

Stability of Gold Nanoparticles in Sol - gel Silica Films

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Submitted: 23rd August 2007; revised: 4th June 2008; accepted: 30th June, 2008

Keywords: Gold nanoparticles, Optical properties, Capping agent, Gans theory, Stability.

Abstract. Sol-gel silica films containing gold ions were prepared with and without citric acid (capping agent). Heat treatment of these films in hydrogen atmosphere (reducing agent) leads to the formation of gold nanoparticles. The experimental optical spectra of the gold nanoparticles prepared with citric acid revealed a surface plasmon resonance band located at 585 nm. Transmission electronic microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) measurements revealed the formation of prolate gold nanoparticles (6.4 nm of average diameter) and aggregates dispersed in silica matrix. On the other hand, gold nanoparticles in sol-gel silica films prepared without citric acid exhibited a splitting in surface plasmon resonance band for the prolate gold nanoparticles with an average size <12 nm. On further annealing the samples in oxygen atmosphere, the gold nanoparticles prepared with citric acid exhibited high stability in contrast to the samples prepared without citric acid. This stability probably depends on the formation of a microporous structure of silica produced by the citric acid. The optical properties of the metallic nanoparticles were modeled using Gans theory.

1. Introduction

The preparation of metallic nanoparticles in dielectric matrices has been a current topic since these materials have many technological applications [1-4]. In general, high concentrations of metallic nanoparticles dispersed in the dielectric medium induce high responses on the properties of interest [5]. Particularly, the sol-gel technique is suitable for preparing films or gels containing high concentrations of metallic nanoparticles [5]. Furthermore, these materials can be produced at low cost, elevated control and high yields. Sometimes, capping agents such as citric acid [6], thiols [7] or CTAB [8] are used to prevent the aggregation of metallic nanoparticles. These capping agents have important influence on the properties of these nanoparticles. Particularly, the linear optical properties of gold nanorods can be controlled for CTAB as capping agent [8]. The optical absorption spectra of these nanorods exhibit two absorption bands corresponding to the oscillation of the free electrons along of the long axis of the nanorod and perpendicular to it. In contrast, a single optical band is observed for spherical gold nanoparticles; but it can be split into two components when the eccentricity of the particle increases [9]. In both cases, the optical absorption of the metallic nanoparticles is due to the coherent oscillation of the conduction electrons named surface plasmon resonance.

The purpose of this work is to improve the stability of metallic gold nanoparticles at high temperature in silica films prepared by the sol-gel process. The influence of citric acid on the stability of the gold nanoparticles was studied in our films. The optical properties of these films were studied by UV-vis spectroscopy and were modeled using Gans theory. The results were supported by TEM and HRTEM images.

2. Experimental

Gold nanoparticles in sol-gel silica films were prepared as follows: Tetraethoxyorthosilicate (TEOS), deionized water and ethanol (EtOH) were mixed in plastic beakers with relative molar concentrations of TEOS:H₂O:EtOH = 1:4:3. Besides, a drop of concentrated HNO₃ (66.4%), 0.58

mM of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ and citric acid were added to the sol under vigorous stirring for 30 minutes at room temperature. Then, silica glass substrates were dipped into SiO_2 sol containing gold ions at withdrawal speed of 5 cm/min, obtaining a homogeneous layer. The same procedure was followed for the silica films prepared without citric acid. Gold ions in these films (prepared with or without citric acid) were reduced in a hydrogen-rich atmosphere at 600°C for 16 minutes. Afterwards, the films containing gold nanoparticles were subsequently heated in an oxygen-rich atmosphere at 600°C for different times. In all cases, the samples were quenched in air by dropping them on a copper plate. The optical properties of the films were recorded with a Thermospectronic Genesys 2 spectrophotometer at room temperature. The TEM and HRTEM analysis were performed in a JEM-2010F FasTEM field-emission transmission electron microscope with an accelerating voltage of 200 kV and with a point to point resolution of 0.19 nm. For the TEM and HRTEM studies, the films were scraped from the silica substrate and dispersed in a vial containing ethanol and subsequently sonicated for 2 minutes. Then a drop was put on carbon-coated copper grids of 3 mm in diameter and dried.

