

Modeling of core-shell silver nanoparticles in nanostructured sol-gel thin films

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ABSTRACT

Silver nanoparticles were obtained by UV radiation of silica films containing Ag^+ ions. 2d-hexagonal nanostructured sol-gel thin films were prepared by dip-coating method using the non-ionic diblock copolymer Brij58 to produce channels into the film, which house the silver nanoparticles. An absorption band located at 438 nm was detected; it corresponds to the surface plasmon resonance. High resolution transmission electronic microscopy measurements show core-shell structures of silver-silver oxide nanoparticles in these sol-gel silica films. These optical properties were modeled and well fitted with the Gans theory considering refractive index higher than the one coming from host matrix. This index is explained because the silver oxide shell modifies the local surrounding medium of the metallic nanoparticles and therefore plays an important role in the optical properties of the films.

KEYWORDS: Gans theory, core-shell, sol-gel, silver nanoparticles, surfactant, thin film

1. INTRODUCTION

Metallic nanoparticles embedded in amorphous SiO_2 glasses (dielectric matrix) exhibit very interesting optical properties because of their technological applications in photo electrodes for solar cells¹, optical switches², electronic and magnetic devices, catalysis or sensor applications³⁻⁶. These properties depend on the size, shape and dielectric environment surrounding the nanoparticles⁶.

The metallic nanoparticles exhibit the property of 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 of several factors as the local refractive index⁶, 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 of 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 nanoparticles⁷⁻¹⁷. The optical absorption can be calculated by the Gans theory, an extended Mie's theory to prolate or oblate particles averaged over all orientations^{10, 11, 18}.

Mesoporous silica materials have been doped with metallic nanoparticles as silver or gold to modify their properties and to improve them¹⁹. In particular, nanostructured 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 as sensors, catalysts, electrochemical or optical devices^{20, 21}. Nanostructured silica films can be synthesized by using a 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 rodlike micelles in water²². 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 architecture²³. Metallic nanoparticles formation carried out in the presence of surfactants frequently leads to the generation of 1-, 2-, or 3-dimensional (1-, 2-, or 3-D, respectively) networks of microporous channels^{24, 25}. Cubic, hexagonal or lamellar mesophases can be obtained controlling the surfactant concentration²⁶. The dimension of the pore can be controlled using different types of block copolymers²⁷.

In this work, long-ordered nanostructured sol-gel films were doped with silver nitrate (AgNO₃) under acidic conditions. An ethylene oxide based non-ionic diblock copolymer Brij58 (C₁₆H₃₃PEO₂₀) was used as template for silica polymerization in the synthesis of uniformly distributed silver-ion-containing nanostructured silica films. The reduction by UV light of Ag⁺ ions embedded into nanostructured silica matrix to silver metallic nanoparticles was monitored by UV-vis absorption spectroscopy. Stable optical properties were obtained from random-oriented silver prolate nanoparticles embedded in nanostructured silica films prepared by the dip-coating method. The reduced size of the silver nanoparticles was obtained by controlling the pore dimension due to the presence of the surfactant, Brij 58. Besides, a block copolymer shell was formed surrounding the silver oxide shell. Gans theory including a variable refractive index^{28, 29} was used to fit the experimental absorption spectra and these results are discussed. They indicate that is necessary to consider the presence of metallic oxidized particles in order to have a successfully fit to the data.

2. EXPERIMENTAL

Glass substrates were cleaned in boiling acidic solution of sulphuric acid-H₂O₂ (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 sol³⁰. Convection-free drying was critical to obtain high optical quality films.

All reagents were Aldrich grade. An initial solution was prepared with AgNO₃ (silver nitrate) dissolved in deionized water and nitric acid. Then was added to the solution 1 g of methanol, 5.4 g of TMOS (Tetramethyl orthosilicate), and 4g of the non-ionic diblock copolymer Brij58 (C₁₆H₃₃PEO₂₀). This solution was refluxed at 50-70 °C for 20 minutes to homogenize the mixture. The final molar ratio was TMOS: MeOH: Nitric acid: H₂O: C₁₆H₃₃PEO₂₀: AgNO₃ = 1:0.9:0.13:6.25:0.1:0.06 to obtain the SiO₂ thin films doped with silver ions. The reduction of Ag⁺ ions embedded into nanostructured silica matrix to silver metallic nanoparticles was obtained by the exposition of the film to UV radiation for 6 hours. The film was placed at 3 cm under to the UV light emitted by a Mineralight lamp Model UVGL-58. The 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 by 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 2 θ and an integration time of 2 s was used. Another characterization of the structure was achieved from conventional transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) by means of a JEM-2010F FASTEM electron microscope at 200kV with 0.19 nm resolution. From the HRTEM micrographs, mean particle size and particle size distribution were calculated, too. The thickness of the films was measured using a SEM microscopy Model STEREOSCAN at 20 kV.

