Optical Properties of Self-Ensemble Monolayers of Gold Metallic Nanostructures

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Abstract. This work analyzes the optical properties of nanostructures metallic surfaces of gold, at different sizes, in glass silanized substrates. Silanized substrates were immersed in the colloid solution for one and half hour at room temperature and dried at room temperature for four hours. The optical properties were analyzed by three spectroscopy techniques and by TEM microscopy. UV/VIS was used to observe changes in absorption due to the aminopropiltrimethoxysilane added to the glass substrate and due to the colloid added to silanized substrate. Infrared vibrational spectroscopy in ATR mode was used to observe the new generation peaks due to substrate silanization and SEIRA effect due to the colloid added to silanized substrate. And finally Z-Scan technique was used to observe the nonlinear properties of these funtionalization metallic nanostructures in function of nanostructures size. TEM images confirm the sizes observed in the UV/VIS spectra.

INTRODUCTION

Ensembles of nanoparticles display unique optical and electrical properties that are distinct from their respective bulk properties and from average measurements of collections of widely spaced particles. To a large extent, however, bulk material properties (i.e., catalytic, biocompatibility, optical and electrical properties) are determined by nanoscale features.

The structural configurations and sizes of these small particles induce new types of physical properties. Therefore, the selection of a synthesis method which can give rise to a particular structural particle configuration is very important for new technological applications [1,2]. Depending on the nanometric particle size, the nanostructures can have different applications. These applications include fields such as: catalysts, photography, medicine, information storage in magnetic devices etc. In our days several biosensors will be development, called last generation biosensors, based in metallic nanostructures in the rank between 5 to 50 nm.

Nanostructured materials of coinage metals such as gold and silver have unique optical properties due to strong surface plasmon absorption in the visible region of light. The wavelength at which a given nanoparticle is resonant depends on the size, shape, chemical nature of the metal, and the embedding environment. [3-5].

Metallic nanostructures, are very attractive for Infrared or Raman scattering analysis, because when such structures are added to a sample, the signal could be increased for almost a million factor, SEIRA and SERS effects [6-8].

Control of the structure and thereby optical properties of gold and silver nanomaterials is especially important for SEIRA and SERS applications; the enhancement factor depends on the optical absorption of the substrate [6,9]. Only nanostructures with absorption on-resonance with the incident light will contribute to the SEIRA or SERS signal, whereas those with absorption off-resonance with the incident light wavelength will contribute none or little to the enhancement factor.

In ensemble average experiments involving a large number of nanoparticles, optical and structural variations from particle to particle average out to yield consistent results from measurement to measurement. However, when examined at the single-nanoparticle or single-molecule level, the spectrum and enhancement can vary significantly from one nanostructure to another because of their different structure and optical absorption. This is often complicated further by the necessity of aggregation of nanoparticles to achieve enhancements large enough for single-molecule observations [10-11]. Because aggregation is generally a random process, structural homogeneity is nearly impossible. It is essential to have high homogeneity or uniformity in the structure and optical absorption of the different nanostructures to achieve good consistency on a single nanostructure level. The solution to this is to design homogeneous SEIRA or SERS substrates that can provide significant single-particle enhancement without aggregation. The first works to realize this goal were the so-called core/shell systems [12-13].

This paper shows the optical properties of self-ensemble monolayers of gold metallic nanostructures at six different sizes. The optical properties were analyzed using UV/VIS absorption (to observe the colloid size), Infrared vibrational spectroscopy in ATR mode (to observe the SEIRA effect due to the colloid added to silanized substrate) and finally Z-Scan technique (to observe the nonlinear properties of these funtionalization metallic nanostructures in function of size nanostructures). Transmission Electron Microscopy (TEM) was used to confirm the colloid sizes in solutions.