3. Results and discussion

3.1. Calculated optical absorption spectra

In order to examine the optical absorption of the gold nanoparticles in the sol-gel silica films, the Gans model for prolate particles [10] was used. In this model, the optical absorption of gold nanoparticles with axial ratio Θ is related with the bulk dielectric constants $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ of the metal and the medium dielectric constant ε_m . For an ellipsoidal shape $R = \frac{1}{2}(abc)^{1/3}$, where a, b, c are the three axes of a prolate particles with $a > b = c$. However, for small particles the dielectric constant $\varepsilon_2(\omega)$ depends on the size R as follows [10]:

$$\varepsilon_2(\omega, R) = \varepsilon_2(\omega) + A \frac{\omega_p^2}{\omega^3} \left(\frac{V_f}{R} \right) \quad (1)$$

Where ω_p is the plasmon frequency and V_f is the Fermi velocity of the conduction electrons. The A parameter includes details of the scattering process of the free electrons. The second term of the Eq. 1 can be obtained starting from the dielectric function of the Drude form [11]:

$$\varepsilon_d(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (2),$$

where γ is the phenomenological damping constant and equals to the plasmon bandwidth for the case of a perfect free electron gas in the limit $\gamma \ll \omega$. The damping constant is related to the lifetimes of the electron for scattering process like electron-electron, electron-phonon and electron-defect. In particular, for small particles γ depends on the size because the scattering of the electrons at the particle surface becomes important. This damping function is defined as [11-13]:

$$\gamma(R) = \gamma_b + A \left(\frac{V_f}{R} \right) \quad (3)$$

where γ_b is the bulk damping constant.

The calculated optical absorption spectra of gold nanoparticles in silica for different axial ratios are shown in Fig. 1. The parameters selected were $\phi = 2.5 \times 10^{-7}$ (volume fraction), $n = 1.5$ (refractive index of SiO_2) and $A = 0.6$. Besides, $\omega_p = 1.08 \times 10^{16} \text{ s}^{-1}$ and $V_f = 1.4 \times 10^6 \text{ ms}^{-1}$ for gold [14] and the dielectric constants of the bulk metal were obtained from Johnson and Christy [15]. Red shift of the surface plasmon resonance with the increasing of the deformation of the nanoparticle was observed. However, the longitudinal mode (intense peak located at longer wavelength) is much more sensitive to deformation than the transversal mode (weak shoulder located at 523 nm).

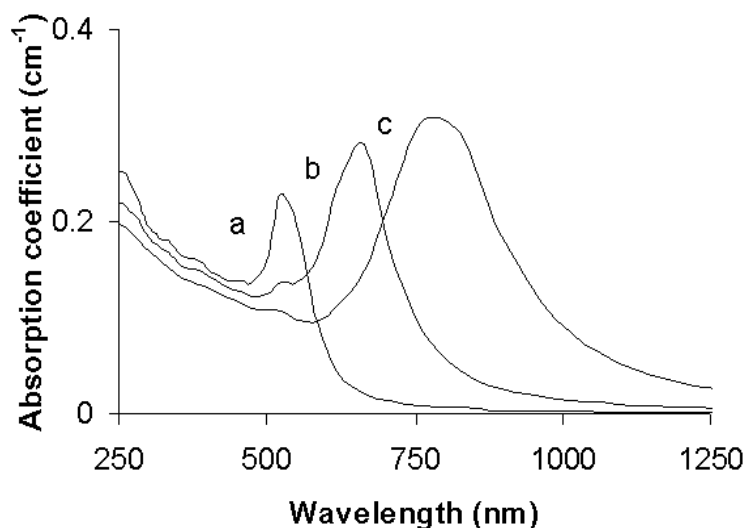


Fig. 1. Calculated optical absorption spectra of gold nanoparticles in silica for several axial ratios: a) $\Theta = 1$, b) $\Theta = 0.4$ and c) $\Theta = 0.25$.

