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Statistical study of Gold Nanoparticles Produced by Laser Ablation in Water

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Abstract: Due to their small dimensions, nanoparticles and materials consisting of nano-sized building blocks exhibit unique mostly superior properties, well differing from their bulk counterpart. Since an effecting method to produce nanoparticles is laser ablation, a study was performed on the generation of particles during laser ablation with emphasis on size distribution measurements. Experimental production of gold nanoparticles upon the ablation of metal targets in deionized water, caused by irradiation with a Nd:YAG laser is studied. The nanoparticles emerging in a liquid were investigated using UV-visible absorption spectroscopy, and transmission electron microscopy. The result display effectiveness of laser ablation in producing uniformly sized and pure gold nanoparticles. Also it was confirmed that colloidal gold nanoparticle solutions exhibit a distinct Plasmon resonance at 530nm respectively.

Key words: Gold nanoparticles, Laser ablation, UV-visible**,** Transmission Electron Microscopy, Particle size distribution.

INTRODUCTION

Metal nanoparticles, with diameters ranging roughly between 1 and 100 nanometers, are natural bridges between molecules and extended solids. They open up a new field in fundamental science and because of their potential technological applications. Due to the significant increase in surface compared with volume, nanoparticles show unique properties. The dominance of the surface behavior provides the possibility to control most material properties without change in chemical composition such as: melting point, magnetic properties and even color of materials. A few applications of nanoparticles include: use as catalysts [Safavi *et al*., 2008], drug carriers [Yuan *et al*., 2008] and production of nanochips [Limon *et al*., 2009], nanotubeds [Zhu *et al*., 2009] and nanowires [Sun *et al*., 2007]. In all these cases in order to use nanoparticles, controlling the size and shape of nanoparticles and their purity is of utmost importance. Therefore special attention should be paid to particle size distribution produced and its purity.

In recent years, metal nanoparticles suspended in a solution to display different optical, magnetic, and electronic properties from bulk materials, have attracted much attention. The most commonly used methods to prepare metal nanoparticles in solution is the chemical reduction of metal ions [Chou and Ren, 2000]. In these chemical methods, the shape and size of nanoparticles produced cannot be controlled. Also, due to the presence of chemicals, colloidal solution of nanoparticles produced is not pure. In recent years a new method for producing metal nanoparticles in solution has been developed. In this method, a target immersed in a liquid is irradiated by a pulsed laser which in turn produces pure nanoparticles in the solution. To control the nanoparticles size, the first important step is to acquire a greater understanding of the process of nanoparticles generation and evolution during laser ablation.

This paper aims to achieve such knowledge using experimental study on creating gold nanoparticles by laser ablation. The results showed that using such experimental setup production of gold nanoparticles with regular spherical shape, well particle size distribution and purity is possible.

2. Experimental Setup:

The experimental apparatus used in this study is shown in figure 1. The output of an Nd:YAG laser was used for ablation. 1 gram gold bullion (Suisse Fine Gold 99.99%) immersed in 5ml deionized water, was irradiated with a focused 1064 nm beam of a pulsed Nd:YAG laser with 5Hz repetition. The spot size of the focused laser beam was 1.0mm. The laser pulse width was 30 ns and irradiation was continued for 15 minutes with an energy output of 50Mj per pulse.

During the irradiation, due to laser beam collision with gold bullion, the material quickly plucked from the surface and was thrown into the ambient fluid. As a result of this process gold colloidal solution was produced. During this process, clear water slowly was converted to a purple color.

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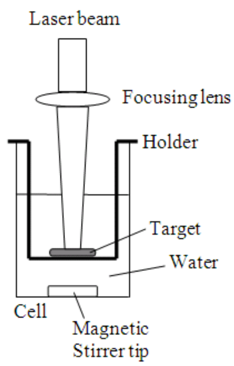


Fig. 1: Experimental apparatus used for production metal nanoparticles by laser ablation in liquid medium.

3. Results and Comments:

3.1. Ultraviolet – visible Spectrometry:

One of the methods used for nanoparticle characterization, especially in liquid medium is a UV-visible Spectrometry. In this study, in order to prepare UV-visible spectra from a gold colloidal solution, Cary-100 spectrometer was used. The comparison between the absorption spectrum of water and gold colloidal solution is shown in figure 2. This spectrum shows a maximum at 530 nm, which corresponds to the surface plasmon absorption that is unique for gold nanoparticles. Maximum absorption of gold nanoparticles obtained in this experiment, has a good agreement with the maximums obtained in other studies [Kazakevich *et al*., 2006, Dolgaev *et al*., 2002].