3. GANS THEORY

For spheroid metallic nanoparticles well separated and which size is $R \ll \lambda$, 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 orientations³¹. 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^{31, 32}.

$$\alpha = -(\alpha_1 + \alpha_2) \quad (1)$$

where

$$\alpha_1 = \frac{3\phi\omega n^3}{9cp^2} \left\{ \frac{\epsilon_2(\omega)}{[\epsilon_1(\omega) + n^2(1/p' - 1)]^2 + \epsilon_2(\omega)^2} \right\} \quad (2)$$

$$\alpha_2 = \frac{3\phi\omega n^3}{9cp^{n2}} \left\{ \frac{2\epsilon_2(\omega)}{[\epsilon_1(\omega) + n^2(1/p'' - 1)]^2 + \epsilon_2(\omega)^2} \right\} \quad (3)$$

Specifically, for prolate nanoparticles we have that:

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

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

$$e = \sqrt{1 - (B/A)^2} \quad (6)$$

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, $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ 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 with $A > B = C$. The ratio B/A is the axial ratio (Θ).

Moreover, the dielectric constant of the metal bulk 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 as²⁸

$$\epsilon_1(\omega, R) = \epsilon_1(\omega) \quad (7)$$

$$\epsilon_2(\omega, R) = \epsilon_2(\omega) + \eta \frac{\omega_p^2}{\omega^3} \left(\frac{V_f}{R} \right) \quad (8)$$

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 on²⁸. Using the equations (1)-(8) we can obtain the calculated absorption spectra of silver nanoparticles in 2d-hexagonal nanostructured sol-gel thin films. Thus, the Gans theory can provide information with regards to size and shape of the metallic nanoparticles as well as of the local refractive index of the medium surrounding the silver nanoparticles.

4. RESULTS AND DISCUSSION

Silver metallic nanoparticles were produced by spontaneous reduction of silver ions deposited on the nanostructured SiO₂ matrix. A colorless film was obtained when only silver ions were present in the matrix. On the other hand, the presence of the silver metallic nanoparticles can be identified by the black color of the sol-gel films acquired after exposition to UV light for six hours.

The thickness of the films was measured by SEM technique (Figure 1). It was 3.272 μm .

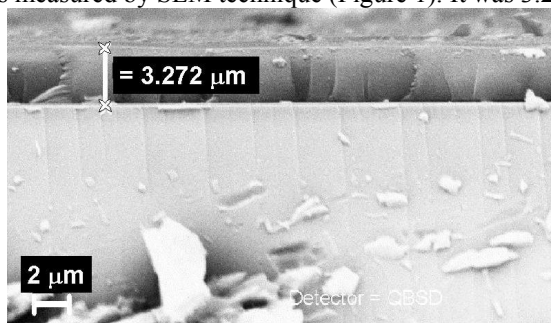


Figure 1. Cross-sectional SEM image of film with silver metallic nanoparticles. The thickness measured is 3.272 μm .

4.1. Optical absorption. Other evidence of the previous process was followed by UV-vis optical absorption. Figure 2 shows the optical absorption spectra taken at room temperature in the range of 300-900 nm. The absorption spectrum of the colorless silica film does not exhibit any band (gray line). The spectrum of the black silica film (black line) shows an absorption band A located at 438 nm. This spectrum shows a broad and asymmetric band suggesting the presence of silver metallic nanoparticles of non-uniform size. For silver nanoparticles under oxidizing atmosphere embedded in silica gels has been reported an absorption peak centred at 425 nm^{28, 29}. A red shift was observed in our spectrum, it can be attributed to deformed silver particles covered with a silver oxide shell.

