Solvent and ligand effects on the optical properties of silver nanoparticles in silica sol−gel films

J. A. García−Macedo [1*], V. M. Rentería−Tapia [1], G. Valverde−Aguilar [1]

1. Departamento de Estado Sólido. Instituto de Física, Universidad Nacional Autónoma de México. México D.F. C.P. 04510

* Contact author:
Dr. Jorge Garcia Macedo
Instituto de Física, UNAM
Circuito de la Inv. Científica s/n
C. P. 04510. Del. Coyoacán
México, D.F.
México.
Tel. (5255) 5622−51−03
Fax (5255) 5616−15−35
E−mail: gamaj@fisica.unam.mx

ABSTRACT

Silver nanoparticles in sol−gel silica films have been synthesized by heat treatment in air atmosphere. We find that the surface plasmon resonance exhibits a principal peak at 534 nm, longer wavelength than that corresponding to the spherical silver nanoparticles in silica (400 nm). The anisotropy in the geometry of the metallic nanoparticles explains this noticeably red shift of the silver nanoparticles. The effect of solvents (ethanol, cyclohexane and toluene) and ligand (pyridine) on the optical properties of these nanoparticles are measured by UV−vis spectroscopy. The position of the surface plasmon resonance varies from 534 nm up to 573 nm depending on the refractive index or the concentration of the solvents. On the contrary, the surface plasmon resonance is gradually shifted to the blue from 534 nm up to 462 nm when the films were immersed in pyridine due to complexing on the surface of silver nanoparticles. These results show highest sensitivity of the surface plasmon to variations in the local environment of the nanoparticles and they suggest that the films can be used as colorimetric sensors.

KEYWORDS: Silver nanoparticles, sol-gel, thin film, colorimetric sensor

1. INTRODUCTION

A great effort has been done to prepare metallic nanoparticles of several sizes and shapes since they exhibit unusual optical, electronic, catalytic and magnetic properties in comparison to those of the bulk materials [1]. In particular, the linear optical properties of metallic nanoparticles have been extensively researched due to their potential in sensors and photonic applications [2−5]. The interesting colors that the metallic colloids exhibit are due to the surface plasmon resonance produced for collective oscillations of conduction electrons. Excitation of these electrons by an electromagnetic field causes scattering and absorption [6]. The resonance depends on the adsorbate−particle interaction, dielectric environment and morphology of the metallic nanoparticles. For example, the interaction of silver nanoparticles with organo−sulfur compounds causes a drastic red shift, broadening and damping of the surface plasmon [7]. Similarly, it has been reported the dependence of the surface plasmon resonance from non−spherical nanoparticles on the refractive index of the medium [8]. On the other hand, the Mie theory in the dipole approximation predicts color changes of

metallic spherical nanoparticles when immersing them in different solvents [9]. Furthermore, the Gans theory provides relatively good predictions of the absorption coefficient α of elongated nanoparticles [10–11]. In this theory, α is calculated in terms of the dielectric constant ε of the metal bulk, the dielectric constant of the medium $\varepsilon_m = n^2$ as well as of the axial ratio AR. In particular, the theory predicts that the surface plasmon resonance of prolate silver nanoparticles is splitted in two modes. One mode is located at short wavelength (transversal mode) and is little sensitive toward the deformation of the nanoparticle (AR < 1). The second mode is located at longer wavelength (longitudinal mode) and is very sensitive toward deformation of the nanoparticle. These modes respond to the changes of the dielectric environment and therefore, can be used for detection of organic molecules [12]. Evidently when AR = 1 (spherical nanoparticles) the Mie theory is obtained in the dipole aproximation.