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EXPERIMENTAL SECTION

Colloids Solutions. Colloidal dispersions of gold (Au) nanoparticles with different sizes were prepared in a typical synthesis; solutions of $HAuCl_4$ (0.096 mmol in 25 ml of water) and poly (N-vinyl-2-pyrrolidone) (PVP, 100 mg in 20 ml of water) were prepared by dissolving the $HAuCl_4$ crystals and PVP in water. Both solutions were mixed to produce an Au (III) ion solution containing PVP as a protective polymer. Then an aqueous solution of ascorbic acid (AA, 0.096 mmol in 5 ml of water) was added to the resulting solution at room temperature. Colloidal dispersions of Au nanoparticles were formed after the addition of AA solution in the mixture solution. The amount of metal ions was altered from 0.096 to 0.186 mmol in order to control the size of Au particles. One solution (sample AU-6) was done at 0.186 mmol six months ago and agglomerates of gold nanostructures are now present.

Functionalized and patch of colloids in glass substrates. The substrates functionalized were done using the aminopropil trimetoxysilane to 1% in an acetic acid water solution. The glasses corning were submerged in this solution by one hour, later were cleaned using water. After that, the substrates with silane were immersed in each one of the colloid solutions at two different times: a half and one hour, at room temperature and dried by four hours at room temperature.

Transmission Electron Microscopy (TEM). A Shimadzu UV-VIS 3101PC double beam spectrophotometer was used to record the absorption spectra of fluids. Particle sizes and size distribution were evaluated by TEM, using a JEOL-JEM200 microscope. For TEM observations, a drop of fluids was spread on a carbon-coated copper microgrid and dried subsequently in vacuum.

UV/VIS Spectrometry. The absorption colloid solutions were performed in a Genesis UV/VIS spectrometer, from 200 to 1100 nm. This technique was applied to colloid solutions and self-ensemble monolayers of gold in silane substrates.

Infrared spectroscopy. Attenuated Total Reflexion mode of the Infrared spectrometer Brucker Vertex 70 was used. The spectrum of a glass substrate was used as background in all the measurements; the crystal used was a Zn Se crystal of one reflection. And the exposure time was 30 seconds for each self-ensemble monolayers of gold in silane substrates.

Z-scan Technique. A 632 nm He-Ne laser was used to improvement this optical technique, the power laser is 20 mW, a lens with 3 cm of focal distance was used to focus the laser beam in the colloid substrates. A Si detector was used to detect the intensity after 120 cm of optical path. Only self-ensemble monolayers of gold in silane substrates were analyzed by this technique.

RESULTS AND DISSCUSION

Transmission Electron Microscopy (TEM)

Figure 1 shows the TEM images and corresponding size distributions of three samples of Au nanoparticles. Similar electron micrographs and particle size histograms of Au nanoparticles (not shown here), are obtained by for other two solutions prepared with concentration of metal ions of 0.176 and 0.186 mmol in 50 ml of water. Formation of nanoparticles is clear from the TEM micrographs.

The average size of the particles ranging from 13.9 to 37.4 nm, is increased with the increase of Au ions in the mixture solution, see Table 1. Gold particles with average size ranging from 13.9 nm to 37.4 nm were measured.

TABLE 1. Nanoparticles sizes obtened by Transmisión Electrón Microscopy (TEM).

Sample	*d* (nm)	*σ (nm)*
AU-1	13.9	4.7
AU-2	23.2	7.0
AU-3	31.5	6.7
AU-4	34.4	7.3
AU-5	37.1	5.6

UV/VIS Spectrometry.

For the absorption analysis by means of UV/VIS spectroscopy, the variations in absorption of the colloidal solutions and the functionalized substrates with nanopartículas were analyzed stuck them. In order to be able to observe with more detail, variations that would be had to do in the spectra, in Fig. 2 we compared one of our colloid solutions with a commercial substrate funcionalizado with gold nanoparticles, the water spectrum also is plotted in Fig. 2.

In our solutions are two peaks very well defined: the peak between 480 and 600 nm associated to gold nanoparticles in solution and the peak of water absorption above of the 900 nm. In comparison with the commercial substrate where only exist two peaks; one of them is due the gold nanoparticles and the other due to the glass substrate.