On the other hand, Fig. 2 shows the calculated optical absorption spectra for gold nanoparticles by using the Gans model with $n = 1.46$, $\phi = 2.5 \times 10^{-7}$, $\Theta = 0.5$, $R = 1.25 \text{ nm}$ and for several values of the A parameter. Increase of intensity, red shift, diminution of the bandwidth and splitting of the surface plasmon resonance band with the reduction of the A parameter were observed. These effects are very noticeable when $A \rightarrow 0$, that is when there is no dependence of the dielectric constant of the metal on the size of the nanoparticle. Similar effects have also been reported by Hövel et al. [12].

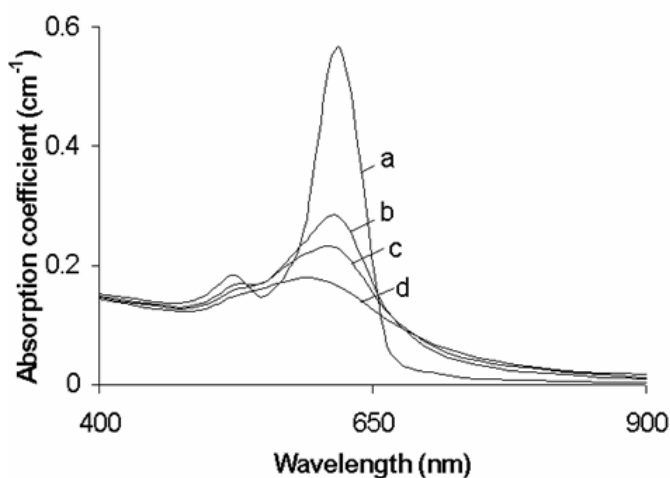


Figure 2. Calculated optical absorption spectra of gold nanoparticles in silica for several values of the scattering factor A : a) $A = 0$, b) $A = 0.4$, c) $A = 0.6$ and d) $A = 1.0$

3.2. Experimental optical absorption spectra

Sol-gel silica films prepared with and without citric acid containing gold ions were heated at 600°C in a hydrogen-rich atmosphere for 16 minutes. The optical spectra of these films are shown in Fig. 3. The electrons supplied by hydrogen gas caused the reduction of Au^{3+} ions in both the

samples. Therefore, the absorption spectra observed in Fig. 3 are due to the formation of gold nanoparticles [8,9]. There are significant differences between the absorption spectra of the samples prepared with citric acid (Fig. 3a) and the samples prepared without citric acid (Fig. 3b). In the first case, the spectrum exhibited an absorption band located at 585 nm with a full width at half maximum (FWHM) of 141 nm. For the second case, the spectrum exhibited a splitting of the surface plasmon resonance band with peaks locating at about 555 and 660 nm, respectively. The optical features observed in the films prepared with and without citric acid could indicate a distribution of different types of particles [16]. In fact, the TEM micrograph for the sample prepared with citric acid (Fig. 4a) showed small prolate gold nanoparticles (tiny particles of 6.4 nm average diameter) and aggregates. In contrast, the TEM image for the sample prepared without citric acid (Fig. 4b) showed prolate gold nanoparticles of about 12 nm average diameter homogeneously dispersed in the film. Consequently, by adjusting the concentration of citric acid, probably it could be possible to control the size and shape of the gold nanoparticles. These results are similar to the results reported for gold nanorods prepared in presence of ascorbic acid [17].

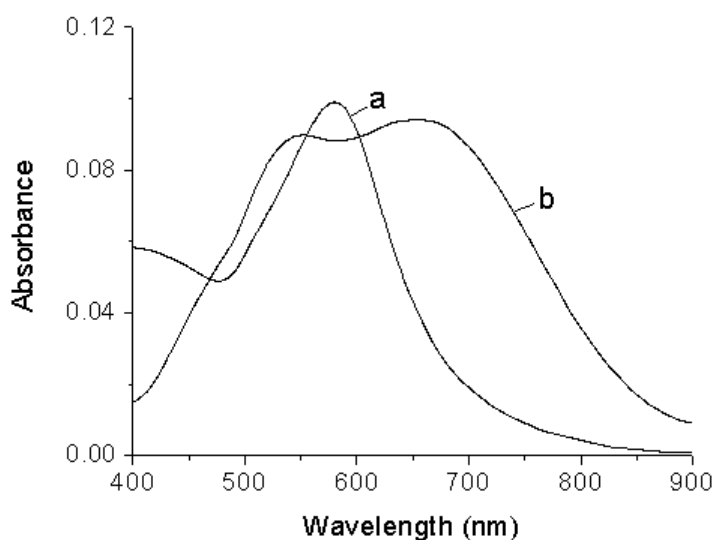


Figure 3. Experimental optical absorption spectra of gold nanoparticles in sol-gel silica films treated in hydrogen atmosphere at 600 °C for 16 min; a) with citric acid and b) without citric acid.