2. 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. In order to prepare the sol–gel silica films containing silver nanoparticles the following procedure was used. Tetraethoxyorthosilicate (TEOS), deionized water and ethanol (EtOH), were mixed in plastic beakers in the relative molar concentrations [TEOS/H_2O/EtOH/]=[1/4/3]. Afterwards, concentrated HNO_3 (66.4%) and the precursor salt (AgNO$_3$) of metallic nanoparticles were added to the mixture. The concentration of AgNO$_3$ was 170 mM. The resulting sol (pH = 1) was stirred for 30 minutes and deposited on the silica glass substrates by the spin–coating method. The films were aged at room temperature around 1 month and then heated in an air atmosphere for 5 min at 280 ^{0}C. Subsequently, the films were immersed in ethanol, cyclohexane, toluene and pyridine at 40 ^{0}C at several concentrations. The optical properties of the films were recorded with a Thermospectronic Genesys 2 spectrophotometer with an accuracy of ±1 nm over the wavelength range of 300–900 nm at room temperature. FTIR spectra were obtained from a film immersed in pyridine using a Bruker Tensor 27 FT-IR spectrometer. They were taken at room temperature in the region 400-1300 cm^{-1}.

3. RESULTS AND DISCUSSION

The sol–gel silica films containing silver ions acquire a pink color when they are heated at 280 ^{0}C in an air atmosphere. In Fig. 1 are shown the experimental optical spectrum of these films and the simulated absorption spectra by Gans theory for silver nanoparticles in SiO$_2$ films (n = 1.46), for several axial ratio. The experimental spectrum (continue line) exhibits a strong resonance about $\lambda_0 = 534$ nm and two weak peaks located at 354 and 387 nm. However, this spectrum is unlike the simulated absorption spectra in dipole approximation (dashed lines) for spherical (AR = 1) or deformed particles (AR < 1). It is observed that the experimental spectrum is noticeably red shift (strong peak in 534 nm) with regards to the simulated spectrum for spherical silver nanoparticles (peak at 400 nm). The simulated spectra with axial ratio 0.4 show that the surface plasmon resonance is splitted in two modes (longitudinal and transversal modes) coming from deformed silver nanoparticles (like nanorods). In no case the calculated optical absorption matched the optical features of the experimental absorption. So, the spectrum observed in Fig. 1 is more complicated than those corresponding to spherical or rod–like silver nanoparticles.
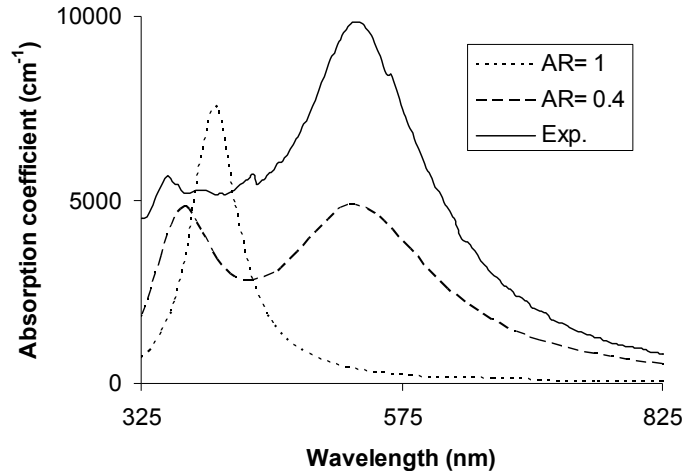
Figure 1. Surface plasmon resonance band of silver nanoparticles in a silica sol-gel film (−). The simulated spectra for spherical (--) and deformed (− −) silver nanoparticles are also shown.

It has been predicted that the anisotropy in the geometry of the metallic nanoparticles (Ag or Au) would have two or more peaks depending of their shape, although some these peaks are enough weak [13−14]. In particular for silver nanoplates, the number of the absorption peaks increases from 3 to 6 and then decreases to 2 as a result of their enlargement [14]. Then, the position of these peaks is correlated with the aspect ratio of silver nanoplates. In fact, the spectrum observed in Fig. 1 is similar to the one coming from of silver nanoplates obtained in aqueous solution [13−14]. Moreover, it has been suggested that these nanostructures are formed starting from spherical or semispherical seeds of silver nanoparticles in presence of oxygen [13]. In our case, a similar process could occur in the formation of these silver nanoplates, according to the next process. A weak surface plasmon resonance located in 450 nm observed in aged films before heat treatment, suggests the formation of seeds of silver. So, the nanoplates are formed starting from these seeds during the heat treatment of the films in an air atmosphere. Furthermore, the optical absorption spectrum registered in Fig. 1 was also reproduced when the films containing silver ions were reduced in a hydrogen atmosphere and subsequently heated in an air atmosphere. So, it is probable that the spectrum observed in Fig. 1 corresponds to silver nanoplates. In order to confirm the presence of these nanostructures the characterization of the films by high resolution transmission electronic microscopy is under process.

