhanced Raman scattering (SERS) spectroscopy is established as a powerful and widely used method for studying vibrational spectra of monolayers and submonolayers of adsorbed molecules on Ag, Au and Cu metal surfaces. It can provide information of the composition, molecular state, and chemical reactivity of adsorbates and surface-adsorbate complexes. Ag hydrosols (colloids), constituted by Ag nanoparticles (nanocrystals) dispersed in an aqueous ambient, are frequently employed as SERS-active surfaces.

In this contribution, we focus on SERS spectra of 2,2'-bipyridine (bpy) in systems with Ag colloids. Two spectrally different forms of Ag-bpy surface complex denoted as f1 and f3 were described in these systems [1]. In the previous studies [1-3], the following characteristics of f1 and f3 were determined:



- f1
- SERS excitation profiles 458-600 nm: no photoinduced CT (charge transfer) [2]
 - spectral analogue of $[\text{Ag}(\text{bpy})_2]^+$ [1-3]
 - detected also in the absence of chlorides, i.e. in Ag colloid/ bpy systems [1-3]
 - detected as the only spectral component in Ag colloid/ HCl/ bpy with HCl concentrations lower than 5×10^{-4} M which is the threshold concentration for changes of Ag nanoparticle morphology [3]

- f3
- SERS excitation profiles 458-600 nm: photoinduced CT at ca 540 nm [2]
 - spectral analogue of $[\text{Ru}(\text{bpy})_3]^{2+}$ (both in resonance and off-resonance spectral patterns) and of some other bpy complexes possessing a photoinduced CT [2]
 - formation is induced by addition of chlorides both in the neutral and acidic ambient, but above a certain threshold chloride concentration [3]
 - generated in Ag colloid/ HCl/ bpy systems with HCl concentrations higher than 5×10^{-4} M which is the threshold concentration above which changes of Ag nanoparticle morphology described as sintering and additional growth were observed [3]

Goal

To find out whether formation of f3 of Ag-bpy in Ag colloid/ HCl/ bpy system results from coadsorption of chlorides and bpy, as proposed in [1], or whether it relates to changes of Ag nanoparticle surface structure and composition accompanying the Ag nanoparticle growth.

Strategy

Investigation of SERS spectra and TEM-images (images of transmission electron microscope) of systems in which Ag nanoparticle were grown in the presence of bpy, but in the absence of chlorides.

Materials and instrumentation

Deionized water, and p.a. grade chemicals were used for all sample preparations.

SERS spectra excited by the 514.5 nm line of an Ar ion laser were collected using a multichannel Raman spectrometer equipped with a monochromator, Monospec-600 (60 cm focal length, 1200 grooves/mm grating), and a liquid N₂ cooled CCD detector (Princeton Instruments). Average laser power at the sample was about 80 mW. Raman scattering was collected in a 90° scattering geometry at room temperature. SERS spectra are the result of 30 spectral accumulations with a 2 s accumulation time. Samples were placed in a quartz cell (10 mm optical path). Ethanol was employed as an internal intensity standard.

A JEOL-JEM 200 CX transmission electron microscope was employed for imaging of the Ag nanoparticles deposited on C-coated Cu grids.

Preparation procedure

4,5 ml 4,42*10⁻³ M AgNO₃

3.5 mg NaBH₄ in 75 ml water and 9.54 ml EtOH

after the preparation of silver colloid added 90 μl bpy in the aqua solution of concentrations: 10⁻² M, 5*10⁻³ M, 2,5*10⁻³ M or 10⁻³ M.

3 min after the last drop of solution bpy to the prepared colloid concentration of bpy in the result solution is 10⁻² M

red = bands of f1
gray = bands of EtOH, borates etc.

New preparation procedure

4,5 ml 4,42*10⁻³ M AgNO₃

3.5 mg NaBH₄ in 75 ml water and 9.54 ml EtOH
+ 90 μl 10⁻² M bpy

same preparation procedure applied for concentrations: 5*10⁻³, 2,5*10⁻³ and 10⁻³ M bpy.

4 min after the last drop of AgNO₃ solution concentration of bpy in the result solution is 10⁻² M

green = bands of f3
cyan = some common bands of both forms
gray = bands of EtOH, borates etc.

