Preparation of Silver Nanoparticles by Pulsed Laser Ablation in Liquid Medium

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Abstract

Silver nanoparticles were synthesized by pulsed laser ablation (Q-switched Nd:YAG, $\lambda=1064$nm, 10 ns pulse duration and E=100-900 mJ) of pure Ag metal plate immersed in double distilled and deionised water DDDW. Spectral measurements, such as surface plasmon extinction SPE spectra of the produced nanoparticles solution were measured. The size and concentrations measurements of produced nanoparticles were estimated. UV-VIS absorption spectra of produced solution show a sharp peak around 400 nm, indicating the produced Ag nanoparticles with a narrow size ranging from 5 to 50 nm with almost spherical shape.

Keywords: Pulsed, Nanoparticles, Ag, liquid, Nd: YAG

تحضير جسيمات الفضة النانوية بواسطة التبخر الانفجاري لليزرالنبضي في وسط سائل

الخلاصة

تم تحضير جسيمات نانوية من الفضة بأستخدام ليزر الياك النبضي، ذو الطول الموجي 1064 nm وطاقة 100-900 ملي جول بطريقة التبخر الانفجاري لقطعة معدنية فائقة النقاوة من الفضة مغمورة في ماء لاأيوني وثنائي التقطير يعرف ب DDDW.تم اجراء القياسات الطيفية مثل SPE لمحاليل الجسيمات النانوية ،كذلك قياسات الشكل والحجم والتراكيز تم حسابها. أطياف أمتصاص الـ UV-Vis للمحاليل الناتجة تظهر قمة أمتصاص حادة ومنفردة حول القيمة 400 nm، والتي تدل على توليد جسيمات نانوية نقية من الفضة بقطر 5-50 nm وهي كروية الشكل .

Introduction

Production of nanoparticles by laser ablation of solids either in gas or in vacuum has been extensively explored during tow last decade. A new methodology based on pulsed laser ablation in liquids medium, denoted by PLAL has received much attention as a novel nanoparticle-production technique. Laser ablation was representing a dramatic laser-material-interaction phenomenon. The amount of mass removed was depending on the laser parameters such as: pulse duration, energy, wavelength, target properties and the surrounding environment [1],[2]

Nanomaterials display unique, superior and indispensable properties and distinct characteristics that are unavailable in conventional macroscopic materials. Their uniqueness arises specifically from higher surface to volume ratio and increased percentage of atoms at the grain boundaries. They represent an important class of materials in the

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development of novel devices that can be used in applications such as: photothermal therapy [3], surface-enhanced Raman spectroscopy [4], biochemical sensors [5].etc.

Noble metal nanoparticles such as Ag have been a source of great interest due to their novel electrical, optical, physical, chemical and magnetic properties [6]. They were very attractive for biophysical, biochemical, and biotechnological applications due to their unusual physical properties, especially due to their sharp plasmon absorption peak at the visible region. Moreover, silver nanoparticle has been for thousands of years, used as a disinfectant; from the other side nobody can neglect its value as a catalyst [7].

Nanoparticles have been prepared by a wide variety of techniques such as pulsed laser deposition [8], chemical reduction [9], photo-reduction [10], electrochemical reduction [11]...etc. Among them, the pulsed laser ablation in liquid medium PLAL has become an increasingly popular top-down approach [12] for producing nanoparticles.

The aims of the work are to preparation of more stable-dispersed and size-controlled of pure silver nanoparticles in easy, fast and simple method with highly ablation efficiency. Also, to optimise the process and improve the formation rate of nanoparticles by studying the effects of experimental parameters such as laser shots, laser energy, liquid thickness and spot diameter, that leads to enhancement of ablation efficiency.

Theoretical Concept

The PLAL process is currently explored as a prospective top-down (dispersion method) strategy of metals nanoparticles preparation [13]. It's simple no chemistry is involved and basically free from limitations because it can generate nanoparticles without counter-ions or surface-active substances [14]. When a high-power pulsed laser beam irradiates on a metal target in a transparent liquid, a local plasma, with super high temperature (about 6000 K) and high pressure (about 1 GPa), will instantly be produced on the solid-liquid interface and quench quickly after one pulse due to adiabatic expansion of the plasma and its interaction with surrounding media.

The intensity of light which propagates through a medium containing small particles is reduced by scattering and absorption. The extinction of the light beam is given by [15]:

$$I(z) = I_0 \exp(-n_0\sigma_{ext}z), \qquad (1)$$

Where $I(z)$ is the intensity of the incoming beam after a distance z, n_0 the number of particles per unit volume and σ_{ext} the extinction cross section of a single particle. It holds [15]:

$$\sigma_{ext} = \sigma_{abs} + \sigma_{sca}, \qquad (2)$$

where σ_{abs} and σ_{sca}: is the absorption and scattering cross sections of a single particle, respectively. The optical properties of such particles, as a consequence of their reduced dimensions, are dominated by a coherent collective oscillation of their conduction band electrons. As a result, the absorption cross section, which scales with their volume, can reach values several orders of magnitude larger compared to common organic dye molecules. Such collective oscillation is known as surface plasmon resonance [15].