On the other hand, the surface plasmon resonance of these nanoparticles is highly sensitive to changes in the refractive index, since strong shifts were observed for films immersed in pure ethanol, cyclohexane and toluene (Fig. 2). In all these cases, λ_0 gradually exhibited a red shift up to achieve a maximum wavelength λ_1 as function of the refractive index of solvents. However, we observe that λ_1 is not linearly dependent on the refractive index and additionally we observed damping of the surface plasmon resonance after immersion of the films in those solvents. For example, in Fig. 3 are shown the optical absorption spectra of the silver nanoparticles in a silica sol-gel film before (a) and after (b) of immersing it in pure toluene (n = 1.5) at 40 °C for 10 min. After immersion of the films the optical absorption band is broadened, diminished and red shifted (from 534 up to 573 nm). However, according to the Mie theory it is expected only a red shift without important influence on the bandwidth [15]. So, the effect of the refractive index on the surface plasmon resonance partially explains the red shift. Since solvents as ethanol, cyclohexane and toluene have not noticeable chemical interaction on the surface of silver nanoparticles, the red shift may result from additional factors such as aggregation of silver nanoparticles [16]. This hypothesis is based on the irreversibility of the UV−vis spectra after colorimetric test of the films. Anyway, the highest sensitivity observed in Fig. 2 is justified because of the shape of the silver nanoparticles. The surface plasma modes in plate or rod−shaped particles have higher oscillator strengths and therefore more sensitivity to the surface perturbations than spherical nanoparticles [15].
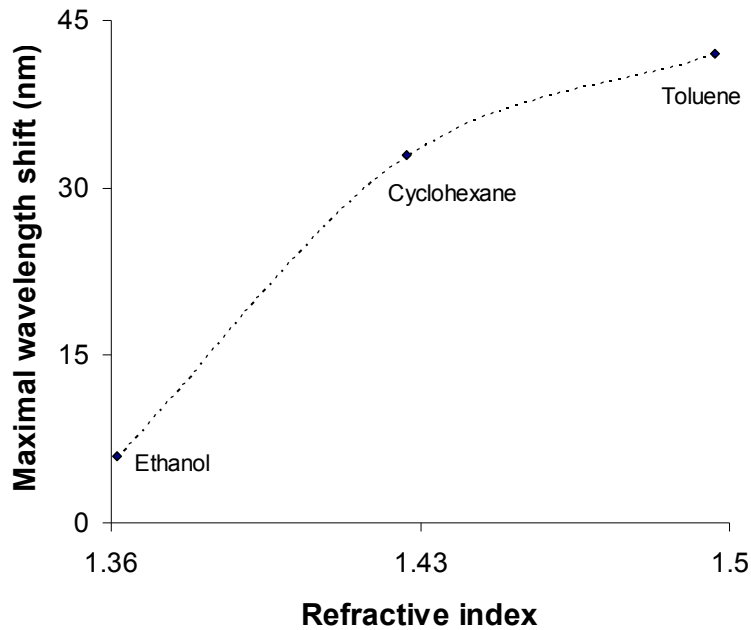
Figure 2. Plot of the maximal wavelength shift of the surface plasmon resonance as function of the refractive index of the solvents. The dashed line is a guide for the eye.
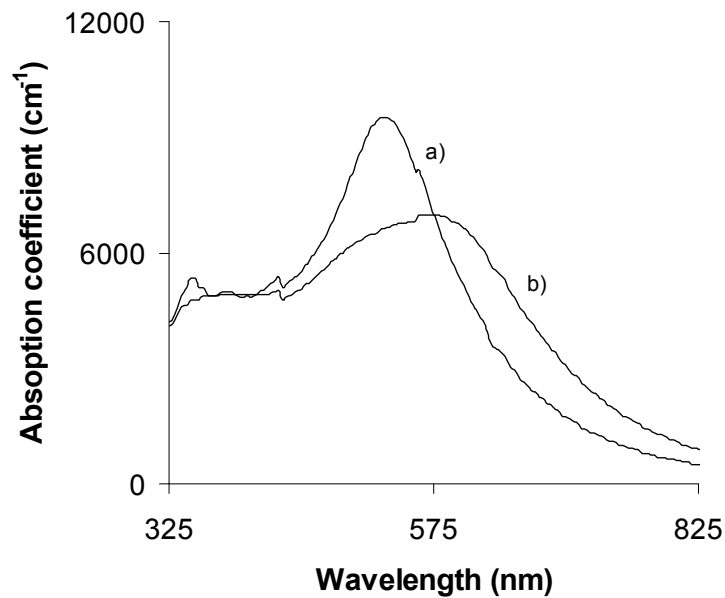

