# Fabrication of Silver Nanoparticles by Laser Ablation in Liquid Solution

Hisham Imam[1], Khaled A.Elsayed[2], Lotfi Z. Ismail[2], Mostafa Afify[2] and M. Atta Khedr[1]

[1]National Institute of Laser Enhanced Sciences, Cairo University, Giza12211
[2]Physics Department, Faculty of Science, Cairo University, Giza12211, Egypt
khaleda4@yahoo.com, moustafa_physics@yahoo.com

**Abstract:** Silver nanoparticles were synthesized by laser (Nd:YAG, 1064 nm) ablation of a silver target immersed in various concentrations of NaCl solutions as well as in distilled water. The silver nanoparticles were prepared by laser ablation in distilled water at different experimental parameters. The effect of ablation time on size and aggregation of AgNPs prepared in distilled water was studied. The average size of the produced particles is increased as ablation time increased. As the ablation time increases the intensity of plasmon peak increase indicating the AgNPs concentration increases. As the fluence increases the size of nanoparticles decreases until they reached their critical size below which above this value the nanoparticles begin to agglomerate again and the size increased.
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**Keywords**: silver nanoparticles, Laser ablation.

## 1. Introduction

Recently, Laser ablation of bulk target immersed in liquid environment which is a simple method to prepare metal nanoparticles has attracted much attention. Laser ablation is an important tool for nanosized material fabrication because its simplicity of procedures and versatility. Nanoscale materials, as an intermediate state between molecular and bulk matter, possess unique chemical and physical properties that drive significant fundamental and technological interest. Materials characteristics drastically change as the size of the constituting particles approaches the nanoscale regime. The change in properties is a result of the presence of a small number of atoms in each particle and a large surface-to-volume ratio due to the large fraction of atoms that reside on the particle surface. Size and shape are the two major factors that determine nanoparticle properties. The characteristics of the metal nanoparticles formed and the ablation efficiency strongly depend upon many parameters such as the wavelength of the laser impinging the metallic target, the ablation time duration, the effective liquid medium and the presence or the absence of surfactants. Moreover, nanoparticles can be modified in shape and size due to the concentrations of the surfactant and the effect of different energies are among the other parameters that effect the shape and size distribution of the silver nanoparticles (AgNPs).Therefore, metallic NPs has the characteristics of SPE (Surface Plasmon Excitation) spectra in the UV–VIS region and the SPE position relates to the particle size. The importance of nanosized material fabrication is increasing today because of such materials' characteristic properties, which differ from those of bulk materials, and because of their efficient utilization of natural resources and energy. Photo-irradiation onto already-prepared metal nanoparticles has been interested as an alternative approach to control morphology of nanoparticles using a simple procedure. At the first time, laser has been used as the irradiation light source due to its high photon-flux. It has been demonstrated that laser irradiation onto gold or silver nanoparticles dispersed in aqueous solution induced fragmentation or fusion of the colloidal nanoparticles [1-5]. The photo-thermal dynamics involved in these processes has been also extensively investigated [6-9]. However, the shape of the produced nanoparticles was almost spherical whatever the shape of the original nanoparticles. In this work we will discuss the fabrication of silver nanoparticles and the experimental parameters that affect the formation of the AgNPs.

## 2.Experimental

Silver nanoparticles were produced by laser ablation of a metal silver plate in distilled water solution. As shown in Fig. 1, the silver metal plate of 3mm thickness (>99.5%) was thoroughly washed with ethanol and deionized water to remove organic contamination. The cleaned target was placed at the bottom of a glass vessel filled with 50 ml of distilled water. The silver metal plate was kept at 15mm below the liquid surface. The metal plate was ablated with an output of the fundamental (1064nm) or the second harmonic (532nm) of Quanta-ray Nd:YAG laser operating at 10 Hz and 8 ns pulse width. The spot size of the laser beam on the surface of the metal plate was adjusted to 0.6mm in diameter, by changing the distance between the focusing lens and

the metal plate. OPHIR- NOVA power meter was used to monitor the laser power. The laser intensity and irradiation was changed from (4 J/cm$^2$ to 53 J/cm$^2$). The ablation time was changed from 10 to 30 min. The laser beam was focused on the surface of the target and it was scanned by using a X–Y stage to avoid the craters on the surface of target. Upon irradiation of the laser beam, the solution gradually turned to gray.