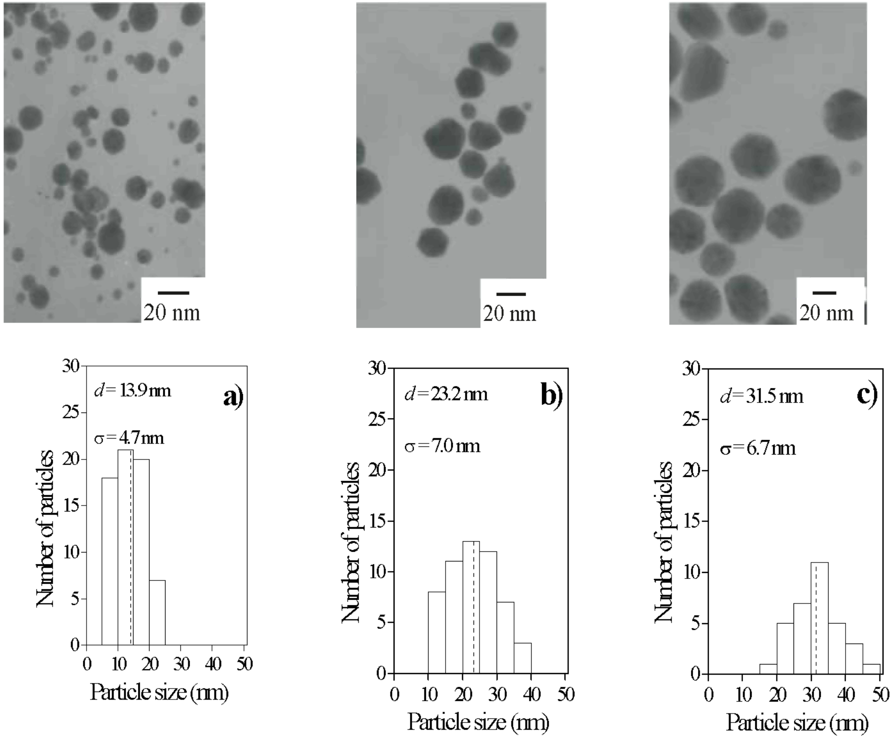

FIGURE 1. Electron micrographs and particle size histograms of Au nanoparticles prepared with different concentration of metal ions: (a) 0.096, (b) 0.126 and (c) 0.156 in 50 ml of water. Average Size *d* and standard deviations σ are reported.

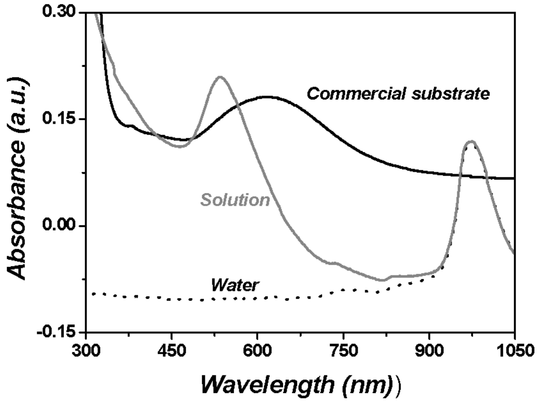

FIGURE 2. UV/VIS absorption spectra of the gold nanoparticles commercial substrate and of our colloid solutions generated. The water absorption spectrum is added too.

Once identified the gold colloids peak, the UV/VIS absorption analysis was done for all colloids solutions and for colloids deposited in the functionalized substrates (colloids film).

Figure 3 presents the UV-Vis absorption spectra of colloidal dispersions of Au nanoparticles prepared with different amount of metal ions. An absorption peak around 530 nm was revealed in these colloidal dispersions, which is generally assigned to the surface plasmon resonance (SPR) of Au nanometric size particles. From this figure we observed that an increase in concentration of Au ions in the mixture solution, corresponds a shift of the optical absorption peak towards higher wavelengths. SPR band position shift are generally assigned to the increase of the Au particles size, which agree with the TEM results.

In Fig. 3a, samples 1 to 5 shows a very well defined peak around the 530 nm associated to the Au nanoparticles generation. The plot AU-1 is centred at 528 nm, the plot AU-2 is centred at 530 nm and the plots AU-3, AU-4 and AU-5 are centred almost at 534 nm. For these solutions the peak position are in agreement with the TEM results. The broad peak centred at 648 nm, for the sample AU-6, means that the solution is not stable for months and nanoparticles of different sizes are now present, the nanoparticles sizes are bigger than to the others five solutions and according to reference 14, the average size is 150 nm.

