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

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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 adsorbrates and surface-adsorbate complexes. Ag colloids (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 distinctly different forms of Ag-bpy surface complex detected as φ and Δ were described in these systems [1]. In the previous studies [1-3], the following characteristics of φ and Δ were determined:

Φ
- SERS excitation profiles 458-600 nm: no photoinduced CT (charge transfer) [2]
- spectral analogue of [Ag(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 systems with HCl concentrations lower than 5x10^-4 M which is the threshold concentration for changes of Ag nanoparticle morphology [5]

Δ
- SERS excitation profiles 458-600 nm: photoinduced CT (charge transfer) [2]
- spectral analogue of [Bis(bpy)]2+ (both in resonance and off-resonance excitation patterns) and of some other bpy complex 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 5x10^-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 Δ 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 microscopy) 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^{-1} focal length, 1200 grooves/mm grating), and 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.

Conclusions

1. Δ 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 reduced 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 Δ generation.
2. Formation of Δ of Ag-bpy surface complex is related to processes of Ag nanoparticle growth.
   * in Ag colloids/HCl/bpy system, the growth of the parent Ag nanoparticles was induced by additions of HCl above the threshold concentration [3]
   * 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 colloidal systems and of Ag colloids/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 relatively prepared borohydride-reduced Ag colloids (~9nm).
4. Reduction of [Ag(bpy)]2+ complex (in the presence of excess Ag) by sodium borohydride yielded systems in which contribution of the SERS signal of Δ varied with bpy concentration.

In summary, growth of Ag nanoparticles in the presence of bpy results in formation of surface adsorption sites on which Δ of Ag-bpy surface complex is formed, characterized by a strong SERS signal typical to Δ of Ag-bpy. These sites were induced by addition of HCl to Ag-bpy colloidal systems which shows the importance of bpy in the process of reduction of Ag+ to Ag0, indicating that the newly formed adsorption sites are most probably the Ag+bpy sites.

Acknowledgement
Financial support of this work by 203/01/1031 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. MSM111300001.

References