Preparation of silver nanoparticles by laser ablation in water

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Abstract: Solutions of silver nanoparticles are obtained by laser ablation in order to analyze the effectivity of this method. The laser used was a Nd:YAG with 1064 nm of wavelength. Characterization of these particles was done using a tranmission electron microscope and a spectrophotometer of double beam, in order to measure both the size and the absorption spectrum of these nanoparticles. The average diameter of the produced nanoparticles increases, from 9 to 22 nm, as the laser pulse energy increases from 9 to 13 mJ. These particles obtained in solution present a strong absorption due to plasmon resonance around 400 nm. It is observed that the peak absorbance of each sample is directly related with the concentration and the size of silver nanoparticles. The position and the maximum value of the peak absorbance variates when ablation time, energy density or laser energy are changed. Ablation efficiency is reduced as time progresses during the process due to the absorption and dispersion of laser light by the nanoparticle solution.

I. INTRODUCTION

Nowadays, there is a growing interest in the study of systems at nanoscale because lots of materials have very different properties when presented in bulk state. Therefore, intensive investigations on metal nanoparticles suspended in solutions have been undertaken because of their size-dependent characteristic properties [1]. Metallic nanoparticles and also colloidal solutions, of these nanoparticles, have plenty of applications in many fields due to their changing optical, magnetic and transport properties with size. These nanoparticles are present in many products such as biosensors, sun creams, inks, solar cells or wound dressings [1].

Currently there are many methods to generate nanoparticles suspended in aqueous solutions. Chemical methods are the most used since they are relatively economical and it is quite easy to control the particle size. Nevertheless, it has recently been demonstrated that laser ablation in liquids is a new promising technique to obtain metal colloids [2-4]. One advantage of laser ablation compared to other conventional methods for preparing metal colloids is the absence of chemical reagents in solutions. Therefore, pure colloids can be produced.

Controlling particle size is a very important factor in the method used for obtaining them, because their properties are very sensitive to their size. In the laser ablation method, the particle size can be controlled by changing the laser wavelength [2].

In this work, the laser ablation method is studied. The objective of this work is to generate nanoparticles with this recent technique and to characterize them in order to study how the particle size, and their concentration, change in different experimental conditions such as laser energy, energy density or ablation time.

II. EXPERIMENTAL

The laser used for ablation was a Nd:YAG (Baasel) working in its fundamental wavelength (λ=1064 nm). This laser was pulsed with a repetition rate of 1 kHz and a pulse width of certain nanoseconds (~150 ns). The current passing through the laser lamp was varied between 15 and 20 A in order to change the laser pulse energy.

The laser pulse energy is measured with a thermopile. This thermopile provides a voltage proportional to laser power (363.7 μV/W). A calibration of the laser was done in order to determine the laser power and pulse energy at different values of the lamp current, Fig. (1).

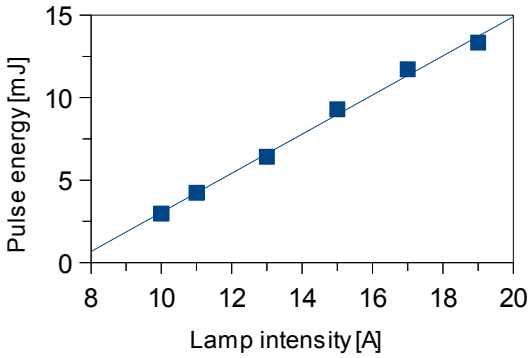

FIG. 1: Calibration curve that relates pulse energy with lamp current. The linear fit was used to correlate the pulse energy from the laser lamp intensity values.

In all the experiments, a colloidal suspension of silver nanoparticles was produced by irradiating with the laser light a silver target (>99.9% purity and rectangular shape) sticked at the bottom of a glass vessel filled with deionized water. The vessel is situated in a plastic recipient larger than the glass. This recipient is filled with water in order to prevent heating of the vessel during the ablation process. A microscope glass slide is placed on top of the vessel in order to avoid splashing of water and protecting laser lenses.

In order to make the nanoparticle generation process more efficient, the laser beam scanned the whole target surface. The laser beam was focused with a convergent lens and moved at a constant speed of 200 mm/s using two galvanometric mirrors that allowed the laser beam to scan the silver target. Two lenses with different focal distance (f= 100 mm and f=160 mm) were used in order to change the energy density.

The characterization of the nanoparticles was performed by a double beam spectrophotometer (Perkin Elmer Lambda 950) and transmission electron microscopy (TEM, Jeol 2010). All the absorption spectra were normalized to the

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absorption spectrum of deionized water. Absorbance values are divided by the optical path of cells the used for spectroscopy (1.1 cm).