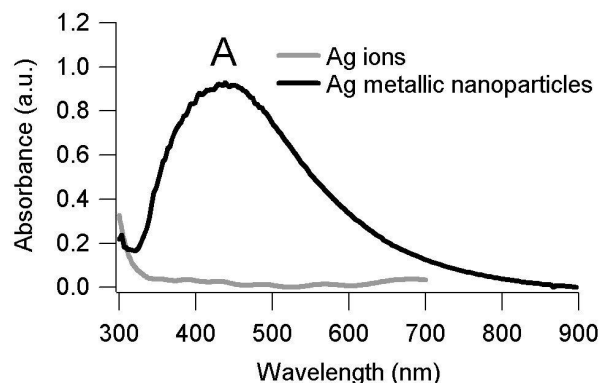


Figure 2. Absorption spectra of the nanostructured sol-gel silica film with silver ions corresponding a colorless silica film (gray line), and a nanostructured sol-gel silica film with silver metallic nanoparticles corresponding a black silica film (black line). The film was exposed to UV radiation for 6 hours.

4.2. TEM and HRTEM measurements. Figure 3 (a) corresponds to the TEM image showing metallic silver small nanoparticles randomly oriented with prolate shape. Figure 3 (b) shows the HRTEM image of one silver nanoparticle. Its diffraction pattern indicates that the particle is crystalline.

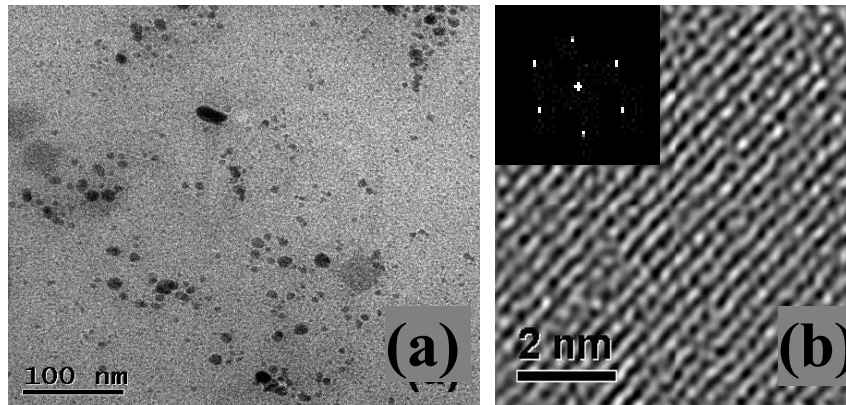


Figure 3. Representative HRTEM micrographs of hexagonal films mesophases. (a) TEM image of the small metallic silver nanoparticles with prolate shape. (b) HRTEM cross-section of hexagonal film formed from the non-ionic diblock copolymer Brij 58.

According to these images, the optical properties observed in the absorption spectrum (Fig. 2) are due to metallic silver nanoparticles. Besides, HRTEM images obtained with filtered energy, shown core-shell structures of metallic silver-silver oxide (Fig. 4). Silver particles covered with a thin block copolymer (surfactant) can be evidently observed. In particular, this particle has a major axis of 29.02 nm, and its minor axis is 18.49 nm. The Ag_2O shell has a thickness of 1.14 nm and the block copolymer shell has a thickness of 1.14 nm, too. A remarkable characteristic is the fact that for particles with diameters between 15-20 nm and small surface area, the shell is very thin; on the other hand for particles with diameters 5 nm and large surface area the shell becomes very thick³³. This effect is due to the chemical reactivity on the surface area.

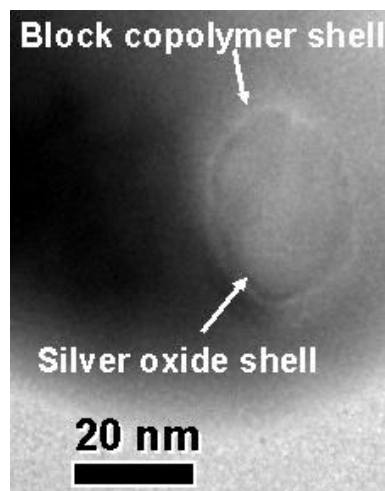


Figure 4. The HRTEM image of the resulting core-shell nanoparticles.

