Colloidal gold nanofilms fabricated via self-assembled monolayer and Langmuir-Blodgett methods

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Colloidal gold nanoparticles have been used as biomaterials since the 1970's. The main goal of developing biological sensors is to identify a number of human diseases and infections with high specificity and sensibility. Two of the most used methods to fabricate biofilms are the Langmuir-Blodgett and the Self-Assembled Monolayer techniques, which are used to obtain homogenous organic and inorganic monolayer films and thin films of organic compounds, respectively. We describe the fabrication of ring-structure colloidal gold nanofilms using both methods. Nanofilms were further characterized by X-Ray Diffraction, Fourier Transformed Infrared Spectroscopy, Ultraviolet-Visible Spectroscopy, and Atomic Force Microscopy.

Keywords: Colloidal gold nanoparticles; SAM; Langmuir-Blodgett method

1. Introduction

Gold is a well-studied material that nowadays has a wide use in medicine due to great advances in Nanosciences and Nanotechnology. Their main contribution in Nanomedicine as biodevices includes biochips, bioelectronics and biosensors. The application that can be given to them is a function of size, shape, and physical properties of the gold nanoparticles. Figure 1 shows some of the possibilities for gold nanoparticles shapes. Gold nanospheres or colloidal gold nanoparticles are synthesized via a chemical reduction method and the surfactant amount used affects their size, varying from 2 nm to 100 nm. Its main application is to detect diseases by means of immunoassays to identify specific binding of antibodies to certain target antigens [1, 2]. Gold nanorods are synthesized using a template method based on electrochemical deposition and its diameter depends on the pore size of the template membrane. One of its applications is as electrodes that have immobilized biological reagents (such as antibodies) on its surface and allows the analysis of molecule interactions (such as antibodies-antigens interactions) with them by measuring current fluctuations in the device [1, 3]. Gold nanoshells are obtained via a seeded growth technique around silica, polymers, ferromagnetic fluids, or other materials according to the desired application; they are usually employed as optical enhanced imaging [1, 4]. The galvanic replacement reaction between a silver template and $HAuCl_4$ in an aqueous solution is used to produce gold nanocages with controllable pores size according to the size of the silver template. Nanocages are used in the photocatalysis field as photothermal transducers, hyperthermia therapeutics or targeting cancer cells [5, 6].

In order to obtain certain devices using gold nanoparticles, it is necessary to arrange these nanoparticles into a thin film that can be used to measure interactions with biological molecules employing optical techniques such as Surface Plasmon Resonance (SPR), Surface Enhanced Raman Spectroscopy (SERS), etc.

There are quite lots methods to fabricate thin films. Selection of the best method depends on the material to be deposited and the future application. There are several methods commonly used to obtain metal, oxide, semiconductor or insulating thin films, including; 1) sputtering deposition, where the sample is eroded by energetic particle bombardment under vacuum or inert atmospheres, 2) spray-pyrolysis in which the deposition is controlled via velocity and droplet size sprayed under a

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specific temperature and inert atmosphere, and 3) chemical vapor deposition (CVD) where gas molecules are chemically decomposed in order to deposit them over the substrate forming a film with the same structure [7]. When organic or biological thin films are required, it is used the self-assembled monolayer (SAM) method. In this procedure the substrate is immersed into a solution of previously activated organic molecules to establish chemical bonds between them and the activated surface of the substrate. The main goal of this method is to keep both structure and properties of organic molecules unmodified [8]. Another method widely used is the Langmuir-Blodgett method (LB) where a surfactant is required to attach the desired material according to its hydrophilic or hydrophobic characteristics [9].

In this work, we constructed thin films using a combination of the SAM and LB methods. Here we used a chemical compound containing a silane group to functionalize the surface and provide free thiol groups to attach gold nanospheres to the glass surface.

2. Methods

As a first step in our methodology, glass coverslips were cleaned with aqua regia for 30 minutes at room temperature (RT), rinsed with plenty of distilled water and methanol. Then, coverslips were submerged in 5% (v/v) 3-mercapto-propyl-methyl-dimethoxysilane in chloroform for 1 hour at RT to functionalize the surface and allow the attachment of gold nanoparticles. These nanoparticles were synthesized by the reduction of an aqueous 1% (w/v) $HAuCl_4$ (Sigma) solution using 4% (w/v) sodium citrate to obtain monodispersed gold nanospheres [10]. To prepare the film for further use as a biosensor and allow its use in SPR or SERS analysis, it was necessary to implement a driven self-organization process that included deposition of metallic nanospheres on the functionalized glass surface and heating at 300°C in an inert atmosphere as shown in figure 2.