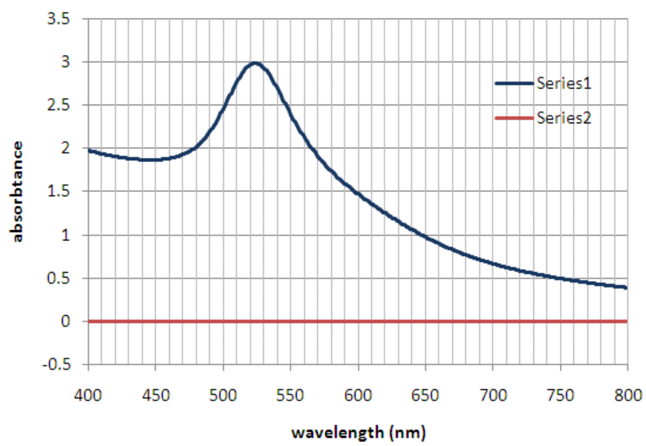


Fig. 2: (Series 1) Absorption spectra of Au colloids obtained by laser ablation, (Series 2) Absorption spectra of water.

Light interaction with the nanoparticles strongly depends on size, shape and composition of the nanoparticles and the environment contains these particles. Solution of the problem of absorption and scattering of light by a small particle involves solving Maxwell's equations with the correct boundary conditions, and also using Mie theory and assuming nanoparticles are spherical, this solution results in calculating the location of the Plasmon peak. After these calculations, the scattering and extinction cross sections can be calculated from:

$$\sigma_{sca} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}(2n+1)(|a_n|^2 + |b_n|^2) \qquad (1)$$

$$\sigma_{ext} = \frac{2\pi}{k^2}\sum_{n=1}^{\infty}\mathrm{Re}(a_n + b_n) \qquad (2)$$

The coefficients a_n and b_n in Eq. (1) and Eq. (2) are given by

$$a_n = \frac{m\psi_n(mx)\psi_n'(x) - \psi_n(x)\psi_n'(mx)}{m\psi_n(mx)\xi_n'(x) - \xi_n(x)\psi_n'(mx)} \quad (3)$$

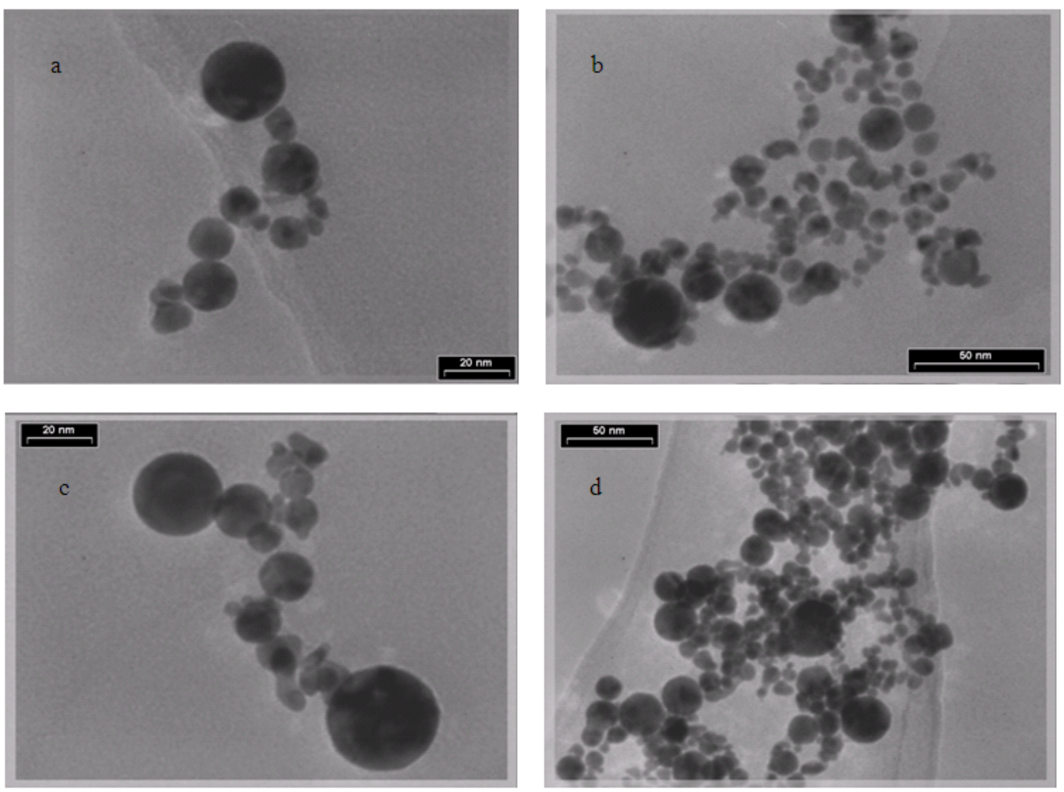
$$a_n = \frac{\psi_n(mx)\psi_n'(x) - m\psi_n(x)\psi_n'(mx)}{\psi_n(mx)\xi_n'(x) - m\xi_n(x)\psi_n'(mx)} \quad (4)$$