3.3. Stability of the gold nanoparticles

In order to observe the stability of the gold nanoparticles prepared with and without citric acid, the samples preheated in hydrogen were subsequently annealed in an oxygen atmosphere at 600 °C for different times. Fig. 5 shows the optical absorption spectra of gold nanoparticles embedded in a silica film prepared with citric acid and annealed for 0 to 10 minutes. The small changes in the position of the absorption maximum and in the shape of the spectra indicate that the morphology of the nanoparticles is very stable after the heat treatment in oxidizing atmosphere. This is probably due to the formation of a microporous structure of silica produced by the citric acid, where the gold nanoparticles are immersed, as observed in Fig. 6. For the samples prepared without citric acid, the absorption maximum initially located at 660 nm, gradually diminished and blue shifted with annealing time (Fig. 7). In particular, the absorption intensity diminished about 11 % and shifted from 660 nm to 648 nm after heat treatment in O₂ atmosphere for 10 min. Such behaviors could be attributed to oxidation process of deformed gold nanoparticles. A similar oxidation process has been reported for deformed gold nanoparticles with higher curvature on

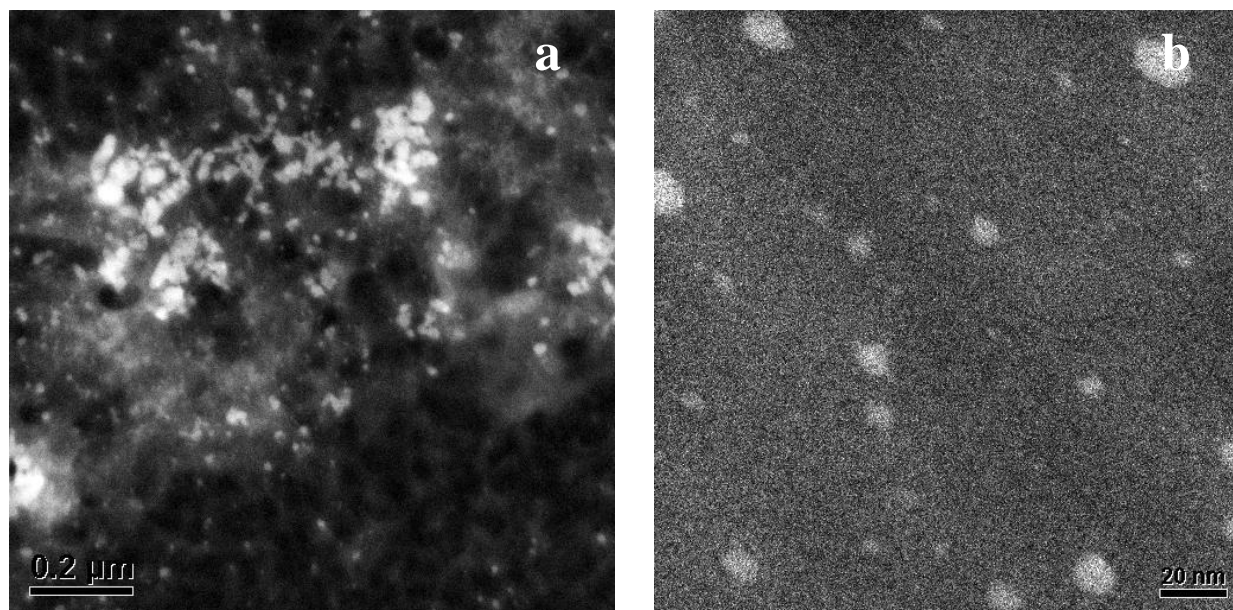


Fig. 4. a) TEM images of gold nanoparticles prepared a) with citric acid and b) without citric acid.

their surface sites [18]. In general, for the samples prepared without citric acid, a blue shift, reduction of the FWHM and damping of the surface plasmon intensity is observed after prolonged heat treatments in oxygen atmosphere.

