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# Synthesis and resizing of silver nanoparticles by laser ablation in liquids

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**Abstract**

Silver nanoparticles are having great attention due to their remarkable optical, electrical and antimicrobial properties, which make them used in many different technological and scientific applications. In this work we present the results of obtaining silver nanoparticles by ablating a silver target submerged in de-ionized water. To resize and get uniform nanoparticles, subsequently laser ablation under different conditions was carried out onto the obtained colloidal solutions. The synthesis of nanoparticles has been carried out using a nanosecond Nd:$YVO_4$ laser operating at 532 nm.
The obtained particles are analyzed and the nanoparticles resizing mechanism is discussed. The obtained nanoparticles were characterized by means of transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), energy dispersive X-ray spectroscopy (EDS) and UV/VIS absorption spectroscopy. The obtained nanoparticles consisted in Ag particles with rounded shape. The size of particles has been reduced by subsequent laser irradiation to give smaller nanoparticles with narrow size distribution. However the irradiation lead to particles melting and formation of agglomerations.

Keywords: Silver nanoparticles; laser ablation, resizing

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## 1. Introduction

There is an increase interest in metal nanoparticles because of their unique physical and chemical properties related to the size effect when compared to bulk material. Due to their special properties, such as good conductivity (Lesyuk et al., 2011), antibacterial and antifungal effects (Pal et al., 2007; Petica et al., 2008; Guzman, M., 2012; Shaban and Abd-Elaal, 2017), catalytic activity (Huang et al., 2011), etc. silver nanoparticles play an important role in many different areas, being extensively used in medicine, industrial applications, photovoltaic energy, etc. For these applications, synthesizing nanoparticles with the adequate size distribution, morphology and crystallinity is very important.

There are different techniques for producing Ag nanoparticles, being chemical the most used method. Many of these techniques of production, use precursors and solvents, or imply chemical reactions which can contaminate the obtained nanoparticles. Laser ablation of solids in liquids (LASL) enables obtaining nanoparticles with no need of chemical precursors. Its simplicity together with the advantage of producing nanoparticles with small size, narrow distribution and weak agglomeration make it suitable for metal nanoparticle fabrication.

In previous works laser ablation of silver plate was carried out in open air and silver nanoparticles with rounded shape and narrow size distribution has been obtained (Boutinguiza et al., 2015). In the present work we report the results of synthesing Ag nanoparticles using laser ablation of silver target in water as well as the irradiation of the obtained colloidal solution.

## 2. Materials and methods

### *2.1. Part 1. Laser Ablation*

Silver foils with 99.99% of purity was cleaned and sonicated to be used as laser ablation targets. The targets were fixed inside a glass vessel filled with milli-Q water up to 1mm over the upper surface of the silver foil. A diode-pumped Nd:$YVO_4$ laser providing pulses at wavelength of 532nm, 0,3mJ of pulse energy and pulse duration of 10ns has been used as energy source to ablate the target. Processing parameters used are listed in table 1. The laser beam was focused on the upper surface of the target to give a fluence of 2 J/$cm^2$, and was kept in relative movement with respect to the metallic plate at 50 mm/s of scanning speed.

Table 1. Processing parameters

| Laser source | Wavelength (nm) | Pulse length (ns) | Frequency (kHz) | Average power (W) | Scanning speed (mm/s) |
|---|---|---|---|---|---|
| Nanosecond laser | 532 | 10 | 20 | 6.0 | 50 |

### *2.2. Part 2. Re-Irradiation*

Part of the obtained solution from the LASL has been re-irradiated using the same laser parameters. In order to irradiate uniformly the colloidal solution, the suspension was kept in a flask and subjected to a constant pressure to leave the flask as a stream of about 1 mm of diameter. The laser beam was focused on the stream.

After each experiment, samples of the obtained colloidal suspension were dropped on carbon-coated copper microgrids and on Si substrates to characterize the particle morphology and microstructure. The scanning electron microscopy (SEM) images were taken using a JEOL-JSM-6700F. Transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS) and high-resolution transmission electron microscopy (HRTEM) images were taken on a JEOL 2010F FEG transmission electron microscope equipped with a slow digital camera scan, using an accelerating voltage of 200kV, to reveal their crystallinity and morphology. The size distribution was derived from a histogram which was obtained by measuring the diameter of about 200 particles from TEM images. The UV-Vis absorption spectra of the obtained particles on glass substrates were measured in a Hewlett Packard HP 8452 A spectrophotometer.