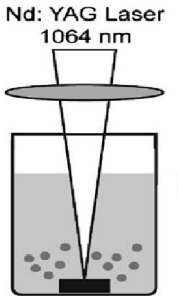



**Fig. 1. Schematic diagram of experimental setup**

## 3.Results and Discussion

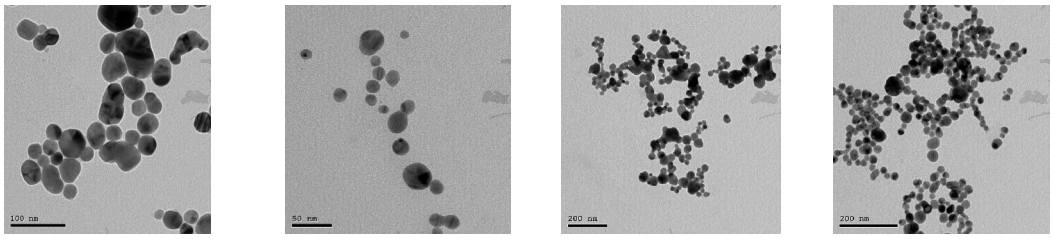
### 3.1. Effect of ablation time on the AgNPs

In this section, we will study the effect of the ablation time on growth, aggregation and optical properties of silver nanoparticles prepared in distilled water. The ablation times were set to (2, 5, 8, 14 minutes).

Fig. 2. (a-d) showed the TEM micrographs of the AgNPs prepared by laser ablation in distilled water for different ablation times at laser fluence 35 J/ cm$^2$. The average diameters of silver nanoparticles were increased as the ablation time increased as shown in the table (1).

**Table 1. The change of the AgNps average size with ablation time.**

| Ablation Time | Average Diameters |
|---|---|
| 2 min | 31 nm |
| 5 min | 43 nm |
| 8 min | 44 nm |
| 14 min | 50 nm |



(a) (b) (c) (d)

**Fig. 2. (a-d). TEM micrographs of silver nanoparticles samples prepared in distilled water (a) 2 min,(b) 5 min, (c) 8 min, (d) 14 min.**

The variation of the ablation time leads to a change in size distribution as well as the rate of nanoparticles generation. When ablation time increased, the ablated mass from the surface of silver metal plate increased and the dispersed nanoparticles increase. The result is the increase in nucleation rate as well as the agglomeration rate leading to the increase in the average size. The nucleation of nanoparticles mostly takes place during ablation. The mechanism of particles formation and growth occur when pulsed laser beam ablates the target during laser irradiation. Ablated particles, known as plume, expand in liquid environment. Fine particles such as free atoms collide with each other and nucleate during ablation. For the first few pulses, only a liquid medium surrounds the plume and silver species in plume nucleate to produce nanoparticles. In this stage two mechanisms contribute to the nucleation process: the first one is the direct nucleation of silver atoms in the condensed plume. The other mechanism is the addition of silver atoms to the produced particles which result in their growth. This leads to broad size distribution [10].

### 3.2. Effect of laser fluencies on size distribution and shapes of AgNPs At ablation time 20 min and irradiation time 20 min

Fig. 3. (a-d) shows the TEM images and histogram of the AgNPs prepared in distilled water and adding 0.2 mM of NaCl before the secondary irradiation with different laser fluences (4, 7, 18, 35, 53 J/cm$^2$) for 20 min.