From HRTEM studies, the corresponding size-distribution histograms were obtained (Figure 5). The distributions from the minor length axis B and major axis A of the metallic nanoparticles are very broad. We obtained as average $B = 5.9 \pm 3.3$ nm (Fig. 5a), $A = 7.8 \pm 4.2$ nm (Fig. 5b) and the mean axial ratio AR was 0.80. The average size of the silver nanoparticles was $2R < 20$ nm and therefore the Gans theory can be used to fit the optical absorption spectrum of the silver metallic silica film.

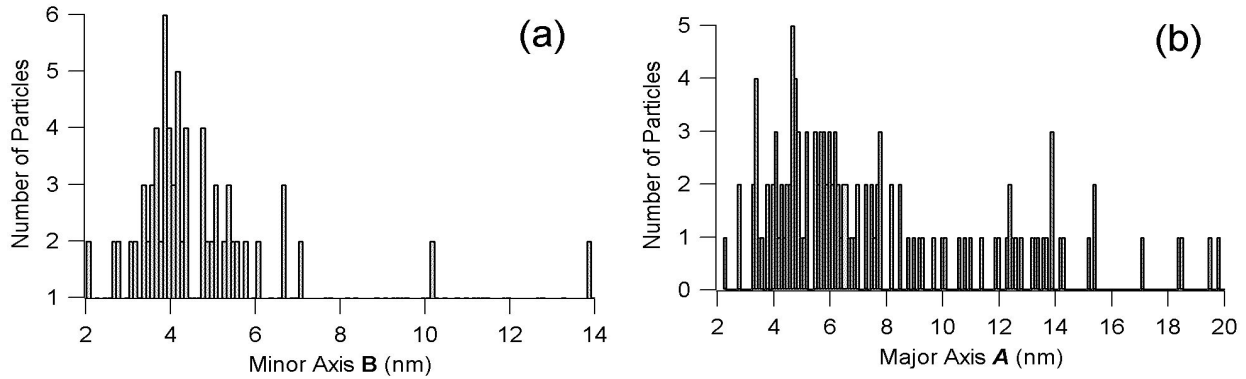


Figure 5. Size-distribution histograms obtained by HRTEM analysis of silver nanoparticles embedded in silica matrix.

4.3. Fits by Gans theory. Renteria et al²⁹ 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. Using this idea, the envelope corresponding to the calculated absorption spectrum can be obtained from adding the absorption bands of prolate nanoparticles 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 to fit the experimental absorption spectrum (Figure 2).

The experimental and calculated spectra of isolated silver nanoparticles in nanostructured silica films are shown in Figure 6. In the fit done with the Gans theory for isolated silver particles, the dielectric constants $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ measured by Johnson and Christy³⁴ were used, and it was considered $\omega_p = 1.38 \times 10^{16} \text{ s}^{-1}$ and $V_f = 1.4 \times 10^6 \text{ ms}^{-1}$ for silver²⁸. This fit was obtained by using the experimental data from size-distribution histograms of Fig. 5. The refractive index $n_1 = 1.47$ corresponding to the silica framework, which covers the silver nanoparticles, and a high refractive $n_2 = 2.04$ were used in eq. (2)-(3) to achieve this good fit. This last index is due to the silver oxide shell ($n = 2.5^{35}$) formed around the silver nanoparticles, and therefore the local refractive index grows with the oxidation process and determinates the maximum wavelength position of the surface plasmon resonance²⁸. Therefore, good fits were obtained using high refractive indexes ($n \geq 1.50$) in films exposed to UV radiation. Consequently, the silver oxide shell modifies the local surrounding medium of the metallic nanoparticles and therefore the optical properties of the films. This high refractive index of the dielectric medium produces the red shift of the peak of the optical absorption from metallic nanoparticles²⁹ observed in Figure 2.

These observed silver oxide shells surrounding the metallic suggest an important influence of the oxygen on the metallic nanoparticles obtained in nanostructured silica films.