To characterize the film of gold nanoparticles we used X-Ray Diffraction (XRD, Siemmens D5000 Diffractometer), Fourier Transformed Infrared Spectroscopy (FT-IR, Nicolet 6700 Spectrometer), UV-Vis spectroscopy (UV-Vis, Perkin Elmer 25 Lambda UV-Vis Spectrometer), and Atomic Force Microscopy (AFM, Veeco Autoprobe Microscope with contact mode operation). All systems are located in the Departamento de Física, Cinvestav-IPN.

3. Results and Discussion

Figure 3 shows the XRD results obtained with our materials. In the first one it is represented the cleaned glass, where it can be observed the main peak of SiO_2 in 21.60 (2 theta). The next one is the diffractogram of the silanized glass which main peaks are in 11.29, 12.27, 12.91, 28.31,

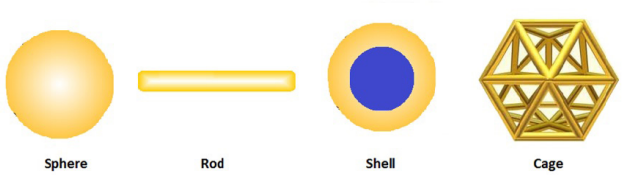

Figure 1. Gold nanoparticles shapes. There are shown some of the different shapes in which gold nanoparticles can be fabricated.

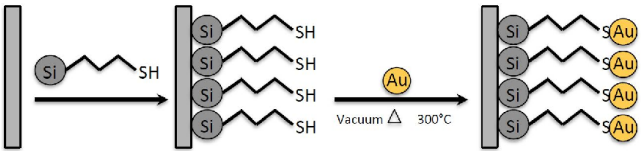

Figure 2. Gold film fabrication process. After cleaning the glass with aqua regia, a) it was submerged in a 5% MPMDMS solution to functionalize the surface, then b)gold nanoparticles were deposited over the silanized glass in a vacuum environment at 300° C, finally c) Gold nanofilm.

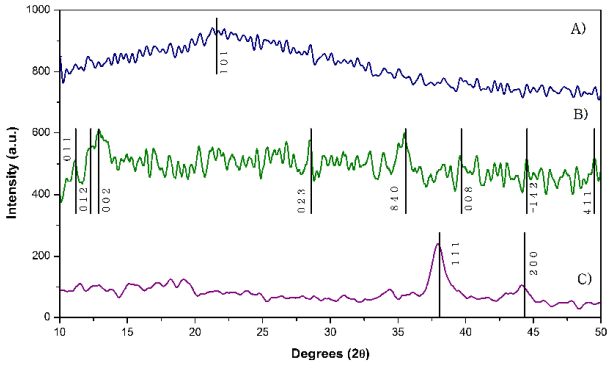

Figure 3. XRD patterns. A) Aqua regia-cleaned glass. B) Silanized glass after 30 min treatment in 5% (v/v) MPMDMS solution. C) Gold nanofilm washed 3 times with methanol. Vertical lines indicate (hkl) planes.

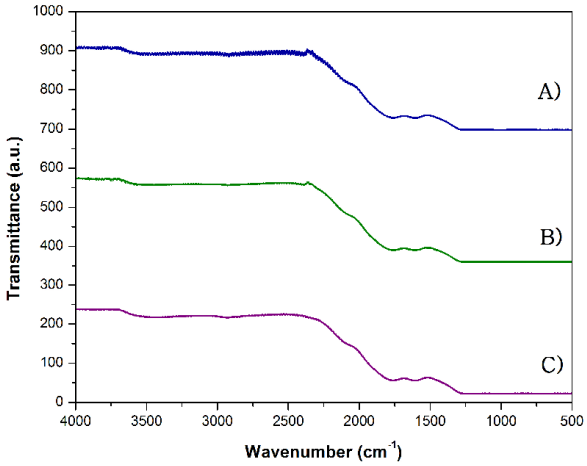

Figure 4. FT-IR spectra showing transmittance in arbitrary units of each stage in the process of the nanofilm fabrication. A) Cleaned glass. B) Silanized glass. C) Gold nanofilm.

