Silver Core - Silver Oxide Shell Nanoparticles Embedded on Mesostructured Silica Films

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Abstract: Metallic silver particles in the nanometer size range were obtained in SiO₂ matrix by the reduction of AgNO₃ with the non-ionic diblock copolymer (Brij 58). Hexagonal mesostructured solgel films were synthesized by dip-coating method using the surfactant Brij58 to produce channels into the film, which house the silver nanoparticles. Optical properties of the metallic nanoparticles were studied by UV-Vis spectroscopy, TEM and HRTEM images. The experimental absorption spectrum of the metallic silver nanoparticles exhibits an absorption band located at 438 nm and a shoulder at longer wavelength. The TEM images show randomly distributed silver nanoparticles (Type I) along with some oriented as long line (Type II). Both distributions exhibit a silver oxide shell around of them. The second shell covering the silver core - silver oxide shell system is related to the surfactant. The optical absorption spectrum was modelled using the Gans theory. The fit shows two main contributions related to metallic silver nanoparticles with different axial ratios, and surrounding of a dielectric medium with high refractive index. Presence of the high refractive index silver oxide shell play important roles in the optical properties of the films.

Introduction

Metallic nanoparticles embedded in amorphous SiO_2 glasses (dielectric matrix) exhibit very interesting optical properties, and have several technological applications in photo electrodes for solar cells [1], optical switches [2], electronic and magnetic devices, catalysis or sensor applications [3-6]. These properties depend on the size, shape and dielectric environment surrounding the nanoparticles [6].

The metallic nanoparticles exhibit optical absorption originated from a collective oscillation of the conduction electrons when they are excited by light. It is named surface plasmon resonance and it is not observed on the bulk metals. The optical response depends on several factors like local refractive index [6], the dielectric constant of the medium (host matrix, coating), morphology (size and geometry) and state of aggregation of the metallic nanoparticles [7,8]. Any change in these physical features will alter the peak position, intensity or shape of the optical response. Many classical models have been used in order to understand the optical absorption spectra of the metallic nanoparticles [7-17]. The optical absorption can be calculated by the Gans theory, and extended Mie's theory to prolate or oblate particles averaged over all orientations [10,11,18].

Mesoporous silica have been doped with metallic nanoparticles as silver or gold to modify their properties [19]. In particular, mesostructured films, due to their high specific area (which can be as high as 500-1000 cm² g⁻¹), the high porosity and the organization of the material, have attracted some interest as materials for nanotechnology to be used as sensors, catalysts, electrochemical or optical devices [20,21]. Mesostructured silica films can be synthesized by using surfactant as template. A surfactant is a molecule with a charged or hydrophilic head group and a hydrophobic tail that can assemble into spherical or rod-like micelles in water [22]. Nonionic alkyl poly(oxyethylene) surfactants and poly(oxyalkylene) block copolymers are important families of surfactants for their ordering properties that can be nearly continuously tuned by adjusting solvent composition, molecular weight, or copolymer architecture [23]. Formation of metal nanoparticles carried out in the presence of surfactants, frequently leads to the generation of 1-, 2-, or 3-dimensional networks of microporous channels [24,25]. Cubic, hexagonal or lamellar mesophases can be obtained controlling the surfactant concentration [26]. The dimension of the pores can be controlled using different types of block copolymers [27].

In this work, long-ordered mesostructured sol-gel films were doped with silver nitrate (AgNO₃) under acidic conditions. An ethylene oxide based non-ionic diblock copolymer Brij 58 (C₁₆H₃₃PEO₂₀) was used as template for silica polymerization in the synthesis of uniformly distributed silver-ion-containing mesostructured silica films. On the other hand, surfactants themselves are known to play an important role in the stabilization of metal colloids [28]. The diblock copolymer Brij 58 was used in the reduction of Ag⁺ ions embedded into mesostructured silica matrix to produced silver nanoparticles. The reduction process was monitored by UV-vis absorption spectroscopy. Stable optical properties were obtained from random-oriented silver prolate nanoparticles (Type I) and silver nanoparticles arranged as long chain (Type II) embedded in mesostructured silica films prepared by the dip-coating method. The small silver nanoparticles were obtained by controlling the pore dimension in presence of the surfactant, Brij 58. The effect of Brij 58 as reductor and as stabilizer of the silver nanoparticles was reviewed. Besides, a block copolymer shell was formed surrounding the silver oxide shell. Gans theory including a variable refractive index [29,30] was used to fit the experimental absorption spectra. The results indicate that it is necessary to consider the presence of oxidized metal particles in order to have a good fit to the experimental data.