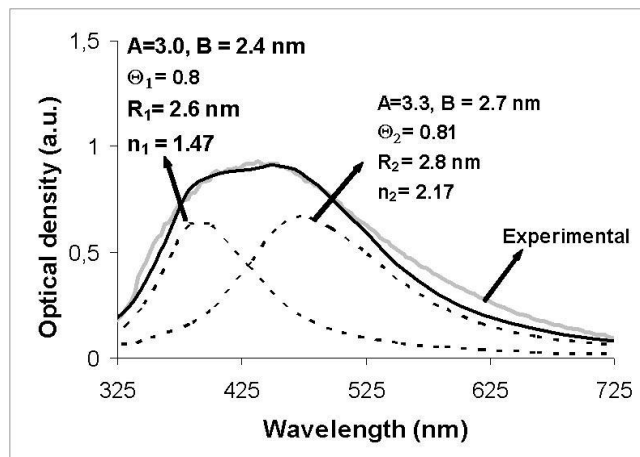


Figure 6. Experimental optical absorption spectrum (gray solid line) from film with silver metallic nanoparticles. Calculated optical absorption spectra (black solid line) for the sample were obtained using the Gans model. The envelope is the result from the convolution of the component bands (black dotted lines) observed in the figure.

4.4. Surfactant effect. The surfactant (Brij 58) allowed the control of small sizes and specific prolate shape of silver nanoparticles. Furthermore, these silver nanoparticles were stabilized by the surfactant shell obtaining an excellent particle size control^{35, 36}. Figure 7 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 (PEO blocks which are water soluble) with residual solvent, and the core that is form by the hydrophobic part of the surfactant.

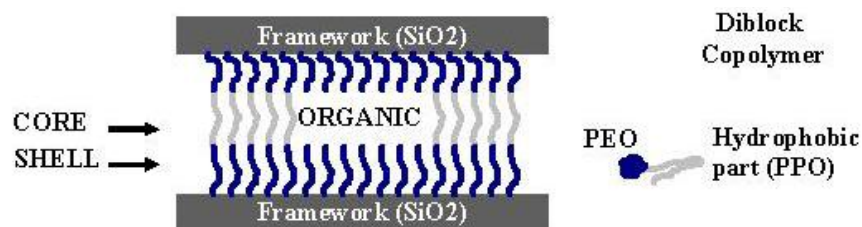


Figure 7. Sketch of the three regions of nanostructured sol-gel thin films prepared with diblock copolymers.

4.5. X-ray patterns. The presence of the silver oxide shell surrounding the metallic particles was confirmed by XRD studies. Figure 8 shows the XRD patterns at high angle of (a) SiO₂:Brij58 thin film, and (b) nanostructured silica film with silver nanoparticles. From Fig. 8 (b), the diffraction peaks located at $2\theta = 27.9, 34.3, 46.35, 50.25, 57.5$ can be indexed as (110), (111), (200), (211) and (220) respectively. The position of the diffraction peaks in the film is in good agreement with those given in ASTM data card (#03-0796) for silver oxide. The diffraction peaks are located at $2\theta = 19.45$ and 23.15 correspond to the surfactant Brij58, and they are marked with asterisk.

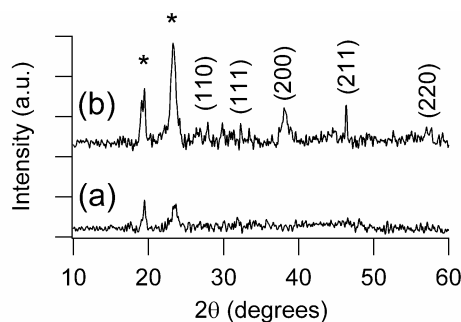


Figure 8. XRD pattern at high angle of (a) block copolymer Brij 58, and (b) nanostructured silica film with silver metallic nanoparticles templated with Brij58.

5. CONCLUSIONS

Silver prolate nanoparticles with size smaller than 10 nm were obtained by UV radiation reduction of silver ions in nanostructured silica films. Based on UV-vis analysis and HRTEM images, it was possible to confirm that the silver nanoparticles randomly dispersed were oxidized obtaining silver core-silver oxide shells nanostructures. The thickness shell grows with the oxidation process. The use of the surfactant (Brij 58) allows to control the size and shape of the silver nanoparticles embedded into the silica matrix. The physical characteristics of the system such as shape and size of the metallic nanoparticles, and the refractive index from silver oxide shell depending of its thickness were taking in account to obtain a good fit to the experimental optical absorption spectrum. The contributions of silver core-silver oxide shell species play an important role in the optical properties of the films.