Once the functionalized films were submerged in colloid solutions, the only sample that shows a film deposition was sample AU-6, which means that the self-ensemble monolayers of gold metallic nanostructures of solution AU-6 have a bigger density than to the others self-ensemble monolayers, where the SPR of Au nanometric size particles smaller than 37 nm can not be detected, see Fig. 3b

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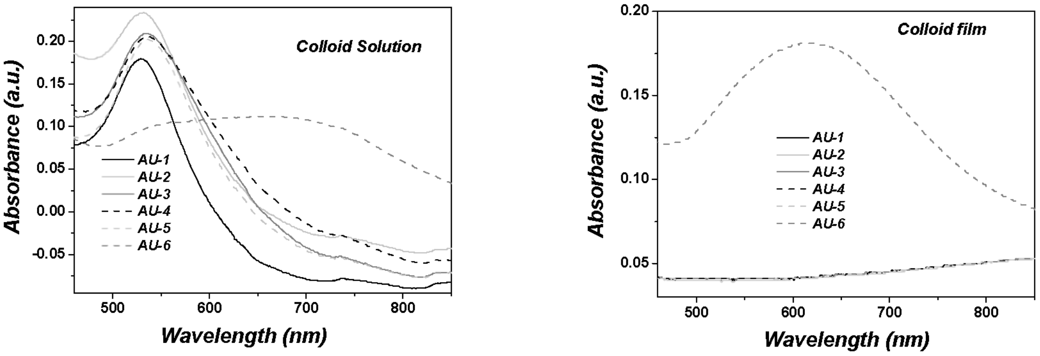

a b

FIGURE 3. UV-VIS absorption spectra of colloidal dispersions of Au nanoparticles a) in solution b) in self-ensemble monolayers.

Infrared Spectrometry.

In Fig. 4, the infrared spectra of the self-ensemble monolayers of gold are showed, for the six different solutions at half and one hour of deposition. In each plot, the spectrum of glass corning with silane is added (functionalized substrates). The functionalized substrates shows: two vibration peaks at 890 and 1060 cm^{-1} associated to the Si-O asymmetric vibrational mode and one lower intensity peak at 750 cm^{-1} associated to the Si-O symmetric vibrational mode. In Fig. 4a and Fig 4b, the black dash line is the plot of the silane deposited in glass, the dark continuous line is for the self-ensemble monolayers of gold metallic nanostructures at one hour (AU-xH) and the grey continuous line is for at half hour (AU-xM); of the functionalized substrate submerged in the colloid solutions.

By comparison of results between UV/VIS spectroscopy and infrared spectroscopy, conclusions are next; although the UV/VIS spectra (see Fig. 3b) do not show the SPR of Au nanometric, except for the solution with the biggest nanoparticles, infrared spectra shows a thin film of gold nanoparticles. This asseveration we can do it due to the effect SEIRA (Surface Enhanced Infrared Absorption) can be observe. Effect SEIRA is observed in the amplification of the Si-O bond peaks (asymmetric and symmetric vibrational mode), in a factor of 10 times the intensity value of the peak without the colloid presence, in the samples of one hour.

Also in this work, for SEIRA effect, the nanoparticles size does not matter, because almost the same enhancement factors were obtained in all the samples at one hour.

The self-ensemble monolayers of gold metallic nanostructures at half hour shows a low SEIRA effect due the lower time of deposition, for this the minimum deposition time must be one hour. But for the sample AU-6, the minimum deposition time should be half hour, because the SEIRA effect is the same when the deposition time is one hour.