TEM-images

Ag-bpy surface complex – form 1

Ag colloid/bpy system 10⁻⁵ M bpy in the system

Ag-bpy surface complex – form 3

Ag colloid/HCl/bpy system; 5*10⁻⁵ M HCl and 10⁻⁵ M bpy

Ag colloid/HCl/bpy system; 5*10⁻⁴ M HCl and 10⁻⁵ M bpy

bpy/growing Ag colloid system; 10⁻⁵ M bpy in the system

New preparation procedure - reduction of complex $[\text{Ag}(\text{bpy})_2]^+$

4,5 ml 4,42*10⁻³ M AgNO₃ and 90 μl 10⁻² M bpy

3.5 mg NaBH₄ in 75 ml water and 9.54 ml EtOH

same preparation procedure applied for concentrations: 5*10⁻³, 2,5*10⁻³ and 10⁻³ M bpy.

SERS spectra are dependent on bpy concentration.

4 min after the last drop of solution of Ag-bpy complex concentration of bpy in the result solution is 10⁻² M

green = bands of f3
red = bands of f1
cyan = some common bands of both forms
gray = bands of EtOH, borates etc.

3 min after the last drop of solution of Ag-bpy complex concentration of bpy in the result solution is 5*10⁻³ M

green = bands of f3
red = bands of f1
cyan = some common bands of both forms
gray = bands of EtOH, borates etc.

Conclusions

1. f3 of Ag-bpy surface complex was generated by growing Ag nanoparticles by reduction of an aqueous solution of silver nitrate by aqueous solution of sodium borohydride in the presence of bpy in the reductant solution and in absence of chlorides or other adsorbing ions. We thus conclude that coadsorption of chlorides (or other adsorbing ions) is not a necessary condition for f3 generation.

2. Formation of f3 of Ag-bpy surface complex is related to processes of Ag nanoparticle growth:

* in Ag colloid/HCl/bpy system, the growth of the parent Ag nanoparticles was induced by additions of HCl above the threshold concentration.

* in our experiments, the overall process of Ag nanoparticle growth was carried out in the presence of bpy.

3. Final morphologies of bpy/growing Ag colloid systems and of Ag colloid/HCl/bpy systems with induced additional Ag nanoparticle growth are similar. TEM images show compact, sintered aggregates of particles larger than the average particle size of the routinely prepared borohydride-reduced Ag colloids (~ 9 nm)

4. Reduction of $[\text{Ag}(\text{bpy})_2]^+$ complex (in the presence of excess Ag⁺) by sodium borohydride yielded systems in which contribution of the SERS signal of f3 varied with bpy concentration.

In summation, growth of Ag nanoparticles in the presence of bpy results into formation of surface adsorption sites on which f3 Ag-bpy surface complex characterized by a stronger Ag-bpy bonding than f1 and by a photoinduced CT is formed.

The fact that in our experiments, f3 is formed in the process of reduction of Ag⁺ to Ag⁰ indicates that the newly formed adsorption sites are most probably the Ag⁰ sites.

We thus tentatively formulate:

f1 as Ag⁺(_m) - bpy surface species,

f3 as Ag⁰(_m) - bpy surface species (complex).

Acknowledgement

Financial support of this work by 203/01/1013 grant awarded by the Grant Agency of Czech Republic is gratefully acknowledged. The study is a part of the long term Research Program of the Faculty of Science Charles University Prague, Grant No. MSM113100001.

References

- [1] M. Kim and K. Itoh, *J.Phys.Chem* **91**, 126 (1987).
- [2] I. Srnová-Šloufová, B. Vlčková, T.L. Snoeck, D.J.Stufkens and P. Matějka, *Inorg.Chem.* **39**, 3551-3559 (2000).
- [3] I. Šloufová: PhD Thesis, Charles University Prague 2000; I. Šloufová, K. Šišková, B. Vlčková, and J. Štěpánek, Proceedings of ICORS 2002, 25-30 August, Budapest, Hungary-accepted (invited lecture); I. Šloufová, K. Šišková, B. Vlčková, and J. Štěpánek, manuscript in preparation.