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REFERENCES

1. H. Kozuka, "Metal nanoparticles in gel-derived oxide coating films: control and application of surface plasma resonance", *SPIE*, 3136, 304-314, 1997.
2. C. Weiping, T. Ming, Z. Lide, "Characterization and the optical switching phenomenon of porous silica dispersed with silver nano-particles within its pores", *J. Phys: Condens. Matter.*, **8** (40), L591-L596, 1996.
3. Y. Masumoto, T. Kawamura, "Biexciton lasing in CuCl quantum dots", *Appl. Phys. Lett.*, **62** (3), 225-227, 1993.
4. Y. Sun, B. Mayers, and Y. Xia, "Transformation of Silver Nanospheres into Nanobelts and Triangular Nanoplates through a Thermal Process" *Nano Letters*, **3** (5), 675-679, 2003.
5. G. Compagnini, L. D'Urso and O. Puglisi, "Structure and properties of silver nanoparticles dispersed in SiO₂ thin films obtained by in situ self-reduction", *Mater. Sci. and Eng.: C*, **19** (1-2), 295-298, 2002.
6. K. Naoi, Y. Ohko, and T. Tatsuma, "TiO₂ Films Loaded with Silver Nanoparticles: Control of Multicolor Photochromic Behavior", *J. Am. Chem. Soc.*, **126** (11), 3664-3668, 2004.
7. C. G. Granqvist, O. Hunderi, "Optical properties of ultrafine gold particles", *Phys. Rev. B*, **16** (8), 3513-3534, 1977.
8. H. Xu and M. Käll, "Modeling the optical response of nanoparticle-based surface plasmon resonance sensors", *Sensors and Actuators B: Chemical*, **87** (2,10), 244-249, 2002.
9. G. W. Arnold, "Near-surface nucleation and crystallization of an ion-implanted lithia-alumina-silica glass", *J. Appl. Phys.*, **46** (10), 4466-4473, 1975.
10. D. C. Skillman, C. R. Berry, "Effect of Particle Shape on the Spectral Absorption of Colloidal Silver in Gelatin", *J. Chem. Phys.*, **48** (7), 3297-3304, 1968.
11. S. Link, M. B. Mohamed, and M. A. El-Sayed, "Simulation of the Optical Absorption Spectra of Gold Nanorods as a Function of Their Aspect Ratio and the Effect of the Medium Dielectric Constant", *J. Phys. Chem. B*, **103** (16), 3073-3077, 1999.
12. M. C. Buncick, R. J. Warmack, T. F. Ferrell, "Optical absorbance of silver ellipsoidal particles", *J. Opt. Soc. Am. B*, **4** (6), 927-933, 1987.
13. G. L. Hornyak, C. J. Patrissi, C. R. Martin, J-C Valmalette, J. Dutta and H. Hofmann, "Dynamical Maxwell-Garnett optical modeling of nanogold-porous alumina composites: Mie and Kappa influence on absorption maxima", *Nanostructured Materials*, **9** (1-8), 575-578, 1997.
14. M. A. Garcia, J. Llopis, S. E. Paje, "A simple model for evaluating the optical absorption spectrum from small Au-colloids in sol-gel films", *Chem. Phys. Lett.*, **315** (5-6), 313-320, 1999.
15. C. A. Foss, G. L. Hornyak, J. A. Stockert, C. R. Martin, *J. Phys. Chem.*, **98**, 2963-2971, 1994.
16. J. A. Creighton, D. G. Eadon, "Ultraviolet-visible absorption spectra of the colloidal metallic elements", *J. Chem. Soc. Faraday Trans.*, **87**, 3881-3891, 1991.
17. A. L. Stepanov, S. N. Abdullin, I. B. Khaibullin, "Optical properties of polymer layers with silver particles", *J. Non Cryst. Solids*, **223** (3), 250-253, 1998.
18. A. Berger, "Prolate silver particles in glass surfaces", *J. Non-Cryst. Solids*, **163** (2), 185-194, 1993.
19. O. Samarskaya, Ö. Dag, "Silver Nitrate/Oligo(ethylene Oxide) Surfactant/Mesoporous Silica Nanocomposite Films and Monoliths", *J. Colloid and Interf. Sci.*, **238** (1), 203-207, 2001.
20. H. Winkler, A. Birkner, V. Hagen, I. Wolf, R. Schmechel, H. Seggern, R. A. Fischer, "Quantum-Confined Gallium Nitride in MCM-41", *Adv. Mater.*, **11** (17), 1444-1448, 1999.
21. A. Bearzotti, J. Mio Bertolo, P. Innocenzi, P. Falcaro, E. Traversa, "Humidity sensors based on mesoporous silica thin films synthesised by block copolymers", *J. of the European Ceram. Soc.*, **24** (69) 1969-1972, 2004.
22. J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London, 1991.
23. D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, "Nonionic Triblock and Star Diblock Copolymer and Oligomeric Surfactant Syntheses of Highly Ordered, Hydrothermally Stable, Mesoporous Silica Structures", *J. Am. Chem. Soc.*, **120** (24), 6024-6036, 1998.
24. C. J. Murphy, T. K. Sau, Anand Gole, C. J. Orendorff, "Surfactant-Directed Synthesis and Optical Properties of One-Dimensional Plasmonic Metallic Nanostructures", *MRS Bulletin*, **30** (5), 349-355, 2005.
25. C. J. Brinker, Y. Lu, A. Sellinger, H. Fan, *Adv. Mater.* **11** (7), 579, 1999.

