Gold nanoparticles size distribution by pulsed laser varying the wavelength

A C Arévalo¹, J H Quintero¹,², S A Rincón²,³, J Rodriguez²,³, and R Ospina¹,²,³
¹ Grupo de Investigación Ciencia de Materiales Biológicos y Semiconductores, Universidad Industrial de Santander, Bucaramanga, Colombia
² Centro de Materiales y Nanociencia, Universidad Industrial de Santander, Bucaramanga, Colombia
³ Centro de Investigaciones en Catálisis, Universidad Industrial de Santander, Bucaramanga, Colombia

E-mail: andrea21arevalo@gmail.com, rospinao@uis.edu.co

Abstract. In this work the influence of the wavelength variation of a pulsed laser on the size distribution of gold nanoparticles, synthesized by laser ablation in liquid medium, was determined, since this technique is the most used due to its simplicity as it is not developed under strict conditions of temperature, pressure, agitation, etc. Three different wavelengths were used: (i) 532 nm, (ii) 355 nm and (iii) 266 nm, due to equipment restrictions. The distributions and sizes of nanoparticles were studied by dynamic light scattering, scanning electron microscopy and atomic force microscopy. In addition, it is shown that the spectra of the gold region determine the chemical state of the nanoparticle. The results showed that the smallest particle size was obtained with the wavelength of 266 nm with a size of 9.6 nm, while for the other wavelengths; sizes of 55.4 nm and 77.3 nm were obtained respectively. Thus, smallest average diameter of gold nanoparticles was obtained with smallest wavelength.

1. Introduction

Materials present different physicochemical properties when found on the nanometer scale (1 nm to 100 nm), the appearance of these properties is related to the great surface energy, the number of atoms on the surface, spatial confinement and the low number of imperfections [1]. This has aroused great interest in researchers, mainly in the production and application of noble metal nanoparticles such as gold (AuNp) due to its great potential in sectors such as biomedicine where nanoparticles are used to fight cancer [2], food industry, where they are an important part of the polymeric nanocomposites of containers [3], in catalysis where, for example, functional supported catalysts are obtained for methane combustion [4], among other areas of scientific knowledge. There are different methods for the synthesis of gold nanoparticles, the two most used are chemical processes and laser ablation, where the first is made from a direct reduction in aqueous solution or phase transfer reactions and the second consists of hitting a target (normally in a solid state) with intense laser radiation [5-7]. In this work, the technique of pulsed laser ablation in a liquid medium (PLALM) was used to obtain gold nanoparticles at different wavelengths, varying the energy; such nanoparticles were characterized by different techniques [8,9].
2. Experimental

2.1. Gold nanoparticles synthesis
The nanoparticles were synthesized using the PLALM technique, where a gold coin (target) (99.99% purity, Kurt Lesker) with 30 mm of diameter and 0.1 mm of thickness was immersed in 5 mL of Milli-Q water (type I) using a 50 mL beaker, the water height was 5 mm. Each sample was located at 29 cm from the mirror to the target. The laser ablation was performed for 5 minutes, with a pulse of 8 ns and a frequency of 10 Hz, with the help of the Q-Smart 850 by Quantel equipment provided by the Optical Laboratory of the Universidad Industrial de Santander, which allows to obtain the laser at different wavelengths using the different harmonics. Figure 1 shows the experimental setup of each configuration. First, it was configured with the 2W harmonic that provides a wavelength of 532 nm and the ablation energy was varied in 70 mJ, 100 mJ, 130 mJ, 160 mJ and 190 mJ. Likewise, with the 3W harmonic that allows to obtain 355 nm of wavelength and the 4W of 266 nm, the ablation energy was varied in 70 mJ, 100 mJ, 130 mJ, 160 mJ and 190 mJ and 70 100 mJ respectively.

2.2. Gold nanoparticles characterization
Size distributions of the nanoparticles were measured using dynamic light dispersion (DLS) in a ZetaSizer nano Zs (Malvern) equipment. The colloidal suspensions were placed in a 2.5 mL disposable cell until reaching a height between 10 mm and 15 mm. Three measurements were made of the average diameter of the particles with different scans defined automatically by the equipment depending on the concentration of the sample. The refractive index of the dispersing agent (water Milli-Q) used was 1.33 and the absorbance of the gold nanoparticles was 0.07.

Morphology was analyzed by scanning electron microscopy (SEM) in a Quanta FEG 650 (FEI) equipment. Colloidal suspensions were dropped on silicon wafers and allowed to dry at a temperature of 40 °C on a heating plate to eliminate excess water, as one drop dried; another was added and so on for 24 hours.

The electronic state of gold nanoparticles was determined by X-ray photoelectron spectroscopy (XPS) using the XPS/ISS/UPS (SPECS) surface characterization platform. The platform is equipped with a PHOIBOS 150 2D-DLD. Samples were fixed in sample holders using double sided carbon conductive tape. The measurements were carried out with a pressure around 1×10^-9 mbar. For each sample, the spectra were recorded using monochromatic Al Kα radiation (hv=1486.6 eV) operated with 100 W and 12 kV. The following sequence of spectra was recorded: survey spectra, C 1s, O 1s, Si 2p, Au 4f and C 1s again to verify the stability of the load compensation in function of time. Survey spectra were recorded at a pass energy of 100 eV, while the high-resolution spectra were recorded at a pass energy of 30 eV. The binding energy of the C 1s at 284.8 eV [10] was used as reference to adjust the binding energy scale of the spectra.

