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Production of silver nanoparticles in liquid by CW and pulsed lasers

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Abstract

The new properties of nanoparticles have accelerated the growth of production of nanostructured materials and their use in many different applications. In particular, silver nanoparticles have attracted much attention as a subject of investigation due to their well-known properties, such as high electrical and thermal conductivity, antibacterial and antifungal effects, etc. They are used in many different areas, medicine, industrial applications, and scientific investigation, etc. The size as well as the shape is very important for certain applications.
Almost all publications reporting synthesis of nanoparticles by laser ablation of solids in liquids use pulsed lasers, especially nanosecond and femtosecond lasers. Nevertheless nanoparticles can be also obtained in liquid media using long pulse lasers and continuous wave (CW) lasers. In the present work we present the results of ablating Ag target in water using a pulsed, as well as, a continuous wave laser.

The obtained particles consist of pure Ag nanoparticles showing rounded shape and uniform size distribution. Crystalline phases, morphology and optical properties of the obtained colloidal nanoparticles were characterized by means of X-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and UV/VIS absorption spectroscopy.

Keywords: laser ablation; silver nanoparticles; pulsed laser; cw laser.

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1. Introduction

Silver nanoparticles have attracted much attention as a subject of investigation due to their well-known properties, such as their high electrical and thermal conductivity [1], antibacterial and catalytic effects [2-4], etc. They are used in many different areas, such as medicine [5-6], industrial applications [7], and scientific investigation [8], etc. The sizes as well as the shapes of nanoparticles, which depend on the synthesis technique, are very important for certain applications. There are different techniques for producing Ag nanoparticles using chemical [9-10], physical [11-12] and biological routes [13-14]. Each method presents its own disadvantages and restrictions, being the chemical one the most used. To prevent the presence of contamination and impurities in obtained products, laser ablation of solids in liquid phase (LASL) has been considered an alternative method to chemical reduction, especially when biological applications are taken into account. Its simplicity together with the advantage of producing nanoparticles with small size, narrow distribution and weak agglomeration make it suitable for metal nanoparticle synthesis.

There are different techniques for producing Ag nanoparticles, chemical, electrochemical, sonochemical, etc. These methods often lead to impurities together with nanoparticles or colloidal solutions. Laser ablation of solids in liquids (LASL) enables obtaining nanoparticles with no need of chemical precursors. In almost all publications reporting synthesis of nanoparticles by LASL a pulsed laser is used, especially nanosecond and femtosecond lasers. Nevertheless nanoparticles can be obtained in liquid media using long pulse lasers and continuous wave (CW) lasers. In previous works we have used the LASL method to obtain and characterize titanium dioxide nanoparticles [15-16]. Herein we report the result of obtaining silver nanoparticles by LASL using CW laser as well as pulsed laser.

2. Materials and methods

Target plates of Ag were cleaned and sonicated to be attached to the bottom of a glass vessel and filled with water up to 0.5 mm over the upper surface of the Ag plate. The first laser was a monomode Ytterbium doped fiber laser (YDFL). This laser works in CW mode delivering a maximum average power of 200 W. Its high beam quality allowed setting an irradiance of 2×10^5 W/cm^2. The laser beam was coupled to an optical fiber of 50 µm core diameter and focused on the upper surface of the target. The second laser source was a diode-pumped Nd:YVO_4 laser system. It provides laser pulses at 532 nm with pulse duration of 1 µs, a repetition rate of 20 kHz and an average output power of 6 W, giving an irradiance of 1×10^8 W/cm^2 in pulsed regime. The laser beam was kept in relative movement with respect to the metallic plate at a scanning speed of 5 mm/s. After each experiment, the obtained colloidal suspensions were dropped on carbon coated copper microgrids substrates for examination of particle morphology and microstructure, while as prepared colloidal solutions were used for UV–vis absorption tests. Transmission electron microscopy (TEM), selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) images were taken on a JEOL-JEM 2010 FEG unit equipped with a slow digital camera scan, using an accelerating voltage of 200 kV, to reveal their crystallinity and morphology.

3. Results and discussion

When using CW laser or long laser pulses the interaction between the laser beam ant the silver target is governed by thermal effects that depend on the characteristics of the laser radiation and the target nature.

When a laser beam strikes a silver target submerged in liquid delivering high irradiance, a thin layer of metal is heated up above its melting point leading to a combination of melting and boiling which give place to nanoparticle formation. This is strictly the case of the CW laser used in this case; since the obtained particles exhibit rounded shape with certain tendency to agglomeration, revealing that the main formation mechanism is melting and rapid solidification in the surrounding water. The appearance of this kind of particles is shown in figure 1. Several microanalysis performed on particles confirmed that the obtained particles are metallic Ag. The HRTEM images of obtained nanoparticles revealed that they are crystalline, as can be seen from figure 1 which shows clearly visible lattice fringes. The average calculated interplanar distances from the Fast Fourier Transform (FFT) corresponding to HRTEM images of several particles obtained using a CW laser, are compared with those of Ag in table 1.