In which ψ and ξ are Ricatti-Bessel functions of order *n*, $x = kR$ is a size parameter (*R* is the radius of the particle) and $m = \sqrt{\varepsilon_p / \varepsilon_m}$ is the square root of the ratio of the dielectric functions of the particle and of the medium. By replacing the values for gold nanoparticle with a radius of 10 nm and parameters for water as the medium nanoparticles exist in, gives the Plasmon peak of 530 nm [Chhatre *et al*., 2012]. This shows good agreement with values obtained from the gold nanoparticles produced in this experiment.

3.2. Transmission Electron Microscopy (TEM):

One of the best methods for nanoparticles characterization is using a Transmission Electron Microscopy (TEM). The TEM images involve appropriate information about the size and shape of nanoparticles [Müller *et al*., 2008].

Gold nanoparticles images shown in the figure 3 were prepared by a TEM model CM200 FEG and Manufactured by Philips Company. The microscope works in the voltage of 200kv. For preparing images of a colloidal solution, Small amounts of colloidal solution were poured on grade and were dried in desiccators. The operation was repeated several times (10 to 20 times) until sufficient numbers of nanoparticles were placed on the grid. Figure 3 shows images of gold nanoparticles colloid in water, prepared by transmission electron microscopy 30 days after production and figure 4 also shows the particle size distribution curve of each image. In these images, the particles were measured by the Microstructure Measurement software and particle size distribution curves of nanoparticles were plotted in Microsoft Excel. It should be noted that the particle size distribution curves were plotted after rounding the primary particle sizes.



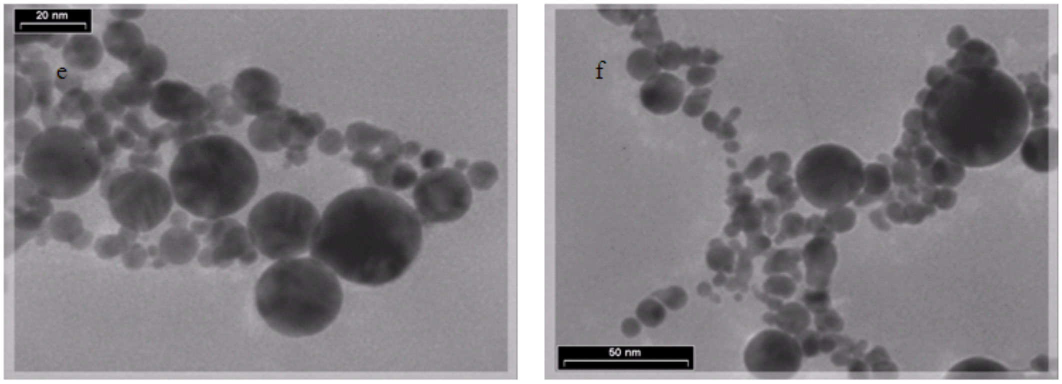


Fig. 3: TEM images of Au nanoparticles produced by laser ablation in water.

