Silver-doped silica colloidal nanoparticles. Characterization and optical measurements

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Abstract

Silver clusters are obtained on the surface of nanosize silica hydrosols by photoreduction of silver nitrate, induced by visible laser irradiation. The formation of Ag-doped silica colloidal particles is confirmed by the UV–visible absorption spectra, which exhibit a large plasmon resonance band at about 410 nm, similar to that observed in pure silver hydrosols, and by the quenching of the fluorescence intensity. These colloids represent suitable substrates for surface-enhanced Raman scattering (SERS), showing stability and enhancement factors comparable with those obtained in pure silver hydrosols. The simplicity of the procedure and the absence of reducing agents represent significant advantages of this method.

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1. Introduction

Metal nanoparticles show peculiar optical, magnetic and electronic properties that bulk solids or isolated molecules do not usually exhibit [1,2], which may find important applications in materials technologies like microelectronics and chemical nanosensors. Colloidal particles of coinage metals (Ag, Au, Cu) have been widely employed as nanostructured substrates for surface enhanced Raman spectroscopy (SERS), where the scattering cross sections are greatly enhanced for the adsorbed molecules [3–5], by $10^{14}$–$10^{15}$ times in the case of single-molecule investigation [6,7]. Hence, SERS spectroscopy is potentially a highly sensitive analytical technique, allowing satisfactory discrimination on the basis of the characteristic vibrational bands of the ligands. This has strongly stimulated research for developing novel nanostructured substrates. For various SERS-active surfaces, including electrochemically roughened metal surfaces, deposited metal layers and crystal island films, metal colloidal suspensions offer significant advantages, such as simplicity of preparation, higher resistance to the damage due to the impact with the laser beam than in solid surfaces and higher Raman enhancement factors. Transmission electron microscopy (TEM) and absorption spectroscopy in the UV–visible region allow the investigation on the shape and size of the colloidal particles. The metal colloidal suspensions

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undergo aggregation by addition of ligand or aging, and this changes the ligand adsorption and the corresponding SERS spectrum. The reagents employed in the colloid preparation could produce spectral interference with the Raman signal of the adsorbate [8] or undesired reactions [9]. Hence, great interest exists in the preparation of stable colloidal materials with metal particles obtained by photochemical reduction, i.e. without using chemical reagents. Nanostructured materials, therefore, were prepared by mixing silica and silver, a typical SERS-active metal, by thermally evaporating silver on fumed silica materials [10,11], by impregnating silica with silver nanoparticles [12], or by depositing [13,14] silver on silica nanospheres. In the latter case, silica besides stabilizing the metal particles supplies the surface roughness needed for the Raman enhancement of the adsorbate. SiO₂-coated silica films were also fabricated to protect the metal surface, avoiding thus the photodecomposition of the adsorbate [15].

In the present study, silica colloidal nanoparticles are doped with metal silver clusters obtained by photoreduction of silver nitrate, in order to create stable substrates and, consequently, improve reproducibility of SERS results. Also, silica gel represents a good supporting material for the SERS-active metals, because it is inert and stable, exhibits optical transparency, from the near UV region through the near infrared, and has a high specific binding capacity [16]. Preliminary results performed on Ag-doped silica colloids have showed SERS performances comparable with those of common silver hydrosols [17]. A characterization of these substrates is given here, along with an investigation on the best conditions for photoreducing silver ions, using optical measurements such as UV–visible absorption, Raman and fluorescence spectroscopy.

2. Experimental

Raman spectra were obtained by using the exciting lines of an Ar⁺ ion laser (457.9, 488.0, 514.5 nm) and a Kr⁺ ion laser (568.2, 647.1 nm), a Jobin-Yvon HG-2S monochromator, a cooled RCA-C31034A photomultiplier and a computer for the data acquisition. UV–visible extinction spectra were obtained with a Cary 5 spectrophotometer and fluorescence measurements with a JASCO spectrofluorometer Model FP-750. Cuvettes with 10 mm path length were used.

To obtain photoreduced silver, a AgNO₃ (Aldrich, 99.9999%) aqueous solution was added to colloidal silica (Aldrich, Ludox TM-40, 40 wt.% suspension in water), resulting in a sample with 10 wt.% SiO₂ content and 2.4 × 10⁻⁴ M Ag⁺ concentration, which was then irradiated for 10 min by various laser lines with 250 mW power density. SERS spectra of 2-amino-5-nitropyrimidine (ANPM) in Ag-doped silica hydrosols were obtained by using the 647.1-nm exciting line.