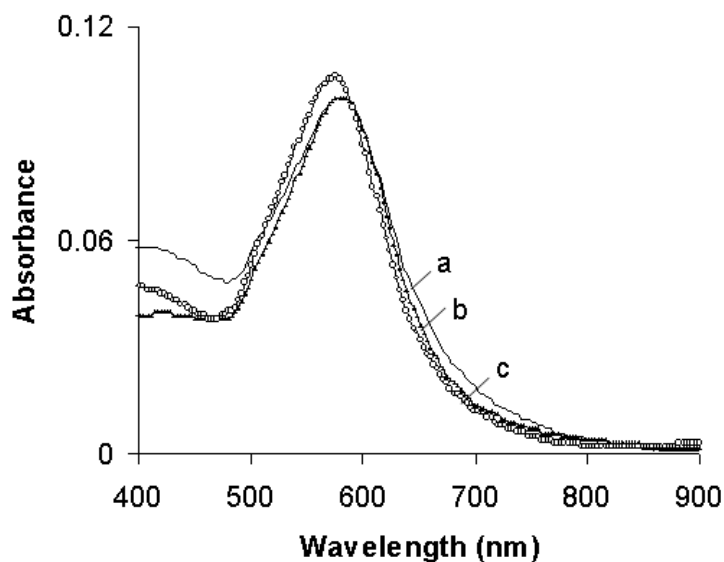


Figure 5. Experimental optical absorption spectra of gold nanoparticles in sol-gel silica films prepared with citric acid and annealed in oxygen atmosphere at 600 °C for a) 0, b) 5 and c) 10 min.

On the other hand, the Fig. 8 shows the evolution of the optical absorption spectra for a sample prepared without citric acid, immersed in ethanol under sonication by a conventional ultrasonic cleaner at different times. The absorption band at shorter wavelength disappeared after prolonged sonication. However, the solution of ethanol revealed an absorption band at 535 nm corresponding to the surface plasmon resonance of gold nanoparticles. So, the ultrasonic treatment alters the optical properties of the films.

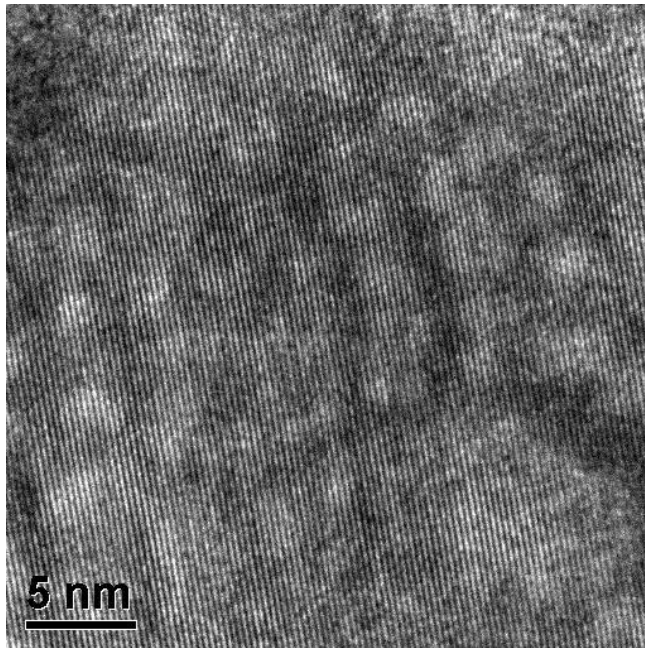


Figure 6. Typical HRTEM image of protective microporous silica, with immersed gold nanoparticles.