Figure 3. a) Surface plasmon resonance of silver nanoparticles in silica sol-gel films. b) Effect of toluene on the optical absorption of silver nanoparticles.

On the other hand, Fig. 4 shows the changes in the position of the maximum of the surface plasmon resonance as function of the toluene concentration. It was observed a red shift of the surface plasmon resonance with the increment of

the toluene concentration. Similar results observed with ethanol and ciclohexane (not shown) suggest that these films can be used as a colorimetric sensor.
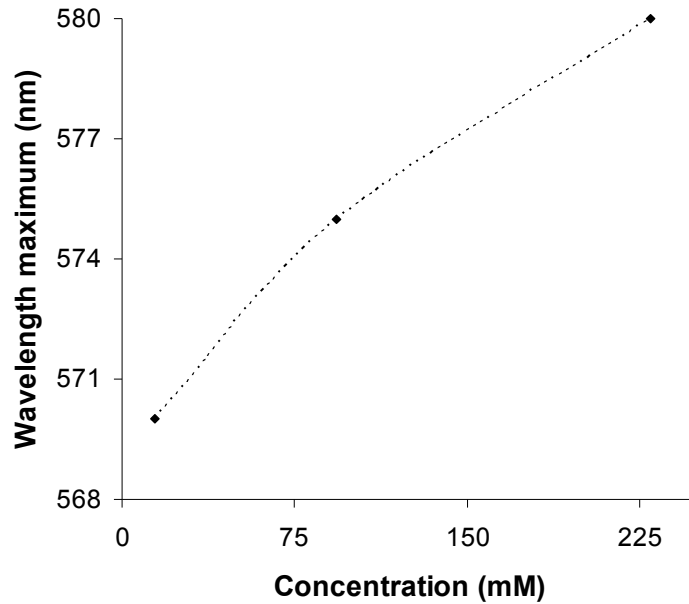

Figure 4. Plot of the maximum wavelength of the surface plasmon resonance as function of the toluene concentration.

Finally, we observed a gradual and strong blue shift of the surface plasmon resonance after immersion of the films in pyridine (Fig. 5). This optical absorption band was shifted from 534 up to 462 nm. This shift is explained by a charge-transfer interaction between pyridine and the silver nanoparticles.
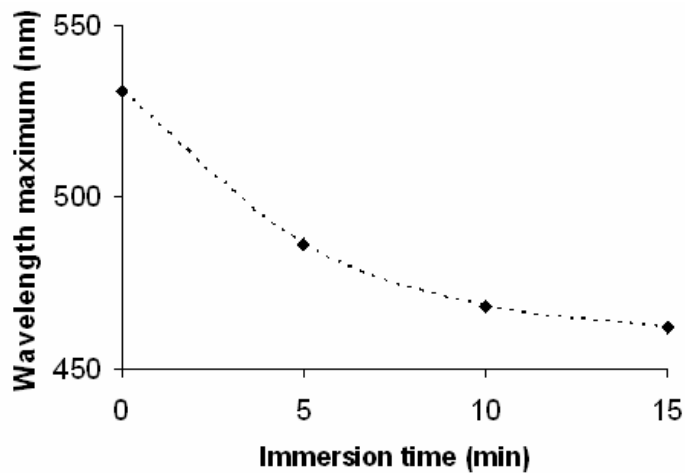

Figure 5. Plot of the maximum wavelength of the surface plasmon resonance as function of the immersion time of the films in pyridine. The dashed line is a guide for the eye.