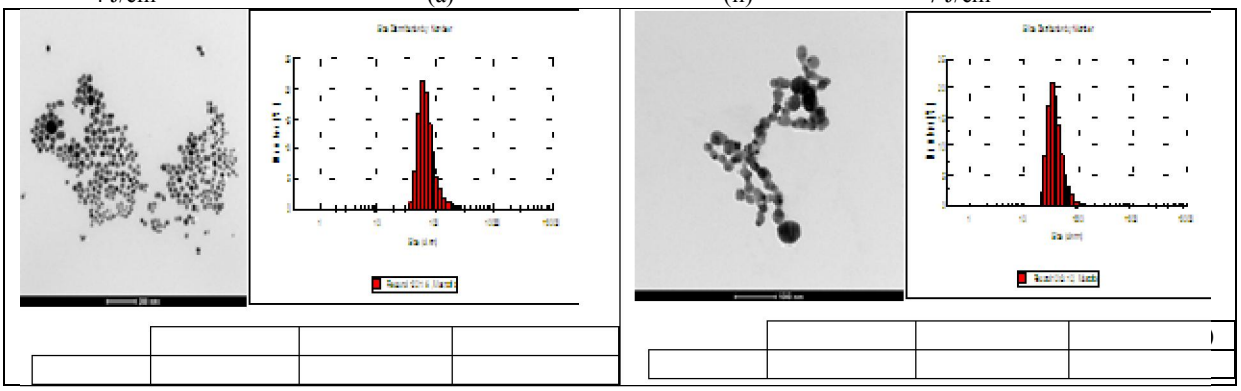
In these figures, number of crystal-shaped particles significantly increased with the energy increase. Nanorods in the figures (3: b / iv, c / v), nanohexagonals in the figures (3: c / vi, d), and other non-spherical particles with rather irregular crystal-like shapes in the other figures of (Fig. 3).

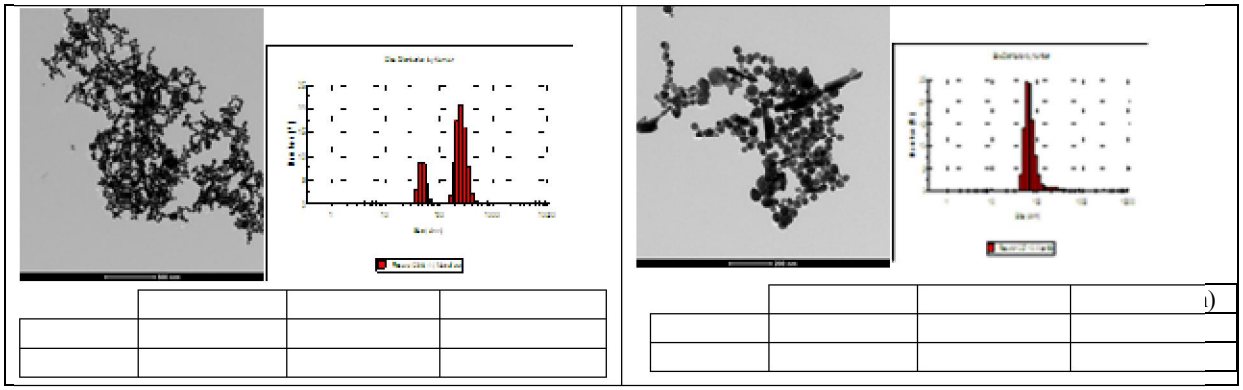
Fig. 4. (a-e), shows the absorbance spectra of silver nanoparticles prepared in distilled water and adding 0.2 mM of NaCl before the second irradiation

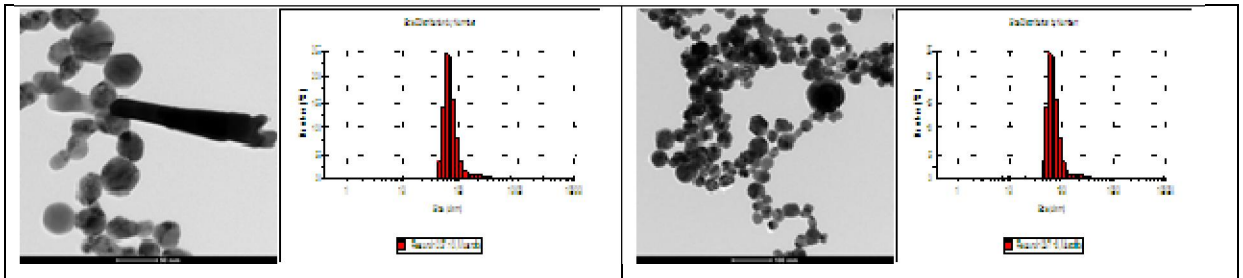
of 532 nm with different laser fluencies (4, 7, 18, 35, 53 J/cm$^2$) for 20 min.