## 3. Results and discussion

After 5 minutes of processing the water turned yellowish, the color intensity increases according to the concentration of the synthesized nanoparticles. The appearance of the obtained particles is shown in figure 1 corresponding to TEM image.

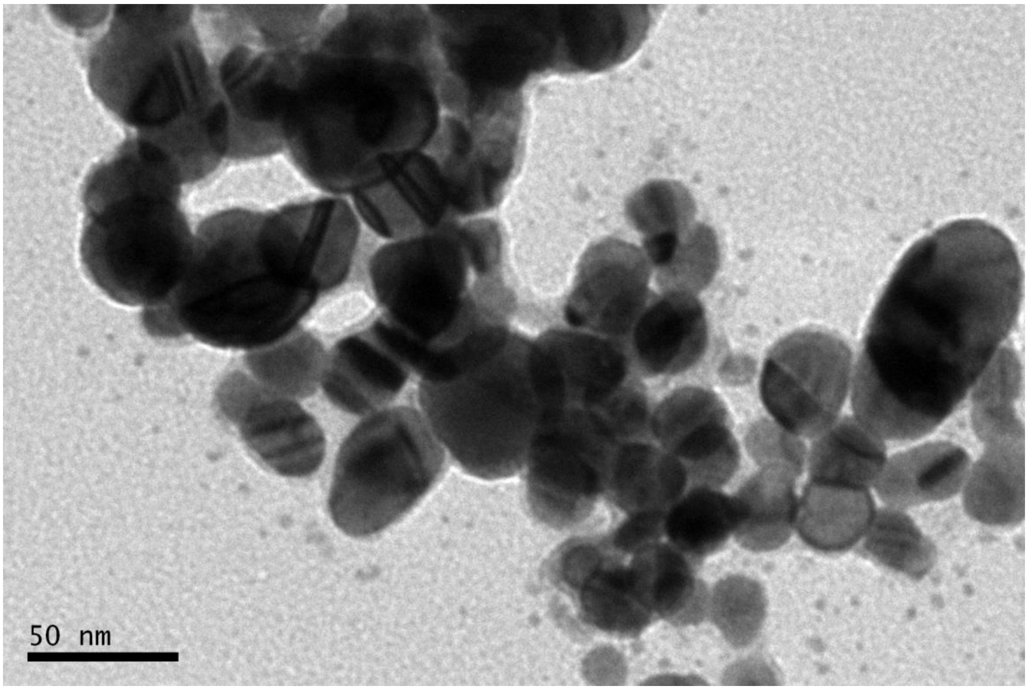


Fig. 1. Ag nanoparticles obtained by laser ablation of Ag foil in water using a $Nd:YVO_4$ laser operating at 532nm.

Note that the silver particles obtained by LASL exhibit rounded shape and homogeneous size with certain tendency to agglomeration. This is due to the formation mechanism of nanoparticles and the regime taking place between laser beam and the target. When the laser beam strikes on the Ag target, the incident radiation is absorbed heating up the target above its melting point. At the same time, a very thin layer of liquid surrounding the droplets is evaporated, which can react with the droplets to give the final particles.

In spite of the most nanoparticles are also spherical, high concentrations of agglomerates are observed where the nanoparticles have an irregular shape, mainly elongated particles. This is due to the interaction between the laser beam and the already formed particles, especially when the nanoparticle concentration in solution is high. Taking into account that the melting point of the nanoparticles is decreased compared to that of starting material, the incident irradiation melts nanoparticles, which solidify forming chains and/or agglomerations. This effect can occur during the nanoparticle formation from the metallic target, but it is clearly observed when the obtained solution is irradiated again. One hand some particles are ablated to give smaller ones, and on the other hand some particles are melted to stick together, as can be seen from figure 2.