The FTIR spectra of the film before (grey solid line) and after (black solid line) immersion in pyridine are shown in Fig. 6. Before and after the immersion of the film in pyridine, the bands for silica and silver are identified. The bands located at 434, 457, 563 and 768 cm^{-1} correspond to the silica [17, 18]. These bands are due to bending and stretching, vibrations. Specifically, the band at 768 cm^{-1} is attributed to the ring structure of the SiO tetrahedra. After the immersion of the film in pyridine, the bands of pyridine are located at 665, 718 and 754 cm^{-1}. These values coincide with those reported by Zingaro $et\ al.$ [19]. The bands from silver are located at 725, 802–810 and 822–831cm^{-1}. These values are in agreement with those reported by Miller $et\ al$ [20]. Table 1 contains the assignments of all bands from silver, SiO$_2$ and pyridine.
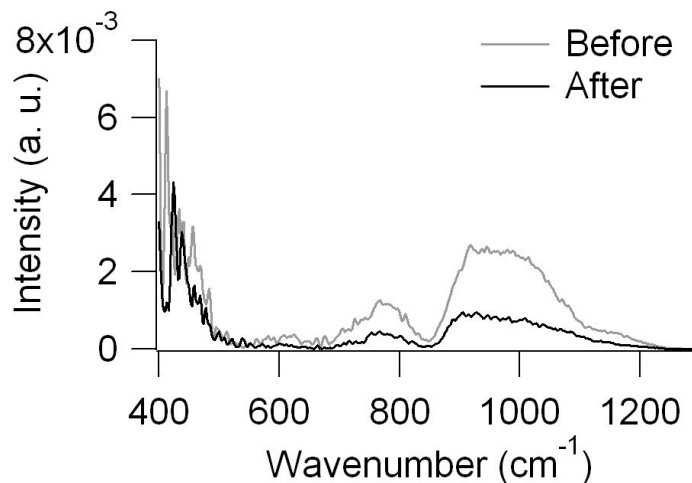

Figure 6. FTIR spectra of the SiO$_2$–Ag film before the immersion in pyridine (grey solid line) and after the immersion in pyridine (black solid line).

Table 1. IR frequencies [in cm^{-1}] from silver, SiO$_2$ and pyridine identified in the SiO$_2$–Ag film.

Before	After		
$\overline{v}_{exp}$ (cm^{-1})	$\overline{v}_{exp}$ (cm^{-1})	description	Ref.
434	438	δ_{as} (SiOC)	17
457	459	δ (Si-O-Si)	18
563	-	v (Si-OH)	18
-	665	pyridine	19
-	718	pyridine	19
725	-	silver	20
-	754	pyridine	19
768	768	v_s (Si–O–Si)	18
810	802	silver	20
831	822	silver	20
987	-	v (Si–OH)	18

4. CONCLUSIONS

Silver nanoparticles in sol−gel silica films were prepared in an oxidizing atmosphere. Their optical properties were studied by Uv−vis spectroscopy. The experimental and calculated data indicated that the silver nanoparticles are deformed (nanoplates−like). These nanoparticles in the sol-gel silica films have highest sensitivity to solvents due to the anisotropy in their geometry.

ACKNOWLEDGMENTS

REFERENCES

[1] Lue J-T, "A review of characterization and physical property studies of metallic nanoparticles", J. Phys. Chem. Solids, 62 (9−10), 1599−1612, 2001.

[2] Ullah M. H., Il K., Ha C-S, "Preparation and optical properties of colloidal silver nanoparticles at a high Ag^+ concentration", Mater. Lett., 60 (12), 1496−1501, 2006.