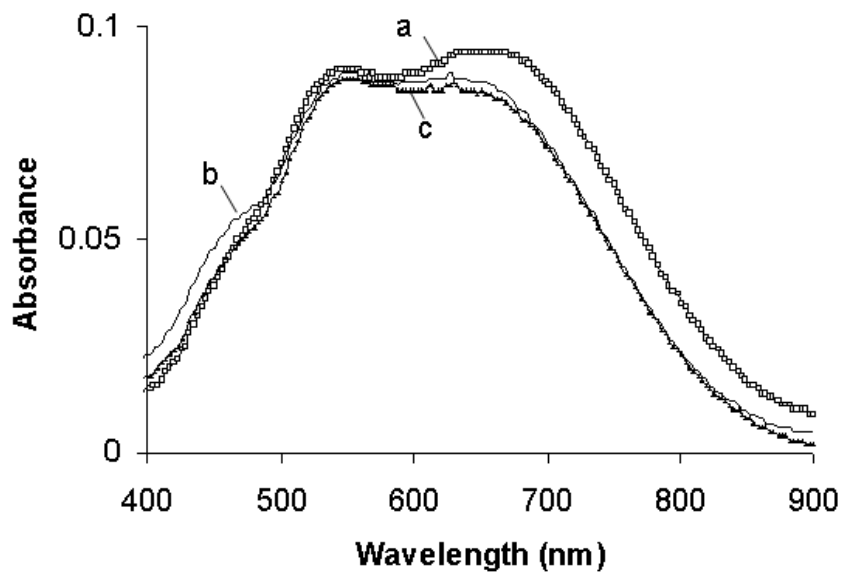


Figure 7. Experimental optical absorption spectra of gold nanoparticles in sol-gel silica films prepared without citric acid and annealed in oxygen atmosphere at 600 °C for a) 0, b) 5 and c) 10 min.

3.4. Comparisons between experimental and theoretical spectra

Theoretical fits to the experimental spectra were poor for the samples prepared with citric acid, considering only prolate particles with several values of the scattering parameter A . However, relatively better fits were obtained using the Gans theory for these samples after annealing in reducing or oxidizing atmospheres considering the prolate shape of metallic nanoparticles and their aggregates, in accordance with the calculated results reported previously [19]. For example, the absorption spectrum of the sample prepared with citric acid and annealed in hydrogen atmosphere was fitted with prolate metallic particles which axial ratio of $\Theta = 0.62$, $n = 1.50$, $R = 2.9$ nm, $\phi = 1 \times 10^{-8}$ and $A = 0.5$. The aggregates were simulated as prolate spheroids using fictitious depolarization factors in the Gans model [10,19]. In this case, we used $L_1^* = 0.250$, and $L_2^* = L_3^* = 0.375$ (Fig. 9a).

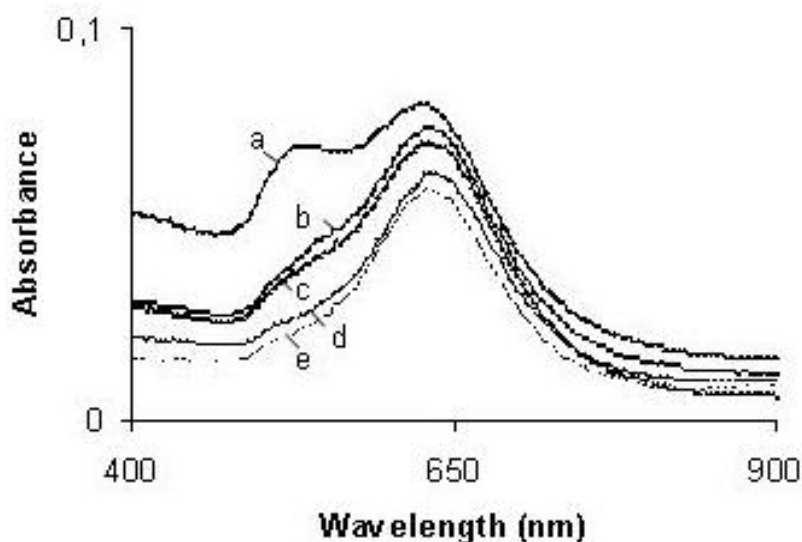


Figure 8. Evolution of the optical absorption spectra for the samples prepared without citric acid under sonication for a) 0, b) 10, c) 15, d) 30, and e) 60 min.