Topography and size of gold nanoparticles were measured using an atomic force microscope (AFM) Hitachi AFM5100N in tapping mode. For these measurements, only a single drop of the colloidal suspension was added on the silicon wafer. Topographic images and nanoparticle size profiles were analyzed by using Gwyddion open software [11].
3. Results and discussion

3.1. X-ray photoelectron spectroscopy analysis

An XPS analysis of the gold nanoparticles supported on silicon wafers synthesized at 100 mJ and wavelengths of 266 nm, 355 nm and 532 nm was performed. The results obtained from each analysis are shown in Figure 2. Figure 2(a) shows the spectra of the Au 4f region of the synthesized nanoparticles with a wavelength of 266 nm and 100 mJ of energy, where the presence of gold in the metallic state is evidenced, with a binding energy of 84.5 eV. Figure 2(b) also certifies the presence of synthesized gold nanoparticles with a wavelength of 355 nm, with a binding energy of 85.2 eV, where there is a chemical shift of gold, since the binding energy is 0.7 eV above of the nanoparticles synthesized at a wavelength of 266 nm, however gold does not lose its metallic state. In Figure 2(c), a low gold intensity is observed, that is, the number of nanoparticles synthesized at 532 nm of wavelength and energy of 100 mJ, although these nanoparticles retain their metallic state with a binding energy of 84.2 eV. Thus, it is verified that gold nanoparticles are being produced and that these retain their metallic state. The literature suggests that gold binding energy is around 84 eV [12].

![Au 4f XPS spectra of gold nanoparticles synthesized at 100 mJ with different wavelengths: (a) 266 nm, (b) 355 nm, and (c) 532 nm.](image)

3.2. Dynamic light dispersion analysis

An analysis of the average diameter of the gold nanoparticles was performed using the DLS technique, the results are presented in Figure 3. Figure 3(a) shows that nanoparticles of different sizes were obtained, since they have a diameter between 16 nm and 5.8 nm; where 34% have the smallest size of 5.8 nm. In the other hand, Figure 3(b) shows a more uniform distribution, since gold nanoparticles with an approximately average diameter of 55 nm were obtained, although these have a larger size compared with those synthesized with the wavelength harmonic of 266 nm (Figure 3(a)). Figure 3(c) shows a size distribution of the nanoparticles around 77 nm; this being the largest nanoparticle size obtained by varying the wavelength of the laser. Therefore, by means of the dynamic light dispersion technique, it is observed that the lower the wavelength of the pulsed laser, the smaller the average diameter of the gold nanoparticles.

![Size distribution of gold nanoparticles synthesized with 100 mJ of energy and different wavelengths: (a) 266 nm, (b) 355 nm, and (c) 532 nm.](image)
3.3. **Scanning electron microscopy analysis**

SEM analysis was performed to determine the morphology and size of the gold nanoparticles. Figure 4 shows the morphology and size of the gold nanoparticles obtained with the harmonic of 266 nm and 355 nm, using the SEM technique. A range of size between 27 nm and 62 nm was observed when the first harmonic was used, and a range of size between 50 nm and 35 nm when the second harmonic was used. An agglomeration of the nanoparticles was evidenced in both samples; the literature suggests that these have a high tendency to agglomerate when they are dried [13] and for this reason, the diameter of the gold nanoparticles synthesized at 266 nm of wavelength are not the same than that seen by DLS. SEM was not performed on the sample obtained at a wavelength of 532 nm and 100 mJ, since in the XPS analysis a low amount of gold was evidenced.

3.4. **Atomic force microscopy analysis**

Figures 5(a) and Figure 5(b) show the topography of the synthesized nanoparticles with a wavelength of 266 nm and 100 mJ of energy in 2 dimensions and 3 dimensions, respectively. It was found that the size of the nanoparticles synthesized under these conditions have a diameter between 9 nm and 20 nm (Figure 5(c)), this wavelength being the one that produces smaller gold nanoparticles.

![Figure 4](image.png)

**Figure 4.** SEM micrography of gold nanoparticles supported on silicon wafer synthesized at 100 mJ of energy and: (a) and (b) 266 nm, (c) and (d) 355 nm.
Figure 5. AFM topography of gold nanoparticles synthesized at 100 mJ and 266 nm: (a) 2D image, (b) 3D image, and (c) Size profiles of gold nanoparticles.

4. Conclusions
The change in wavelength influences the size of gold nanoparticles. It is evident that with smallest wavelength was obtained the smallest diameter of the synthesized nanoparticles. In this work were obtained average diameters of 9.6 nm, 55.4 nm and 77.3 nm for the wavelength of 266 nm, 355 nm and 532 nm, respectively. By the XPS analysis it can be concluded that due to the change of the harmonic, a chemical shift in the gold can be generated, although it does not lose its metallic state.

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