Experimental

Glass substrates were cleaned in boiling acidic solution of sulphuric acid- H_2O_2 (4:1) under vigorous stirring for 30 minutes. They were then placed in deionized water and boiled for 30 minutes, rinsed three times with deionized water, and stored in deionized water at room temperature. Films were dip-coated on glass substrates (9 cm x 1 cm x 1 cm) at a rate of 3.5 cm/min. The films were drawn with the equipment described previously that uses hydraulic motion to produce a steady and vibration-free withdrawal of the substrate from the sol [31]. Convection-free drying was critical to obtain high optical quality films.

All the used reagents were of LR grade (Aldrich). An initial solution was prepared with AgNO₃ (silver nitrate) dissolved in deionized water and nitric acid in a Nalgene plastic beaker. Then 1 g of methanol, 5.4 g of TMOS (Tetramethyl orthosilicate, the silicate precursor), and 4g of the non-ionic diblock copolymer Brij 58 ($C_{16}H_{33}PEO_{20}$) were added to the solution. This solution was refluxed at 50-70 °C for 20 minutes to homogenize the mixture. To obtain the SiO₂ thin films doped with silver ions, the final molar ratio of TMOS, methanol, nitric acid, H₂O, $C_{16}H_{33}PEO_{20}$, and AgNO₃ was adjusted to 1:0.9:0.13:6.25:0.1:0.06. The reduction of Ag⁺ ions embedded into mesostructured silica matrix to silver metallic nanoparticles was detected by the typical sequence of color changes from colorless to black. This reduction process was monitored by UV-Vis absorption spectroscopy. UV-Vis absorption spectra were obtained on a Thermo Spectronic Genesys 2 spectrophotometer with an accuracy of ± 1 nm over the wavelength range of 300-900 nm.

The structure of the final films was characterized with X-ray diffraction (XRD) patterns. These patterns were recorded on a Bruker AXS D8 Advance diffractometer using Ni-filtered CuK α radiation. A step-scanning mode with a step of 0.02° in the range from 1.5 to 10° in 2θ and an integration time of 2 s was used. Characterization of the morphology and microstructure was achieved from conventional transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) by using a JEOL FEG 2010 FasTem electron



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microscope with 1.9 Å resolution (point to point) and high angle annular dark-field detector (HAADF) attached. For TEM and HRTEM studies, the sample was suspended in ethanol in order to disperse the powders and a drop of the sample was deposited on a lacey carbon copper grid as a TEM support. From the HRTEM micrographs, mean particle size and particle size distribution were calculated. The thickness of the films was measured using a SEM microscope Model STEREOSCAN at 20 kV.

Gans Theory

For spheroid metallic nanoparticles well separated and with size $R << \lambda$, where λ is the wavelength of the incident light, the optical properties depend mainly on the axial ratio AR=B/A (A is the length of the axis of rotation of the spheroid and B is the shorter transversal axis). On these conditions, the optical absorption can be calculated by the Gans theory, an extended Mie's theory to prolate or oblate particles averaged over all orientations [32]. According with the Gans theory a splitting of the surface plasmon is predicted in one longitudinal mode along of the major axis and one transversal mode, perpendicular to the first axis. Assuming that the extinction coefficient is only due to the absorption from silver nanoparticles, the absorption coefficient α can be written as [32,33]:

$$\alpha = -(\alpha_1 + \alpha_2) \tag{1}$$

where

$$\alpha_{1} = \frac{3\phi\omega_{n}^{3}}{9cp'^{2}} \left\{ \frac{\varepsilon_{2}(\omega)}{\left[\varepsilon_{1}(\omega) + n^{2}(1/p'-1)\right]^{2} + \varepsilon_{2}(\omega)^{2}} \right\}$$
(2)

and

$$\alpha_{2} = \frac{3\phi\omega_{n}^{3}}{9cp^{"^{2}}} \left\{ \frac{2\varepsilon_{2}(\omega)}{\left[\varepsilon_{1}(\omega) + n^{2}(1/p"-1)\right]^{2} + \varepsilon_{2}(\omega)^{2}} \right\}$$
(3).

Specifically, for prolate nanoparticles we have:

$$p' = \frac{1 - e^2}{e^2} \left\{ \frac{1}{2e} \ell n \frac{1 + e}{1 - e} - 1 \right\}$$
(4)

$$p'' = (1-p')/2$$
 (5)

$$e = \sqrt{1 - \left(\frac{B}{A}\right)^2} \tag{6}$$

where α_1 and α_2 are the components of the absorption coefficient parallel and perpendicular to the longer principal axis of the particle, respectively; ϕ is the volume fraction, *c* is the light velocity, *n* is the local refractive index of the medium surrounding the silver nanoparticles. $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary part of the dielectric constant of silver in bulk, respectively. The parameters



p' and *p*" are the depolarization factors for the three axes *A*, *B*, *C*, of the prolate shape particles with A > B = C. The ratio B/A is the axial ratio (Θ).