26. P. C. A. Alberius, K. L. Frindell, R. C. Hayward, E. J. Kramer, G. D. Stucky, B. F. Chmelka, "General Predictive Syntheses of Cubic, Hexagonal, and Lamellar Silica and Titania Mesostructured Thin Films", *Chem. Mater.*, **14** (8), 3284-3294, 2002.
27. B. Smarsly, S. Polarz, M. Antonietti, "Preparation of Porous Silica Materials via Sol-Gel Nanocasting of Nonionic Surfactants: A Mechanistic Study on the Self-Aggregation of Amphiphiles for the Precise Prediction of the Mesopore Size", *J. Phys. Chem. B*, **105** (43), 10473-10483, 2001.
28. V. M. Renteria, J. Garcia-Macedo, "Modeling of optical absorption of silver prolate nanoparticles embedded in sol-gel glasses", *Materials Chemistry and Physics*, **91**, 88-93, 2005.
29. V.M. Rentería, J. García-Macedo, "Influence of the local dielectric constant on modelling the optical absorption of silver nanoparticles in silica gels colloids", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **278** (1-3), 1-9, 2006.
30. F. Nishida, J. M. McKierman, B. Dunn, J. I. Zink, C. J. Brinker, A. J. Hurd, "*In Situ* Fluorescence Probing of the Chemical Changes during Sol-Gel Thin Film Formation", *J. Am. Ceram. Soc.*, **78** (6), 1640-1648, 1995.
31. C.F. Bohren, D.R. Huffman, *Absorption and Scattering of Light by Small Particles*, John Wiley & Sons, New York, 1983.
32. J. Pérez-Juste, I. Pastoriza-Santos, L. M. Liz-Marzán, P. Mulvaney, "Gold nanorods: Synthesis, characterization and applications", *Coordination Chemistry Reviews*, **249** (17-18), 1870-1901, 2005.
33. V. M. Renteria, J. Garcia-Macedo, "Optical properties of metallic nanoparticles in sol-gel films silica annealed under reducing and oxidizing atmosphere", Submitted on *J. Nanoscience and Nanotech.* June 2007.
34. P.B. Johnson, R.W. Christy, "Optical Constants of the Noble Metals", *Phys. Rev. B*, **6** (12), 4370-4379, 1972.
35. J. F. Rivadulla, M. C. Vergara, M. C. Blanco, M. A. López-Quintela, J. Rivas, "Optical Properties of Platinum Particles Synthesized in Microemulsions", *J. Phys. Chem. B*, **101** (44), 8997-9004, 1997.
36. S. Brimaud, C. Coutanceau, E. Garnier, J.-M. Leger, F. Gerard, S. Pronier, M. Leoni, "Influence of surfactant removal by chemical or thermal methods on structure and electroactivity of Pt/C catalysts prepared by water-in-oil microemulsion", *J. Electroanalytical Chem.*, **602** (2), 226-236, 2007.