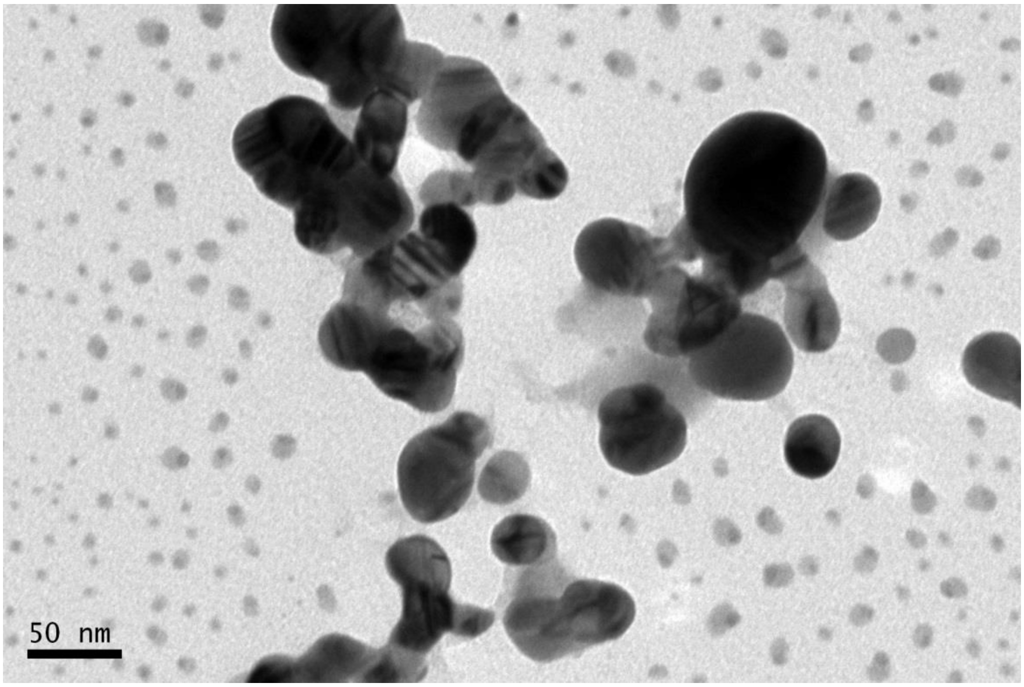


Fig.2. Ag nanoparticles obtained by re-irradiation .

According to the obtained results the re-irradiation process enables obtaining smaller nanoparticles than those obtained in starting solution, but contributes also to the formation of irregular and bigger particles as consequence of re-melting of initial nanoparticles. This behavior is clearly represented in figures 3 and 4 showing the nanoparticle size distribution in processes, initial irradiation and re-irradiation of colloidal solution. The latter process leads to obtaining smaller particles together with wider size distribution.

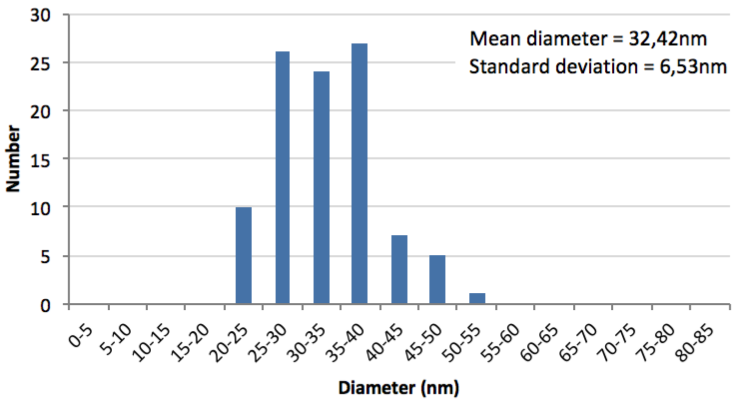


Fig.3. Histogram of more than 100 particles obtained by laser ablation of Ag in water using a pulsed Nd:YAG laser.

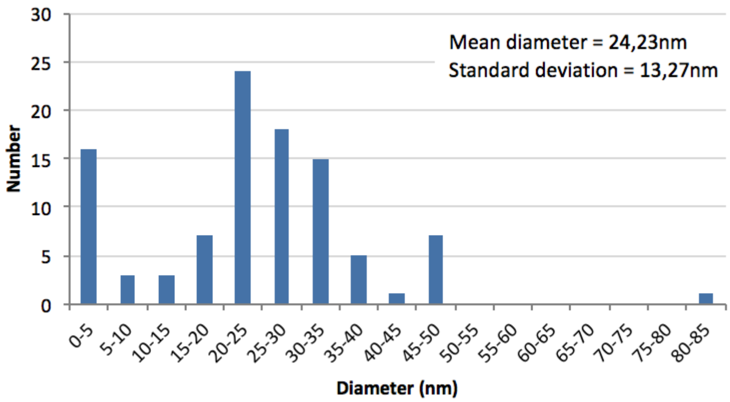


Fig.4. Histogram of more than 100 particles obtained by re-irradiation of the colloidal solution using a pulsed Nd:YAG laser.