Moreover, the dielectric constant of the bulk metal must be modified to take in account the decreasing of the electron mean free path in the small particles. This effect will produce an increment in the predicted half-width of the absorption band. The complex dielectric constant correction due to the dependence on the frequency ω and particle size *R* from the spherical nanoparticles is given as [29]:

$$\boldsymbol{\mathcal{E}}_{1}(\boldsymbol{\omega},\boldsymbol{R}) = \boldsymbol{\mathcal{E}}_{1}(\boldsymbol{\omega}) \tag{7}$$

$$\varepsilon_{2}(\omega, R) = \varepsilon_{2}(\omega) + \eta \frac{\omega_{p}^{2}}{\omega^{3}} \left(\frac{V_{f}}{R}\right)$$
(8)

where $R = 1/2(ABC)^{1/3}$, ω_p is the plasmon frequency and V_f is the Fermi velocity of the conduction electrons. The η parameter is relating with the scattering rate of the free electrons against other electrons, the particle surface, phonons, defects and so on [29]. Using the Eq. (1)-(8) we can obtain the calculated absorption spectra of silver nanoparticles in 2d-hexagonal mesostructured sol-gel thin films. Thus, the Gans theory can provide informations on to size and shape of the metallic nanoparticles as well as of the local refractive index of the medium surrounding the silver nanoparticles.

Results and Discussion

Metallic silver particles in the nanometer size range were obtained in SiO_2 matrix, by the reduction of AgNO₃ with the non-ionic diblock copolymer (Brij 58) [28]. A colourless film was obtained when only silver ions are present in the matrix (left side in Fig. 1). On the other hand, the presence of the silver metallic nanoparticles can be identified by the black colour of the sol-gel films acquired after aging in air in the darkness at room temperature for two months (right side in Fig. 1). The thickness of the films was about 3.272 μ m, as measured by SEM (Fig. 2).



Figure 1. Mesostructured sol-gel silica films with silver ions showing a colourless silica film (left side), and with silver metallic nanoparticles showing a black silica film (right side).







Optical absorption

Other evidence of the silver metallic nanoparticles generation was followed by UV-Vis optical absorption spectroscopy. Fig. 3 shows the optical absorption spectra taken at room temperature in the range of 300-900 nm. The absorption spectrum of the colourless silica film does not exhibit any absorption band (solid line). The spectrum of the black silica film (dotted line) shows an absorption band A located at 438 nm and a shoulder B at longer wavelength (~ 660 nm). This spectrum shows a broad and asymmetric band, suggesting the presence of silver metallic nanoparticles of inhomogeneous size. For silver nanoparticles embedded in oxidizing atmosphere like in silica gels, an absorption peak centred at 425 nm [29,30] has been reported. A red shift was observed in our spectrum, which can be attributed to deformed silver particles covered with a silver oxide shell.



Figure 3. Absorption spectra of the mesostructured sol-gel silica film with silver ions corresponding a colorless silica film (solid line), and a mesostructured sol-gel silica film with silver metallic nanoparticles corresponding a black silica film (dotted line).

X-ray diffraction patterns

The presence of the silver oxide shell surrounding the metallic nanoparticles was reviewed by XRD studies. Fig. 4 shows the XRD patterns at high angle of (a) SiO₂:Brij 58 thin film without silver particles, and (b) mesostructured silica film with silver nanoparticles. The peaks corresponding to surfactant were detected in both the films, and they were identified with asterisks.



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From Fig. 4 (b), the diffraction peaks of silver oxide are located at $2\theta = 27.90$, 29.85, 32.25, 33.4, 46.30, 52.60, 57.05 degrees, and can be indexed as (110), (111), (120), (031), (13 -2), (051) and (132) planes, respectively. For metallic silver, two diffraction peaks are located at $2\theta = 38.05$ and 44.50 degrees, and they were indexed as (111), (200) planes, respectively. The position of the diffraction peaks in the film is in good agreement with those given in ASTM data card (# 40-1054) for silver oxide, and ASTM data card (# 01-1167) for metallic silver. The intensity of the surfactant peaks is more intense than those from silver oxide and silver nanoparticles.