3. Characteristics of the colloidal silica

Colloidal silica appears as a cloudy colorless liquid. The aqueous solution is alkaline (pH ~ 9.0, at 25 °C), as in Ag hydrosols obtained by reduction of silver nitrate with excess borohydride [18]. The colloidal particles are discrete uniform spheres of silica with 22 nm average diameter, and 140 m² g⁻¹ specific surface area. The particle charge is negative, due to the presence of >Si-O⁻ groups on the surface. Because of the electric charge, the particles repel one another, resulting in a stable product. Na⁺ is the stabilizing counter ion; chlorides (as NaCl) and sulfates (as Na₂SO₄) are present in small quantities, 0.03 and 0.08 wt.%, respectively. The stability increases generally with dilution and decreases with temperature, resulting in gelation or aggregate formation. The greatest tendency to gel occurs at pH 5–6, but when the pH is further reduced the sol becomes more stable. Small additions of salts up to 10⁻² M concentrations hardly affect the sol stability, while keeping the other variables unchanged.

4. Photoreduction of silver ions

After the addition of silver nitrate, silver ions could adsorb on silica [19], but in alkaline medium they are hydrolyzed to AgOH, giving rise to a
5. UV–visible extinction spectra

During the photoreduction process of the silver ions, an absorption broad band in the UV–visible extinction spectrum occurs at about 410 nm (Fig. 1), progressively increasing with the irradiation time. This band, which is not present in the pure colloidal silica, is attributable to the surface plasmon absorption of metal nanoclusters, obtained by photoreduction onto the silica particles. Preliminary TEM measurements indicate that silver clusters are formed onto the silica particles, with 20–30 nm average diameter, but with a significant amount of larger aggregates, also indicated by the broad tail of the plasmon resonance band in the visible region. The efficiency of the laser lines for the photoreduction process is monitored, as described in Section 2, by observing the intensity of the band at 410 nm. The maximum intensity was obtained using the 514.5-nm laser line. The irradiation with yellow light (568.2 nm) induces a small effect, whereas the red light (647.1 nm) does not produce any observable photoreduction from the absorbance curves.

6. Surface-enhanced Raman scattering

The Ag-doped silica colloids, obtained by various laser lines, have been employed as substrates for ANPM, whose SERS spectra were recently studied [23]. Here, SERS measurements (Fig. 2) have been performed by using the 647.1-nm exciting radiation, which is not photoreducing the residual silver nitrate. A strong SERS effect is found for colloids irradiated by laser lines in the
457.9–514.5 nm region, whereas the colloid irradiated by yellow light (568.2 nm) shows a negligible Raman enhancement. This latter depends on the number of silver particles formed by laser irradiation, as revealed by the UV–visible absorption spectra. Hence, a close correspondence is found between the SERS intensity, as evaluated by the integrated area of the strongest SERS band of ANPM at \( \approx 1324 \text{ cm}^{-1} \) and the absorbance of the plasmon resonance band observed at 410 nm (Fig. 3). In order to evaluate the enhancement factors, the SERS intensities are compared with the weak Raman intensity observed in the colloid irradiated by the 647.1-nm line, without photoreduction of silver nitrate. These values cannot represent the effective enhancement factors, the evaluation of which requires knowledge of the amount of ligand adsorbed on silver. However, for the colloid irradiated with the 514.5-nm laser line the relative enhancement factor, with respect to the colloid without silver particles, is found larger by two size orders (about \( 1.1 \times 10^2 \)). This agrees with enhancement factors usually detected in pure silver hydrosols [24] compared to the aqueous solutions containing the same ligand concentrations.

7. Fluorescence measurements

Fluorescence quenching near metal surfaces was observed and interpreted on basis of various electrodynamics models [25–27]. In the case of the colloidal silica, a fluorescence band occurs with maximum at about 480 nm (Fig. 4). After photoreduction of silver ions, a drastic quenching of the fluorescence is observed in the Ag-doped silica colloids along with a shift of the peak to 495 nm. This evidence can be interpreted on the basis of the formation of a non-fluorescent complex between the fluorophore and the quencher [28], i.e. the silver clusters obtained by photoreduction onto the silica surface.

8. Conclusions

New SERS-active substrates have been obtained by photoreduction of silver nitrate in silica hydrosols. The photoreduction process, which usually occurs in water solutions by UV irradiation [29], is obtained here with visible light, because of the presence of silica nanoparticles, where silver ions are adsorbed. The formation of silver nanoclusters adhering to the colloidal silica is proved by optical measurements using UV–visible absorption, Raman and fluorescence spectroscopy.

![Fig. 3. SERS intensity of ANPM in silica/AgNO₃ hydrosols irradiated with various laser lines compared with the absorbance of the plasmon band at 410 nm. SERS intensities, denoted as stars, and absorbances, denoted as open circles, in arbitrary units.](image-url)

![Fig. 4. Fluorescence spectra (330-nm exciting line) of a silica/AgNO₃ colloid irradiated with 514.5-nm laser line for: 0 (A); 30 (B); 90 (C); 600 s (D).](image-url)
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References