All the particles obtained under the conditions mentioned before are crystalline, as can be seen from figure 5 showing a HRTEM of a single particle exhibiting clear fringes. The measurements of the corresponding interplanar distances of 0.237 nm, which could be assigned to {111} family planes (0.237 nm).

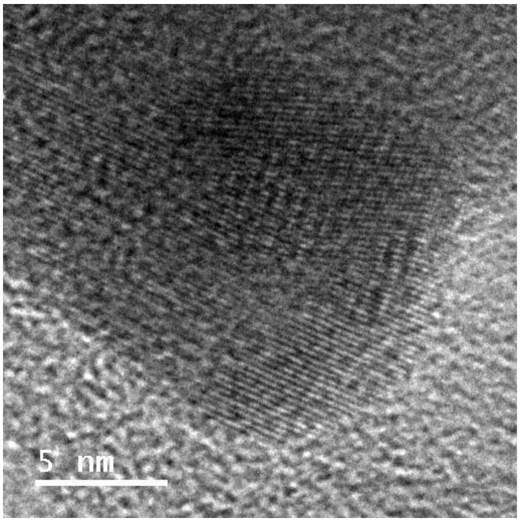


Fig.5. HRTEM image of Ag crystalline nanoparticles showing lattice fringes.

Concerning the optical properties of the colloidal solutions obtained under radiation and re-irradiation processes, the characteristic plasmon resonance peak of spherical nanoparticles is shown in the uv-visible spectrum around 400 nm. The increase of the surface plasmon resonance intensity indicates an increase of the colloidal concentration-

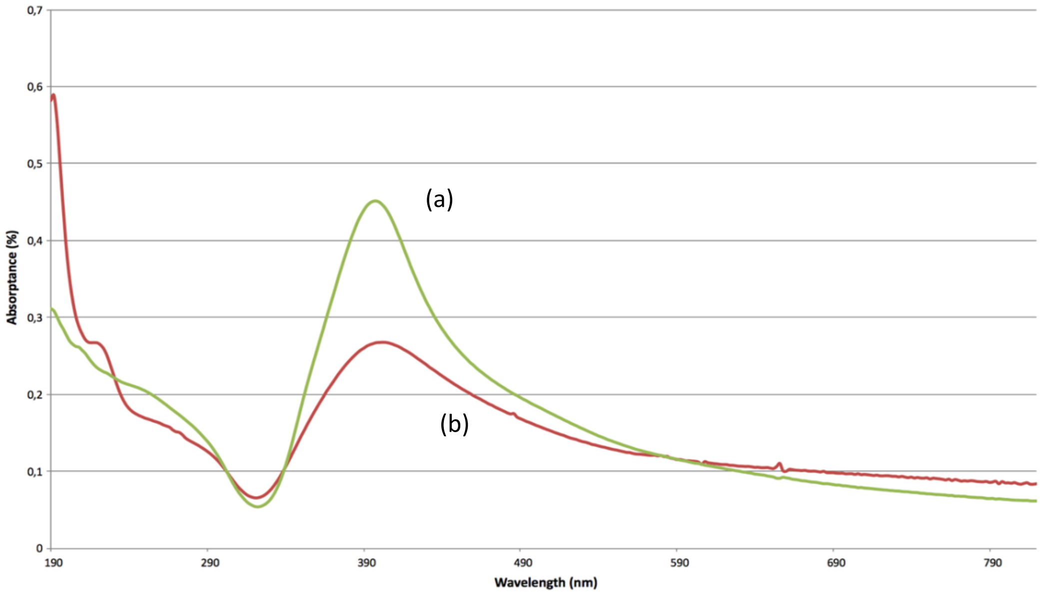


Fig.6. UV-vis spectrum of Ag nanoparticles: (a) obtained by laser ablation of metallic silver in water and (b) after re-irradiating the colloidal solution of a)..

## 4. Conclusions

Crystalline nanoparticles of Ag without any chemical reagent or contamination have been obtained by means of LASL technique as well as re-irradiation, using a nanosecond Nd:$YVO_4$ laser operating at 532 nm of wavelength. The particles obtained by laser ablation of silver target in water show rounded shape and narrow size distribution, while those obtained by re-irradiating the initial colloidal solution contributes to reduce the size of part of nanoparticles as well as to widen the size distribution by the formation bigger nanoparticles with irregular shape. This is due to the effect of nanoparticles re-melting.

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