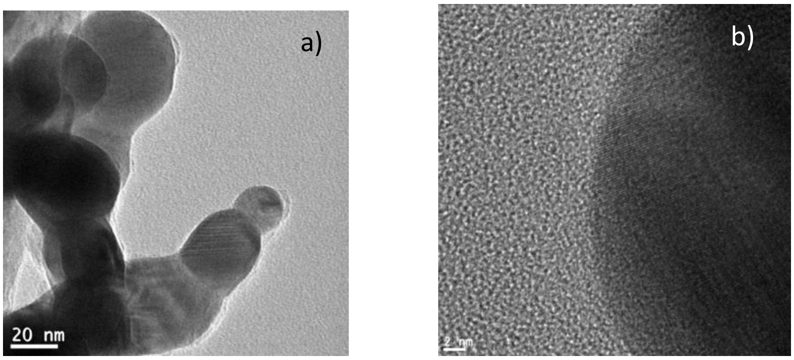

Fig. 1. Nanoparticles obtained by ablating Ag plate submerged in water with a CW laser: (a) TEM micrographs Ag nanoparticles appearance. (b) HRTEM of Ag nanoparticle showing clear fringes.

Table 1. Measured interplanar distances from the FFT of figure 1 compared to those of Ag.

Measured d_{hkl} (nm)	Ag d_{hkl} (nm)
0.235	0.235
0.212	0.204

The shape of particles obtained when using pulsed laser is similar to that obtained by CW laser, but with smaller size. As the pulse duration is shorter than the time needed for heat dissipation in the target, the process is fundamentally governed by thermal effects. This condition together with the high repetition rate leads to a relatively large layer of melted material. With the increase of temperature, evaporation and eventually formation of plasma can take place; and part of the melted liquid can be superheated to generate phase explosion. Consequently, clusters and droplets directly ejected from the target and aggregations formed in the ablated plume lead to the nanoparticle formation via solidification and condensation. The mechanism is similar to that mentioned before when using CW laser, but with more presence of phase explosion and vaporization, which contributes to the formation of smaller nanoparticles, as can be observed in the TEM picture in figure 2 (a). All the obtained particles with the use of the pulsed laser are also crystalline, as can be seen from the HRTEM image in figure 2 (b), showing clearly the presence of lattice fringes corresponding to their crystalline planes.

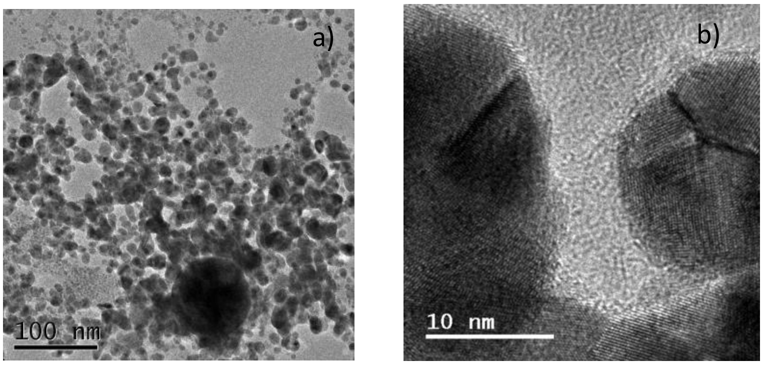

Fig. 2. Nanoparticles obtained by ablating Ag plate submerged in water with a pulsed laser: (a) TEM micrographs of Ag nanoparticles showing general appearance. (b) HRTEM of Ag nanoparticle showing clear fringes.

To characterize the crystalline structure of the obtained Ag nanoparticles when a pulsed laser was used, an analysis of the SAED patterns was performed on various groups of particles. Their interplanar distances were compared with those of Ag, as is depicted in table II. The measured interplanar distances show good agreement with those corresponding to pure metallic silver.

Table 2. Measured interplanar distances from the SAED of a group of particles obtained by pulsed laser compared to those of Ag.

Measured d_{hkl} (nm)	Ag d_{hkl} (nm)
0.235	0.236
0.204	0.204
0.143	0.145

Regarding the optical properties of the colloidal nanoparticles, the two groups obtained by both lasers showed similar behavior. Their typical UV-vis is represented in figure 3, showing a pronounced peak around 400 nm, which is characteristic of spherical nanoparticles; while the peaks at lower wavelengths are due to the presence of smaller particles as well as particle agglomeration.

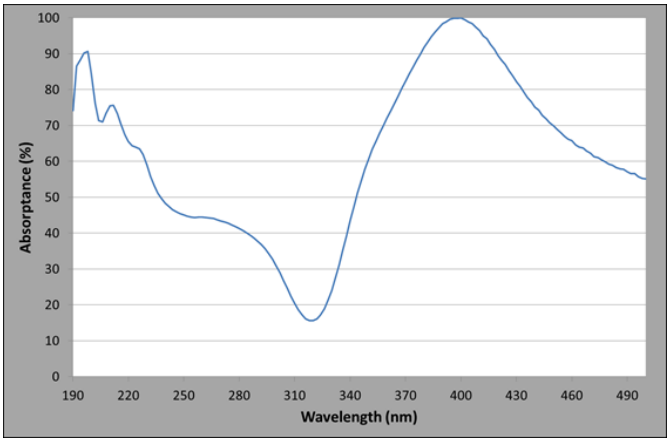

Fig. 3. UV-vis spectrum of colloidal nanoparticles obtained by laser ablation Ag plate submerged in water.