Figure 4. XRD pattern at high angle of (a) SiO₂:Brij 58 thin film without silver particles, (b) mesostructured silica film with silver nanoparticles templated with Brij 58.

Fig. 5 shows the XRD pattern at low angle of mesostructured silica film with silver nanoparticles. The peak at $2\theta = 1.77^{\circ}$, or a *d*-spacing of 50.0 Å, corresponds to the (100) peak of the 2-D hexagonal structure of the SiO₂ matrix.



Figure 5. XRD pattern at low angle of mesostructured silica film with silver nanoparticles. The (100) peak with $2\theta = 1.77^{\circ}$ corresponds to a *d*-spacing equal to 50.0 Å.

TEM and HRTEM measurements

TEM images of small metallic silver nanoparticles with prolate shape are presented in Fig. 6. Fig. 6 (a) shows randomly oriented silver nanoparticles (Type I) and Fig. 6 (b) shows the silver nanoparticles arranged in a long line (Type II) with lengths of \sim 600 nm. Fig. 6 (c) shows the HRTEM image of a silver nanoparticle. Its electron diffraction pattern (inset) indicates that the particle is crystalline and it corresponds to the fcc Ag [34]. As evidenced from these images, the optical properties revealed in the absorption spectrum (Fig. 3) are due to metallic silver nanoparticles.



Figure 6. (a) TEM image of the small metallic silver nanoparticles with prolate shape (Type I); (b) TEM image of the silver nanoparticles oriented in long lines (Type II); and (c) The electron diffraction pattern of a silver nanoparticle correspond to the fcc Ag.

Fig. 7 show the SEM image of the silver metallic nanoparticles embedded in the silica film. Two populations (Type I and Type II) of silver nanoparticles can be distinguished from their contrasts, which are immersed in the silica matrix and in the regions of the surfactant.







HRTEM images obtained with energy filtering at 10 eV, show metallic silver - silver oxide core-shell structures (Fig. 8). It is easy to identify that the dark shell corresponds to the silver oxide which is surrounding the silver particle. In turn, a thin bright shell is covering the metallic silver - silver oxide shell system. This bright shell is related to the used copolymer which reveals a SERS (Surface-enhanced Raman scattering) effect [35]. It is well known that the SERS is a process in which the Raman scattering cross-section of molecules absorbed onto the surfaces of metals such as silver, copper and gold is increased by as much as six orders of magnitude compared with the cross-section for normal Raman scattering.





In particular, the particle in Fig. 8 has a major axis of 29.02 nm, and minor axis of 18.49 nm. The AgO_2 shell has a thickness of 1.14 nm and the block copolymer shell has a thickness of 1.14 nm, too. It must be noted that for the particles with diameters between 15-20 nm with small surface area, the shell is very thin. On the other hand, for the particles with 5 nm and large surface area, the shell becomes very thick [36]. This effect is due to the distinct chemical reactivity of the surfaces.



From HRTEM studies, the corresponding size-distribution histograms were obtained (Fig. 9). The distributions of the minor axis B and major axis A of the metallic nanoparticles are very broad. For the Type I particles, we obtained $B = 5.9 \pm 3.3$ nm (Fig. 9a), $A = 7.8 \pm 4.2$ nm (Fig. 9b) and the mean axial ratio AR was 0.80. For distribution Type II, we obtained $B = 4.2 \pm 1.2$ nm (Fig. 9c), $A = 6.0 \pm 1.7$ nm (Fig. 9d) and the mean axial ratio AR = 0.52. In both the cases, the average size of the silver nanoparticles were 2R < 20 nm, and therefore the Gans theory could be used to fit the optical absorption spectrum of the films containing silver particles.



Figure 9. Size-distribution histograms obtained from HRTEM analysis of silver nanoparticles embedded in silica matrix.

Fits by Gans theory

Renteria et al. [30] have demonstrated that the Gans theory is adequate for sol-gel systems. They considered the case of the interactions between silver nanoparticles and the dielectric medium by using two principal refractive indexes in their fits. By using this idea, the experimental absorption spectrum in Fig. 3 has been fitted. The envelope corresponding to the calculated absorption spectrum is obtained from adding the component absorption bands of prolate nanoparticles (Type I and II). These component bands are calculated with pairs of optical parameters: radii R_1 and R_2 , axial ratio Θ_1 and Θ_2 and two principal refractive indexes n_1 and n_2 .