Sample have to be prepared in order to be observed by TEM. A single droplet of the solution of interest was placed on a copper mesh that has a very thin film of carbon at the bottom. After drying the samples (when the water is evaporated) only the nanoparticles will remain on top of the carbon thin film.

In most samples, the ablated mass cannot be measured with a precision balance (0.1 mg resolution). For this reason, the ablated mass and concentration was calculated from the absorption spectrum. For calibration, three dissolutions were prepared from a sample in which the ablated mass was enough for being measured with balance. These dissolutions were prepared in order to have 1/2 , 1/4 and 1/8 of the reference concentration.

If we represent the absorption spectrum of these dissolutions we observe that the value of the maximum absorbance is proportional to the concentration. This phenomenon is used for calculating concentrations from the maximum value of absorbance, Fig. (2).

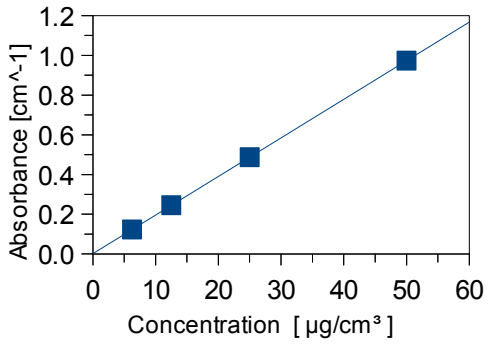

FIG. 2: Maximum value of the absorption peak as a function of concentration of silver nanoparticles.

III. RESULTS AND DISCUSSION

As a result of the ablation process, the water solutions acquired a yellowish colour which is characteristic of the presence of Ag nanoparticles. The yellow intensity depended on the laser energy, energy density and ablation time.

A. SERIES OF DIFFERENT ENERGIES

In this experiment, the ablation time was fixed at approximately 20 min. Laser energy and energy density are the parameters that were changed. In order to vary the energy density we changed the lens used to focus the laser beam, obtaining a spot size of ~ 300 µm (f=160 mm) or ~ 100 µm (f=100 mm).

Fig. (3) shows micrographs and the diameter distribution of various solutions of nanoparticles obtained by ablation of the silver target at different energies with the lens of f=160 mm. From left to right, the pulse energy was 9.2 mJ, 11.7 mJ and 13.3 mJ respectively.

The formation of nanoparticles in liquid solution is observed in the images obtained with TEM, Fig. (3). We can note that all the particles are spherical, regardless of the laser energy with which the sample was irradiated.

An increase of the particle diameter is observed when the pulse energy increases. This phenomenon is also reflected in a variation of the size distribution, the distribution center tends to move to higher values of the particle diameter when pulse energy is increased, Fig. (3).

The standard deviation also changes. According to histograms in Fig. (3) , the standard deviation increases at the same time that laser energy is increased too, Table I. This is reflected in TEM images, in which the range of particle size is higher in 13.3 mJ sample than in 9.2 mJ sample. If we observe TEM image of the sample prepared with 13.3 mJ, Fig. (3.c), particles of many sizes can be found (maximum particle diameter found was 70 nm and the minimum was