4. Conclusions

Colloidal nanoparticles have been obtained by laser ablation of Ag targets submerged in water using CW and pulsed lasers. The particles exhibited rounded shape with tendency to agglomeration and with bigger size when the CW was used. The main formation mechanism of the obtained nanoparticles was explosive phase, which favored the formation of continuity between particles.

Acknowledgements

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References

1.- Yu A Krutyakov, A A Kudrinskiy, A Yu Olenin, G V Lisichkin, Russ. Chem. Rev. 77 (2008), p 233 – 257. Synthesis and properties of silver nanoparticles: advances and prospects.

2.-. A. Petica, S. Gavriliu, M. Lungu, N. Buruntea, C. Panzaru, Materials Science and Engineering: B. Vol. 152, No. 1-3, 2008, p 22-27. Colloidal Silver Solutions with Antimicrobial Properties.

3.- P. Gupta , M. Bajpai, and S. K. Bajpai, The Journal of Cotton Science 12, 2008, p 280–286. Investigation of Antibacterial Properties of Silver Nanoparticle-loaded Poly (acrylamide-co-itaconic acid)-Grafted Cotton Fabric.

4.- Z. L. Jiang, C. Y. Liu and L. W. Sun, The Journal of Physical Chemistry B, Vol. 109, No. 5, 2005, p 1730-1735. Catalytic Properties of Silver Nanoparticles Supported on Silica Spheres.

5.- M. Bosetti, A. Massè, E.Tobin, M. Cannas, Biomaterials 23 (2002) , p 887–892. Silver coated materials for external fixation devices: in vitro biocompatibility and genotoxicity.

6.- Douglas Roberto Monteiro, Luiz Fernando Gorup, Aline Satie Takamiya, Adhemar Colla Ruvollo-Filho, Emerson Rodrigues de Camargo, Debora Barros Barbosa, Int. J. Antimicrob. Agents. 34 (2009), p 103–110. The growing importance of materials that prevent microbial adhesion: antimicrobial effect of medical devices containing silver.

7.- Maqusood Ahamed, Mohamad S. AlSalhi, M.K.J. Siddiqui, Clin. Chim Acta 411 (2010), p 1841–1848.. Silver nanoparticle applications and human health.

8.- Yang, J,; Pan, J., Acta Mater 60 (2012), p 4753–4758. Hydrothermal synthesis of silver nanoparticles by sodium alginate and their applications in surface-enhanced Raman scattering and catalysis.

9.- Y. Badr, M.G. Abd El Wahed, M.A. Mahmoud, Appl. Surf. Sci. 253 (2006) p, 2502–2507. On 308 nm photofragmentation of the silver nanoparticles..
10.- Yujie Han, Zhimin Luo, Lihui Yuwen, Jing Tian, Xingrong Zhu, Lianhui Wang, Appl. Surf. Sci. 266 (2013), p 188–193. Synthesis of silver nanoparticles on reduced graphene oxide under microwave irradiation with starch as an ideal reductant and stabilizer.
11.- L D'Urso, V Nicolosi, G Compagnini, O Puglisi, Appl. Surf. Sci. 266 (2004). p 131-136. Size distribution of silver nanoclusters induced by ion, electron, laser beams and thermal treatments of an organometallic precursor.
12.- Giuseppe Compagnini, Elena Messina, Orazio Puglisi, Valeria Nicolosi, . Appl. Surf. Sci. 254 (2007), p 1007-1011. Laser synthesis of Au/Ag colloidal nano-alloys: Optical properties, structure and composition
13.- S.V. Otari, R.M. Patil, N.H. Nadaf, S.J. Ghosh, S.H. Pawar, . Mater. Lett. 72 (2012), p 92–94. Green biosynthesis of silver nanoparticles from an actinobacteria Rhodococcus sp.
14.- Amit Kumar Mittal, Jayeeta Bhaumik, Sanjay Kumar, Uttam Chand Banerjee, . J. Colloid. Interface Sci. 415 (2014), p 39-47 Biosynthesis of silver nanoparticles: Elucidation of prospective mechanism and therapeutic potential.
15.- M. Boutinguiza, B. Rodríguez-González, J. del Val., R. Comesaña., F. Lusquiños, J. Pou, Nanotechnology 22 (2011) 195606 Nanotechnology 22 (2011) 195606. Laser-assisted production of spherical TiO2 nanoparticles in water.
16.- M. Boutinguiza, R. Comesaña, F. Lusquiños, A Riveiro, J. del Val, J. Pou, Applied Surface Science, 302 (2014), p19–23. Palladium nanoparticles produced by CW and pulsed laser ablation in water. Appl. Surf. Sci. 258 (2012) 9484-9486.