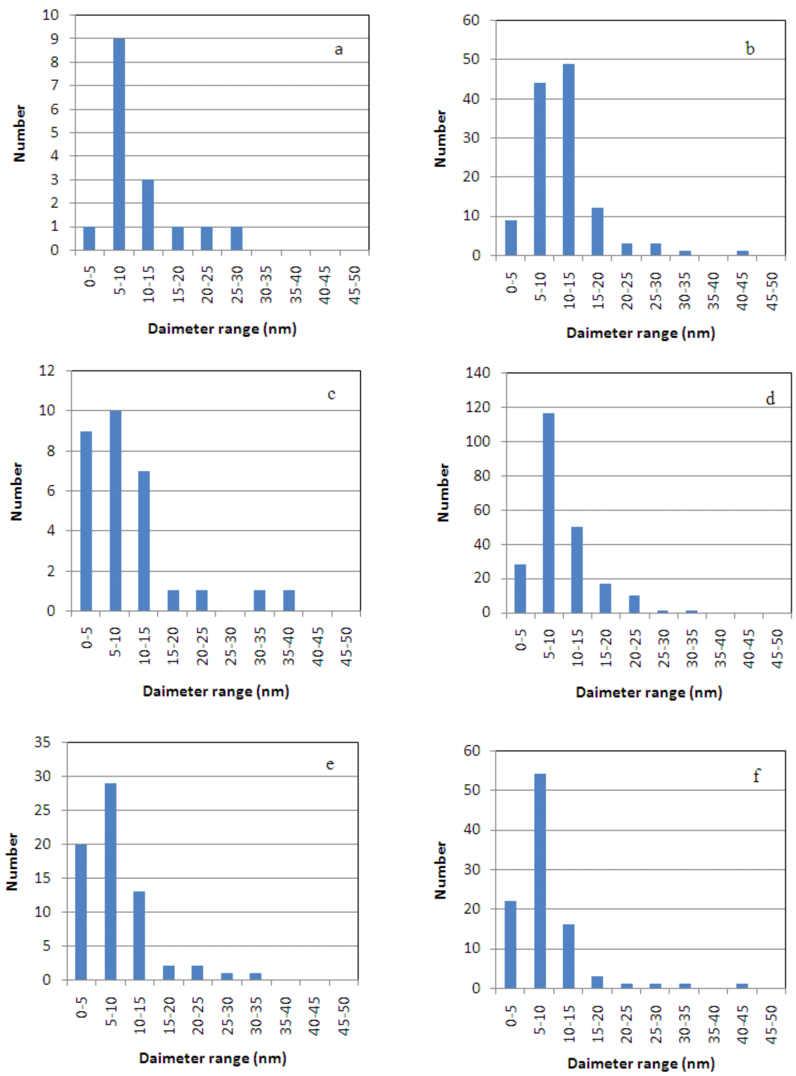


Fig. 4: The particle size distribution curve of Au nanoparticles.

Figure 5 shows the distribution of particle size related to 1529 gold nanoparticles colloid in water that was studied using the 30 TEM images.

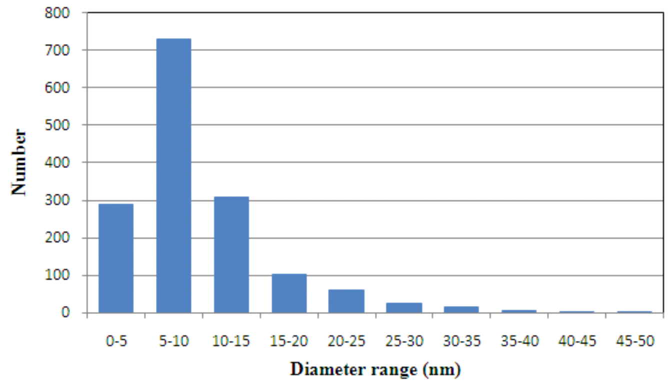


Fig. 5: The distribution of particle size related to 1529 gold nanoparticles colloid in water that was studied using the 30 TEM images.

4. Conclusion:

Experimental production of gold nanoparticles using laser ablation in water medium was studied in this research. Notable features of gold nanoparticles produced via this method are their regular spherical shape and purity of the resulting colloidal solution. Results show that most particles have a size range from 0 to 15 nm, with the average size equal to 9.49 nm and standard deviation is 5.93. These values are indicative of very good size distribution.

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