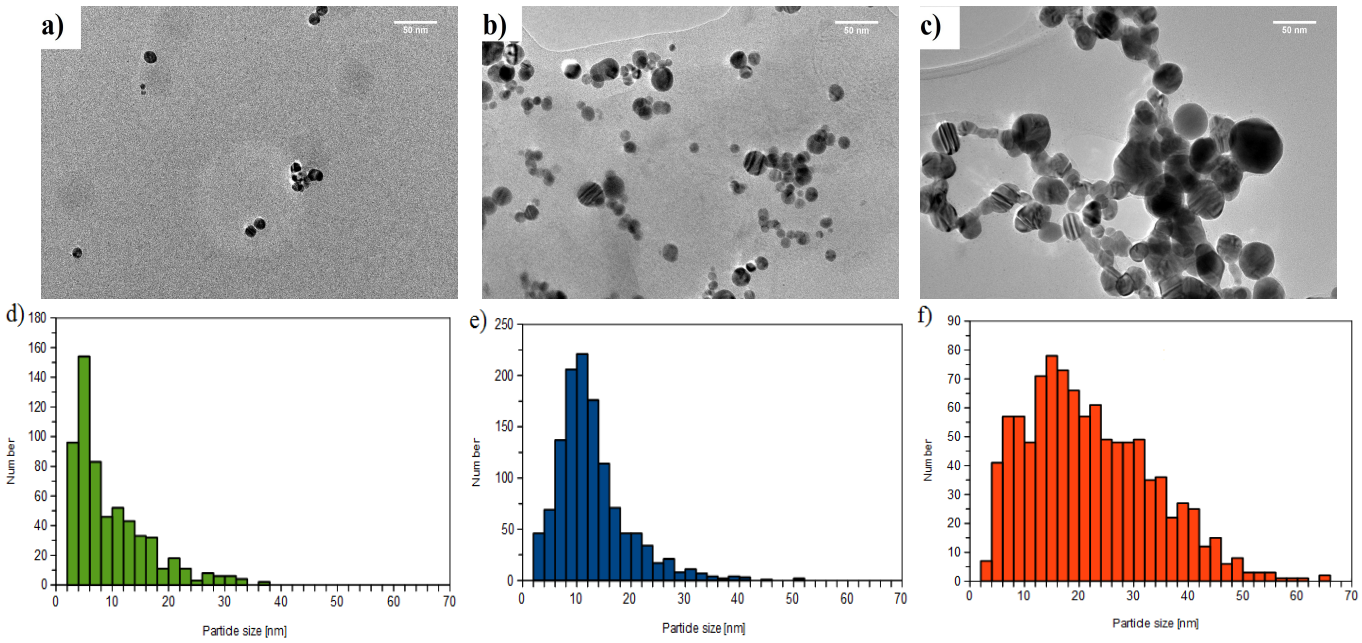

FIG. 3: Images obtained with TEM and size distributions of the silver nanoparticles produced by laser ablation with a laser energy of: a) and d) 9.2 mJ, b) and e) 11.7 mJ, c) and f) 13.3 mJ. Histograms are obtained by counting of 20 images from each sample. TEM was operating in image mode at 200 keV.

3-4 nm approximately). However, this does not happen in the image on the right, in which the particles that can be found have approximately the same diameter.

The number of nanoparticles in each specimen also varies. In samples obtained with a low pulse energy it is more difficult to find regions with nanoparticles. This means that the concentration in the samples obtained with a higher laser energy is greater. For this reason the number of nanoparticles that could be counted for obtaining the histograms is lower in the sample prepared with laser working at 9.2 mJ than in the other two samples, Fig. (3).

Pulse energy [mJ]	Mean diameter [nm]	Standard desviation [nm]
9.2	9	6
11.7	12	6
13.3	22	11

TABLE I: Size distributions of solutions prepared by laser ablation. In this table three specimens prepared with different laser energy and lens of f=160 mm are compared.

Fig. (4) shows the absorption spectra of six solutions of silver nanoparticles obtained with different laser energy. The spectra consist of strong absorption due to plasmon resonance around 400 nm in all samples [2-3]. It is observed that the absorption peaks tend to be higher when the laser energy is increased. As we know, a higher peak absorbance implies more concentration of silver nanoparticles in solution, Fig. (2). For this reason, it can be said that the higher the laser power, the higher the concentration of nanoparticles in solution. This is the cause for which the samples have a distinctive yellowish tone, the absorption peak is placed around 400 nm, absorbing the wavelengths corresponding to the blue and green colours. This colour is more intense in samples in which the absorption peak is higher.

A peak shift is also observed in the absorbance spectra, Fig. (4). The samples generated at lower laser pulse energies show a displacement of the absorption peak to lower wavelengths. In Fig. (3), we observe that the size of nanoparticles increases when the laser energy is increased too, for this reason if we look to absorption spectra, Fig. (4), it seems that there is a correlation between particle size and the position of the absorption peak. Absorption peak tends to be moved to higher wavelengths when laser energy is increased.

Small particles will have plasmon resonance at lower wavelenghts than bigger particles. If we compare two solutions of silver nanoparticles with different size, we will observe that the absorption peak is placed at higher wavelengths in the sample that contains bigger particles, Table. II. That is because smaller particles have higher surface/volume ratio than bigger particles.

Pulse energy [mJ]	Peak position [nm]
9.2	398 ± 2
11.7	402 ± 2
13.3	414 ± 2

TABLE II: Position of the absorption peak at different laser energies for samples in Fig. (4a.). Error corresponds to spectrophotometer resolution.