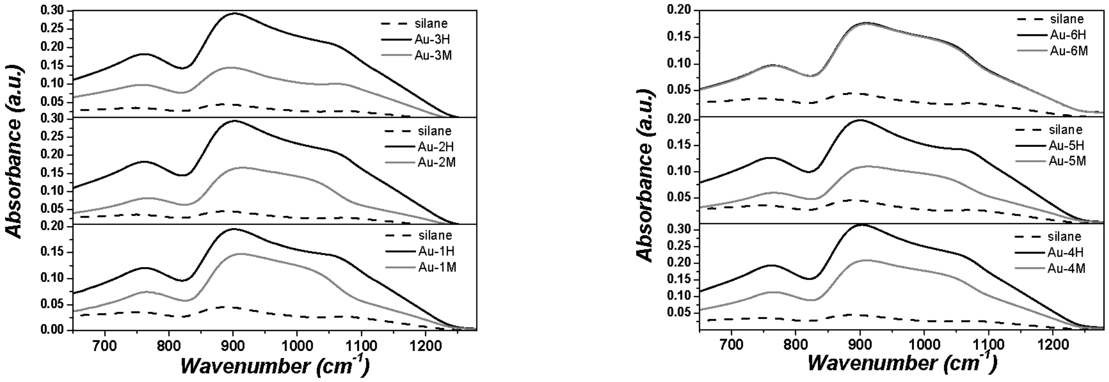

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FIGURE 4. Infrared spectra of self-ensemble monolayers of gold metallic nanostructures at two different deposition times; a half hour (Au-XM) and a one hour (Au-XH) of the functionalized substrate submerged in the six colloid solutions.

Z-scan Technique.

Z-Scan technique is a method for measuring both real and imaginary part of the nonlinear index of the optical materials. It is based on self-focusing and self-defocusing of an optical beam by a nonlinear sample. In this technique the sample is scanned along the optical axis (Z direction) in the focal region of a single focused laser beam, the transmitted intensity is recorded in the far field by a photodetector with or without a small aperture.

A typical plot of the transmitted intensity versus sample position, using a small aperture, is show in Fig. 5. Continuous line show a valley in prefocus and a peak in postfocus, behavior given by a sample with positive nonlinear refractive index. The opposite behavior, dash line, is expected for a negative nonlinearity.

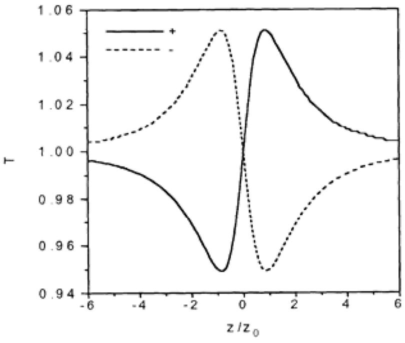

FIGURE 5. Typical Z-scan of positive and negative nonlinear behavior.

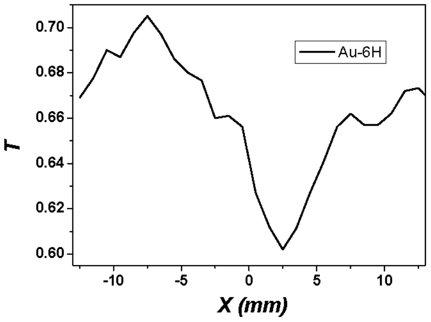

FIGURE 6. Z-scan spectrum of the sample at 0.186 mmol old (generated six months ago).

In Fig. 6, the intensity response of the sample AU-6H, to prefocus and postfocus, is plot. In this figure a negative nonlinear behavior is present for the gold nanoparticles with the bigger size. The others five samples not show a nonlinear defined behavior main by the thin film of gold colloid deposited in the functionalized substrates. We think that with a large laser power, the same behavior must be obtained.

CONCLUSIONS

The obtaining of self-ensemble monolayers of gold metallic nanostructures between 13.9 to 37.1 nm in recent prepared colloid samples and of 150 nm in an aged sample (aggregates gold metallic nanostructures) was present. The nanostructure size was determinate by UV/VIS spectroscopy and TEM microscopy. In the middle infrared spectra are observed only Si-O bonds associated to the aminopropil trimetoxysilane, but the self-ensemble monolayers of gold induce the SEIRA effect in the functionalized substrates. The aged sample showed the biggest SEIRA effect compared with the rest of the samples at the minimum time deposition. Due the dense gold colloid thin film deposited on functionalized substrate, the aged sample was the only sample that had a negative nonlinear behavior, in the z-Scan analysis. With these studies, now we have self-ensemble monolayers of gold metallic nanostructures to make biosensors or only SEIRA substrates, and also these self-ensemble monolayers of gold could be used for optical devices, due to their nonlinear behavior.

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