[3] Dubas S. T., Pimpan V., "Optical switch from silver nanocomposite thin films", Mater. Lett., 62 (19), 3361−3363, 2008.

[4] Babapour A., Akhavan O., Moshfegh A.Z., Hosseini A.A., "Size variation and optical absorption of sol-gel Ag nanoparticles doped SiO_2 thin film", Thin Solid Films, 515 (2), 771−774, 2006.

[5] Daniels J. K., Chumanov G., "Spectroelectrochemical studies of plasmon coupled silver nanoparticles", J. Electroanal. Chem., 575 (2), 203−209, 2005.

[6] Bratescu M. A., Saito N., Mori H., Takai O., "Localized surface plasmon resonance of silicon compounds adsorbed on silver nanoparticles", Surf. Sci., 601 (18), 3886−3891, 2007.

[7] Henglein A. and Meisel D., "Spectrophotometric observations of the adsorption of organosulfur compounds on colloidal silver nanoparticles", J. Phys. Chem. B, 102 (43), 8364–8366, 1998.

[8] Miller M. M. and Lazarides A. A., "Sensitivity of metal nanoparticle surface plasmon resonance to the dielectric environment", J. Phys. Chem. B, 109 (46), 21556–21565, 2005.

[9] Underwood S. and Mulvaney P., "Effect of the solution refractive index on the color of gold colloids", Langmuir, 10 (10), 3427–3430, 1994.

[10] Sprünken D. P., Omi H., Furukawa K., Nakashima H., Sychugov I., Kobayashi Y., and Torimitsu K., "Influence of the local environment on determining aspect-ratio distributions of gold nanorods in solution using Gans theory", J. Phys. Chem. C, 111 (39), 14299–14306, 2007.

[11] Link S. and El-Sayed M. A., "Spectral properties and relaxation dynamics of surface plasmon electronic oscillations in gold and silver nanodots and nanorods", J. Phys. Chem. B, 103 (40), 8410–8426, 1999.

[12] Cheng C-S, Chen Y-Q, Lu C-J, "Organic vapour sensing using localized surface plasmon resonance spectrum of metallic nanoparticles self assemble monolayer", Talanta 73 (2), 358−365, 2007.

[13] Tang B., Xu S., An J., Zhao B. and Xu W., "Photoinduced shape conversion and reconstruction of silver nanoprisms", Phys. Chem. C, 113 (17), 7025–7030, 2009.

[14] Zou X., Ying E., Chen H., Dong S., "An approach for synthesizing nanometer- to micrometer-sized silver nanoplates", Colloids and Surf. A: Physicochem. Eng. Aspects, 303 (3), 226−234, 2007.

[15] Jiang X. C. and Yu A. B., "Silver Nanoplates: A Highly Sensitive Material toward Inorganic Anions", Langmuir, 24 (8), 4300–4309, 2008.

[16] Kulkarni A. P., Munechika K., Noone K. M., Smith J. M. and Ginger D. S. , "Phase transfer of large anisotropic plasmon resonant silver nanoparticles from aqueous to organic solution", Langmuir, in press, 2009.

[17] Mondragón, M. A., Castaño, V. M., Garcia, J., Téllez, C. A., "Vibrational analysis of $Si(OC_2H_5)_4$ and spectroscopic studies on the formation of glasses via silica gels", Vibrational Spectroscopy 9, 293−304 (1995).

[18] Jitianu, A., Raileanu, M., Crisan, M., Predoi, D., Jitianu, M., Stanciu, l., Zaharescu, M., "Fe_3O_4–SiO_2 nanocomposites obtained via alkoxide and colloidal route", J. Sol-Gel Sci. Techn., 40, 317−323 (2006).

[19] Zingaro, R. A., Tolber, W. E., "Infrared Spectra of Pyridine Coordinated Iodine (I) Salts", J. Am. Chem. Soc. 81 (6), 1353–1357 (1959).

[20] Miller, F. A., Wilkins, C. H., "Infrared spectra and Characteristic Frequencies of Inorganic Ions", Anal. Chem. 24 (8), 1253−1294 (1952).