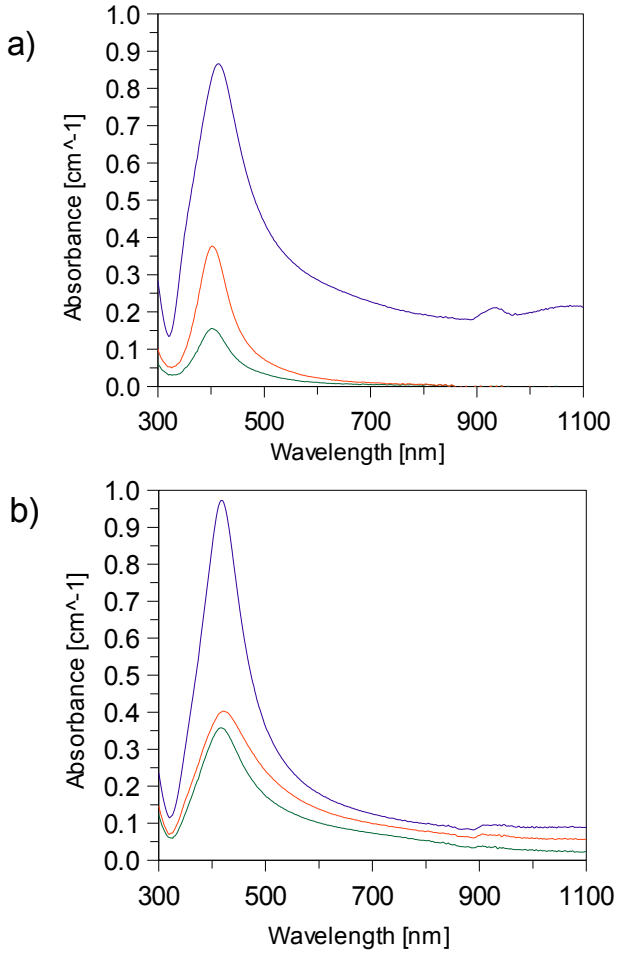

FIG. 4: Absorption spectra of silver colloidal solutions prepared by laser ablation with an energy of: (green) 9.2 mJ, (red) 11.7 mJ and (blue) 13.3 mJ. The lens used to focus the laser beam was: a) 160 mm, b) 100 mm. The vessel was filled with: a) 10 ml, b) 15 ml of deionized water.

Note that the absorption peaks in Fig. (4b) are higher than the ones in Fig. (4a). This implies that the concentration is higher in samples of Fig. (4b) because the energy density is greater due to the focal used was 100 mm, even though there is a larger volume of water.

Fig. (5) illustrates how many material is ablated from the silver target under different conditions of laser pulse energy and energy density.

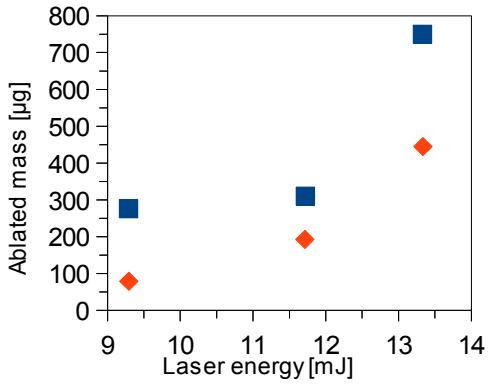

FIG. 5: Ablated mass as a function of pulse energy for samples prepared with a lens of [■] 100 mm, [♦] 160 mm. They correspond to the same samples in Fig. (4).

It is observed that the ablated mass is higher when the laser density increases. When spot size is the same and laser energy is changed, the same is observed. A higher laser energy implies a higher energy density, this is reflected in an increase of the ablation speed. Therefore more mass was extracted from the target. We can see that increase is not linear with energy, Fig. (5).

B. EVOLUTION OF ABLATION PROCESS

In this experiment the laser energy was fixed at 13.3 mJ/pulse and the lens used for obtaining all the samples was f=160 mm. The parameter studied is the ablation time. A set of solutions (10 ml) were prepared with different ablation time: 47, 94, 235, 470, 705 and 940 s, in order to study how the sample changes through time.

Fig. (6) shows the evolution of the absorption spectra of Ag nanoparticles suspensions after different ablation times. Absorption peak is increased when ablation time is increased too. As expected, more time means that more nanoparticles are generated and, consequently, their concentration increases. In the solutions is observed that higher ablation time, the more intense the color becomes.

A peak shift is also seen in Fig. (6). If we relate this fact with that seen in the previous section, it seems that the particles tend to be bigger increasing ablation time.