The experimental and calculated absorption spectra of silver nanoparticles in mesostructured silica films are shown in Fig. 10. For the calculated absorption spectra, the dielectric constants $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ measured by Johnson and Christy [37] were used, and $\omega_p = 1.38 \times 10^{16} \text{ s}^{-1}$ and $V_f = 1.4 \times 10^6 \text{ ms}^{-1}$ for silver were considered [29]. An excellent fit was obtained by using the experimental data from size-distribution histograms of Fig. 9. Higher refractive indices ($n_1 = 1.97$ for nanoparticles of Type I, and $n_2 = 2.04$ for nanoparticles of Type II) were used in Eq. (2)-(3) to achieve this good fit. The refractive index n_2 is due to the silver oxide shell (n = 2.5 [38]) formed around the silver

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nanoparticles. This oxide shell therefore increases the local refractive index and determinates the maximum wavelength position of the surface plasmon resonance [29].



Figure 10. Experimental optical absorption spectrum (gray line) of the silica film containing two types of silver nanoparticles. The components bands (black solid lines) corresponds to the silver nanoparticles Type I ($n_1 = 1.97$) and Type II ($n_2 = 2.04$). By adding these component bands, the calculated optical absorption spectrum (black dotted line) was obtained.

For the surfactant Brij 58, a refractive index ~1.24 is reported in the literature [39]. This refractive index value is smaller than the silver oxide shell $n_{AgO_2 shell} > n_{surfac \tan t shell}$. Then, the silver oxide shell has a more notable effect than the surfactant shell on the interactions between silver nanoparticles and the dielectric medium (SiO₂). Therefore, good fits were obtained using high refractive indexes (n > 1.50) in films aged at room temperature. This high local refractive index of the dielectric medium, due to the silver oxide shell, which produces the red shift of the absorption band of the metallic nanoparticles [30] observed in Fig. 3. For both type I and type II distributions, the surfactant - silver oxide shells surrounding the metallic core were observed.

Surfactant effect

The surfactant (Brij 58) was used as reductor and as stabilizer preventing the aggregation of the nanoparticles. The surfactant allowed the control of small sizes and specific shapes (prolates and almost spherical) of silver nanoparticles. At the same time, these nanoparticles were oriented in a long line due to the hexagonal mesophase generated in the SiO_2 matrix, although in some regions they were not oriented. Furthermore, the silver nanoparticles were stabilized by the surfactant shell obtaining a good particle size control [38,40]. The nature and concentration of the surfactant are crucial parameters for controlling the stability and optical properties of the particles.

Marzán et al. [28] have reported the reduction of silver ions with several surfactants dissolved in different solvents. They indicated that the oxyethylene groups are responsible for the reduction and stabilization process. The amount of reduced silver (as indicated by the height of the plasmon absorption band) is roughly proportional to the concentration of surfactant. They proposed that the surfactant reduces the silver ions to the neutral state through oxidation of oxyethylene groups to hydroperoxides. Surfactant molecules subsequently adsorb onto the surface of the particles, promoting a steric stabilization. In turn, the presence of the relatively large concentration of Ag^+ ions can induce their adsorption onto the surface of the particles, causing a red shift of the plasmon band [41]. This mechanism and the absorption of the surfactant molecules onto the particle surface are the most likely reasons for the measured red shift of the absorption band.



Fig. 11 shows a schematic representation of the three distinct regions created by the block copolymer: the framework that consists of silica or modified silica, the shell that is formed by the hydrophilic part of the surfactant (EO blocks which are water soluble) with residual solvent, and the core that is formed by the hydrophobic part of the surfactant.





Conclusions

Prolate silver nanoparticles with sizes smaller than 10 nm were synthesized into a SiO_2 matrix through the reduction of AgNO₃ with the non-ionic diblock copolymer, Brij 58. The use of the surfactant (Brij 58) allows to control the size and shape of the silver nanoparticles embedded into the silica matrix. The AgNO₃/Brij58 ratio has an important effect on the extent of the reduction. A high surfactant concentration is necessary for a complete reduction.

Based on our UV-Vis analysis, XRD, and HRTEM results, it was possible to confirm that the silver nanoparticles were oxidized forming silver core - silver oxide shell type nanostructures oriented as a long line or randomly dispersed. The second thin bright shell covering the metallic silver - silver oxide shell system corresponds to the surfactant.

The observed red shift of the silver plasmon absorption band can be due to (i) the size and shape distribution of the particles, (ii) the high local refractive index of the medium surrounding the nanoparticles and (iii) the presence of free Ag^+ ions adsorbed onto the surface of the particles.

The physical characteristics of the system such as shape and size of the metallic nanoparticles and the refractive index of silver oxide shell should be taken into account to obtain a good fit to the experimental optical absorption spectra. The contributions of silver core–silver oxide shell structures play an important role on the optical properties of the films.

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