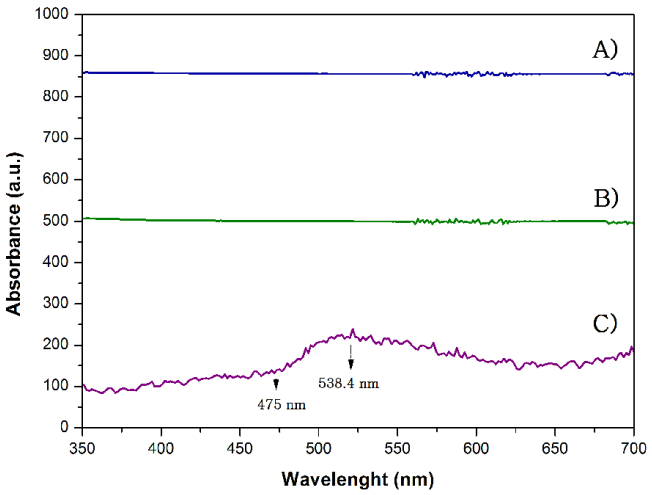

Figure 5. UV-Vis Spectra. A) Cleaned glass without any significant traces in the interest region (500nm – 560 nm). B) Silanized glass with almost the same spectra obtained in A). C) A significant absorption in 538.4 nm.

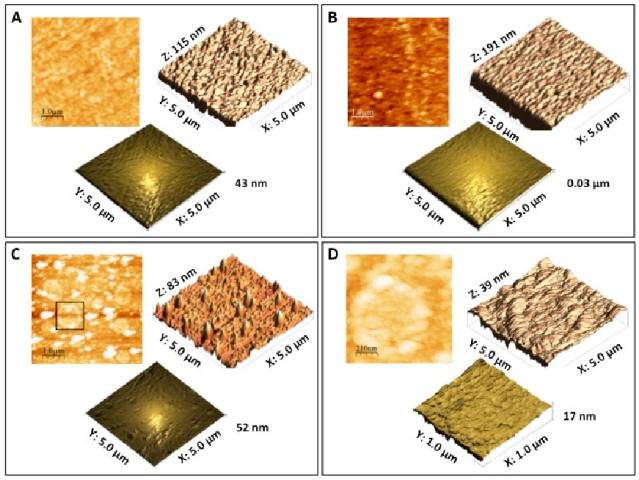

Figure 6. AFM images. A) Cleaned glass showing damage over its surface because of the aqua regia. B) In the silanized glass is observed a smoother surface thanks to the MPMDMS solution. C) Micrograph of the nanofilm showing different structures. D) Close-up of the black rectangle marked in C) where a ring formed by the gold nanoparticles can be seen.

35.45, 39.66, 44.53, and 49.49 (2 theta degrees). These peaks do not correspond to a specific compound in the ICSD patterns, and they match some of the peaks for Si, S, O, C, and H according with the same database. The last one is the diffractogram of the colloidal gold film where it is possible to observe the peaks in 38.18, and 44.39 (2 theta degrees) at corresponding to the gold chart.

Figure 4 represents the FT-IR spectra in which are easily identified the progressiveness in the thin film fabrication. With glass we observed abundant noise. When the surfactant was added, the surface became smoother. Finally, when the colloidal gold nanoparticles were present we could not see bands between 4,000 and 3,600 cm^{-1}, and the one in 2,300 cm^{-1} disappeared.

Figure 5 displays the UV-Vis spectra where it was possible to identify the peak of maximum absorption of colloidal gold film at 538.4 nm. Using the regression equations of curves *a* and *b*:

$$y = 516.43 + 0.75\,x \quad (1)$$

$$y = 431.6 + 1.7x \quad (2)$$

Substituting in Eq. (1) y with the maximum absorption and in Eq. (2) with the minimum absorption of the colloidal gold film it was possible to calculate that the approximate size of nanoparticles was between 24.4 and 29.94 nm.

Figure 6 shows AFM images of a) the cleaned glass where it can be observed how the cleaning solution eroded the surface, b) the glass functionalized with 3-mercapto-propyl-methyl-dimethoxysilane showing a smoother surface than the previous one, c) the gold film where several structures such as mounds, double hills, and rings standing out were seen; according with the WSxM [11] and Gwyddion programs the average roughness is 83 nm, and d) a close-up of a ring in the gold film, where it is possible to observe how the gold spheres agglomerate and form clusters of 40 nm high and 300 nm wide.

The different patterns observed in the AFM images might indicate inefficiency in the deposition process, which could be affected by the shape of nanoparticles and the combination of the inert atmosphere, temperature and negative ions present in solution generating ring-like structures.

4. Conclusions

With the combination of Self-Assembled Monolayer and Langmuir-Blodgett methods in an inert atmosphere, it is possible to obtain colloidal gold films with different patterns. The ring-like structures obtained in this work are influenced by negative ions in solution and the sphere colloidal gold nanoparticles according to Ye et al. [12]. These patterns could be useful as templates for obtaining layers of different materials showing this kind of organization. Our results show that we have to improve the deposition process in order to get an optimal surface suitable for biosensors as suggested [13].

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