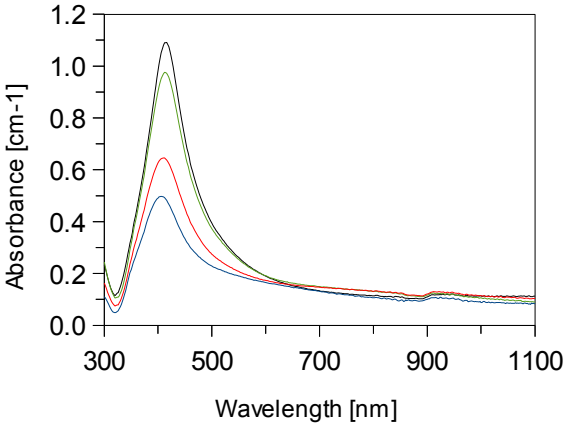

FIG. 6: Absorption spectra of silver colloidal solutions prepared by laser ablation during: (blue) 47s, (red) 235s, (green) 470s and (black) 940s.

The evolution of the concentration is not linear, Fig. (7). We can see that it is during the first seconds of the process that ablation is more efficient. As time passes, the concentration increases, but at a much slower pace than at the beginning. It seems that as time passes, the concentration tends to a saturation value.

Since the laser beam is focused on the target surface through the colloidal suspension, this could be related to the increased absorption and dispersion of the laser beam by the colloidal sample during the process, Fig. (6). Therefore, as time passes, the sample absorbs and disperses more and more laser light, decreasing the intensity of the light reaching the silver target. This fact results in a decrease in the ablation rate, Fig. (8).

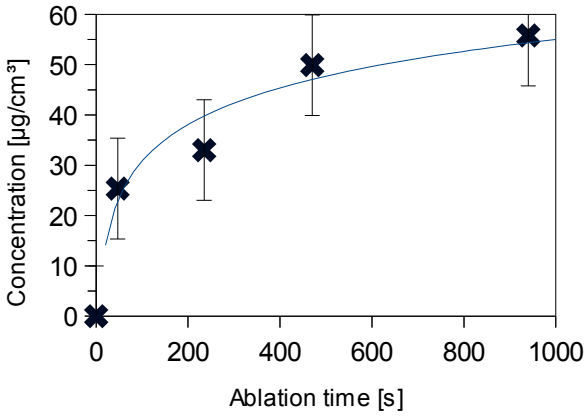

FIG. 7: Evolution of the concentration of a solution during the ablation process. Concentration is calculated from the fit obtained in Fig. (2).

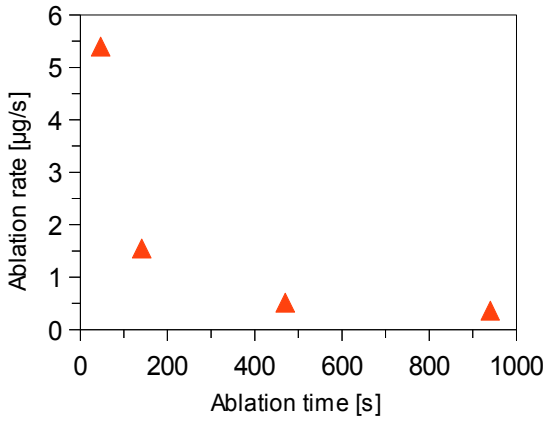

FIG. 8: Evolution of ablation rate during the process. The ablation rate is calculated from the values in Fig. (7).

Taking all this into consideration, we can make the hypothesis that the peak shift seen in the absorbance spectra, Fig. (6), is because the particles tend to aggregate when ablation time is increased. According to Fig. (7) and Fig. (8), it seems clear that the dispersion due to the colloidal suspension increases with ablation time. Therefore, the laser loses energy on its way to reach the target. For that reason, the laser energy at the surface of the silver target is lower as time passes. Based on the previous results, less laser energy means smaller particles, Fig. (3), so we can say that the smaller particles tend to aggregate more than bigger particles [3].

IV. CONCLUSIONS

Silver nanoparticles have been prepared by laser ablation in water. TEM observations and absorption spectra obtained with a spectrometer indicates that the spherical shape of these nanoparticles do not change. The size and concentration of these nanoparticles change by changing parameters such as laser energy or ablation time. In our experiment we obtained nanoparticles from 3 nm to 70 nm. Nanoparticles larger than 100 nm have not been observed.

Moreover, the dynamics of the ablation process has also been studied. The efficiency of ablation is reduced as time passes due to self absorption and dispersion of the liquid solution.

Taking all of this into consideration, we can conclude that laser ablation is a good method for obtaining pure silver nanoparticles in a controlled way. We were able to obtain stable particles in pure water without chemical reagents.

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