The previous figures show that as the energy increases, the intensity of the plasmon band increases while their position doesn't vary significantly. In figure (4:a, b) the laser fluence used was low at 4 and 7 J/cm$^2$, so the absorption band of the silver nanoparticles was around 400 nm and the band width was decreased due to the low fluence. But at the higher fluences like 18, 35 and 53 J/cm$^2$ in figures (4:c, d) and (4: e) the absorbance band of the silver nanoparticles were also around 400 nm, but the difference is in the width of the band is very broad. The wide visible band in the spectra of AgNPs indicates the presence of chains with various aspect ratios. Coagulated AgNPs are characterized by the appearance of wide absorption band.

4 J/cm$^2$ (a) (ii) 7 J/cm$^2$



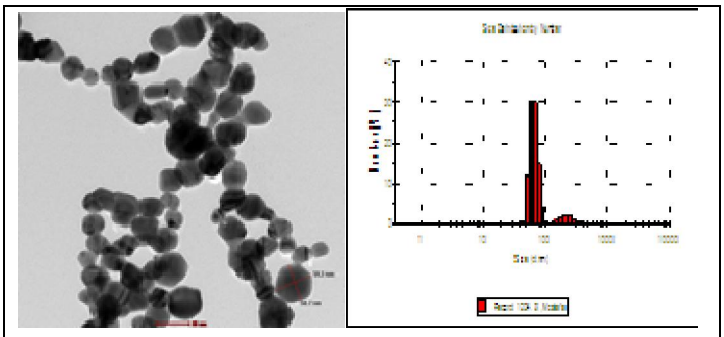




| | Size (d.nm) | % Number | Width (d.nm) |
|---|---|---|---|
| -Peak 1 : | 190.1 | 4.2 | 67.58 |
| -Peak 2 : | 58.77 | 95.8 | 19.35 |

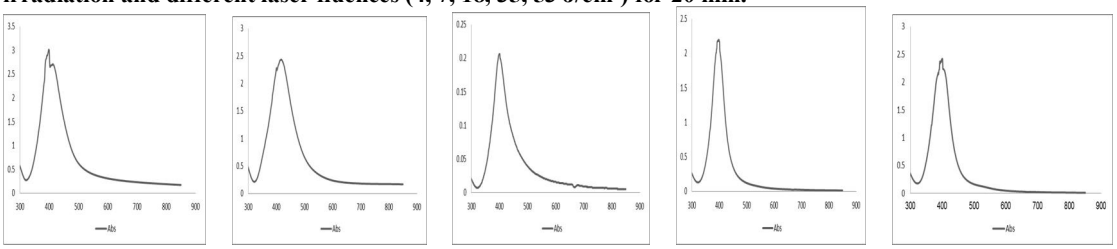
| | Size (d.nm) | % Number | Width (d.nm) |
|---|---|---|---|
| -Peak 1 : | 190.1 | 4.2 | 67.58 |
| -Peak 2 : | 58.77 | 95.8 | 19.35 |

(d) 53 J/cm$^2$



| | Size (d.nm) | % Number | Width (d.nm) |
|---|---|---|---|
| Peak 1: | 78.82 | 80.1 | 54.72 |
| Peak 2 : | 21.04 | 19.9 | 5.610 |

**Fig. 3. (a-d). TEM and histogram of AgNPs prepared in distilled water and adding 0.2 mM of NaCl before the secondary irradiation and different laser fluences (4, 7, 18, 35, 53 J/cm$^2$) for 20 min.**



Wavelength (nm) Wavelength (nm) wavelength (nm) wavelength (nm) wavelength (nm)

(a) (b) (c) (d) (e)

**Fig. 4. (a-e). The absorbance spectra of AgNPs prepared at different laser fluencies for 20min.**
**(a) 4 J/cm$^2$. (b) 7 J/cm$^2$. (c) 18 J/cm$^2$ (d) 35 J/cm$^2$. (e) 53 J/cm$^2$.**

## 4. Conclusion

Silver nanoparticles (AgNPs) were successively prepared by laser ablation in distilled water at different ablation times. The produced average diameter is ranged from 30-50 nm. The average size of the produced particles is increased as ablation time increased. As the ablation time increases the intensity of plasmon peak increase indicating the AgNPs concentration increases. As the laser power increases the size of nanoparticles decreases until they reached their critical size below which the fluence increases above this value the nanoparticles begin to agglomerate again and the size increased.

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