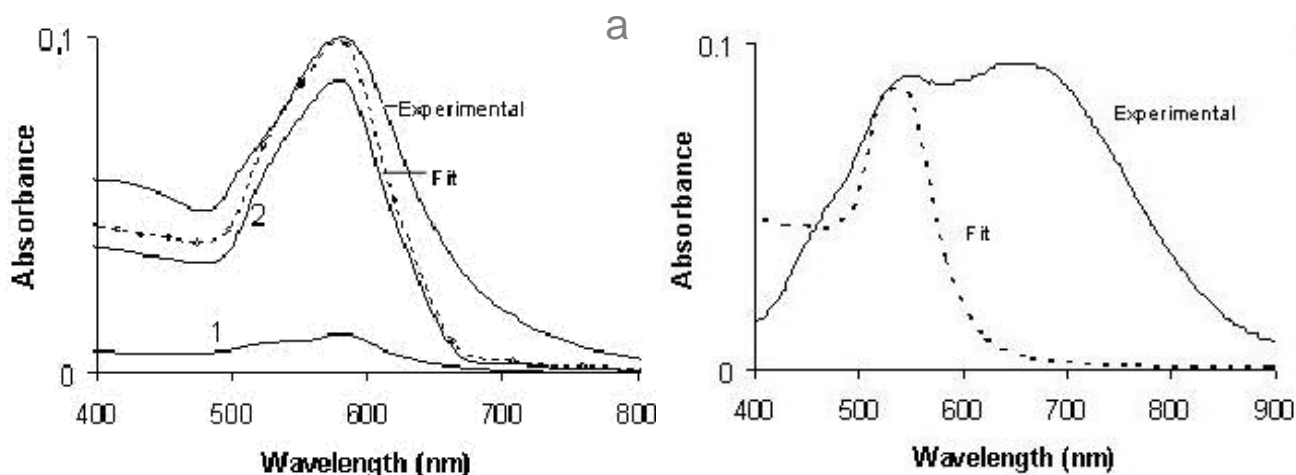


Fig. 9. Gans theory fit to the optical absorption spectra of gold nanoparticles obtained after annealing at 600 °C in reducing atmosphere for 16 min. a) Fit performed with single particles (1) and aggregates (2) for the sample prepared with citric acid, and b) Fit performed with single particles for the sample prepared without citric acid.

For the samples prepared without citric acid it was not possible to obtain a good fit to the optical absorption spectra after annealing in reducing or oxidizing atmosphere. For example, Fig. 9b shows the experimental and calculated spectra of gold nanoparticles in sol-gel silica films after annealing in hydrogen atmosphere. While using the Gans model, we included the experimental data obtained from the TEM images. The peak at shorter wavelength was fitted very well, but the fit to the peak at longer wavelength was very poor. This can be explained considering that a sonication process was used during the preparation of the samples for TEM measurements, losing some of the metallic particles from the clusters. The sonication altered the optical properties of the films and consequently the distribution of the nanoparticles observed in Fig. 8.

4. Conclusions

Stable gold nanoparticles in sol-gel silica films prepared with citric acid were obtained by annealing in reducing or oxidizing atmosphere at high temperature. Their optical properties were

studied by TEM, HRTEM, UV-vis absorption spectroscopy and modeled using the Gans theory. The experimental and calculated data indicate that the citric acid is probably a good capping agent to control the size and shape of gold nanoparticles under oxidation process. Citric acid produces microporous silica protecting the prolate gold nanoparticles in them, and therefore plays an important role on their stability. Conversely, we observed poor stability of gold nanoparticles in sol-gel silica films prepared without citric acid.

Acknowledgments

The authors gratefully acknowledge the financial support for this work from the CONACYT 79781, NSF-CONACYT, PUNTA, PAPIIT 116506-3 (México). VRT and GVA thank to Conacyt and ICyTDF for postdoctoral fellowship. We also thank to Luis Rendón and Edilberto Hernández for their technical assistance.

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Journal of Nano Research Vol. 3

doi:10.4028/0-00000-025-6

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doi:10.4028/0-00000-025-6.115