Experimental Works

Silver nanoparticles were synthesized by laser ablation process, which is a combination of focused

pulsed laser ablation of a piece of silver metal plates (purity: 99.999%, Aldrich Co.) placed on the bottom of quartz vessel containing 1ml of double distilled deionised water DDDW. The Nd-YAG laser (type HUAFEI) of 1064 nm at energy set in the range of (100-900 mJ) per pulse, with a positive lens having a focal length of 110 mm, was utilized as an ablation source. The pulse duration and the repetition rate of the laser pulse were 10 ns and 10 Hz respectively. The effective spot size of the laser beam on the surface of the metal plate was varied in the range of 2.37-0.4 mm in diameter to increase the laser fluence. The liquid thickness was changed in the range from 2-14 mm to increase the shock wave. The liquid thickness adjusted by using different dimensions of cells. The number of laser shots applied for the metal target ranged from 5 to 90 pulses. A transmission electron microscope TEM (CM10 pw6020, Philips-Germany) was employed to study the structure of nanoparticles. Absorbance spectra of the nanoparticles solution were measured by UV-visible (UV-VIS) double beam spectrophotometer CECIL, C. 7200 (France). Atomic absorption measurement was carried out using atomic absorption spectroscopy AAS type GBS 933.To obtained reference solution, a standard solution with concentration 1000 µg/l of silver was prepared by dissolving 1.57 g of $AgNO_3$ powder in 10 ml of HNO_3 (40%), which is mixed gently. Five standard samples were prepared by applying the dilution equation $(C_1V_1=C_2V_2)$, for concentrations (C) range from (1.5, to 5.5 µg/ml).

Result and Discussion

Fig.1 shows surface plasmon resonance SPR absorption spectrum of colloidal solutions of silver nanoparticles, synthesized by pulsed laser ablation at different laser shots of a piece of silver plate placed on the bottom of quartz vessel containing 1ml of ultra pure DDDW. The liquid thickness was selected 8 mm above the target. The piece of metal was irradiated by focused energy of 600 mJ/pulse and 1064 nm wavelength of Nd: YAG laser. The beam spot diameter at the metal surface was 1.27 mm. The number of pulses applied for the Ag metal target ranged from 5 to 90 pulses. The height and the width of the SPR peaks were found to be dependent upon the laser shots. Also the width of the SPR peak is broadened and the height is increased more greatly by introducing more laser shots. This spectral change indicates that the abundance of the nanoparticles is enhanced more under irradiation of the laser. The Figure displays a quasisymmetric absorption band centred at 400 nm, which indicates that the nanoparticles in the growth solution are quasispherical [16]. The size of nanoparticles is approximately 8 nm which estimated by TEM. The silver nanoparticles, was faint yellow in color. The height and the width of the SPR peaks were found to be dependent upon the laser shots.

Fig.2 (A) shows the maximum absorbance of silver nanoparticles at 400 nm, as a function of the laser shot. The absorbance was found to increase exponentially, attributed to the effect of accumulation nanoparticles which attenuates the laser intensity. The ejected NP remains in the liquid that surrounds the target resulting in formation of so

called colloidal solution and prolonged interaction with laser radiation proceeds via its absorption by free electrons. Thus, the particles have a considerable extinction coefficient at wavelength of laser light, they can absorb energy of laser light and the interacting intensity of the incident laser light will be reduced.

Fig.2 (B) shows the PLAL efficiency, in terms of the maximum absorbance, as a function of laser shot. It was found that ablation efficiency of samples is very weak, and found increases almost linearly with the number of laser shot until 15 pulses, then turns to decrease. The linearly increase of the efficiency is interpreted as that initially the target surface of silver was smooth and very shining, so that it reflects some of incident photon and reduces the ablation efficiency . But after application of the first few laser shots 2 to 3 pulses, the surface roughness and area increase respect to surface corrosion. Under optimum conditions, the formation efficiency was enhanced compare with results was reported by **Siskova** [26,37,38,39].

To obtain the concentration of silver nanoparticles in liquid, atomic absorption spectrometer AAS was employed. Fig. 3(A) shows the calibration curve, referring to atomic absorbance values obtained from AAS, as a function of silver standard concentration samples. The silver concentration exhibited an almost linear increase with atomic absorption. Fig. 3(B) shows the amounts of ablated silver nanoparticles as a function of SPE peak, corresponding to the samples shown in Fig. 1. The amount of ablated silver nanoparticles exhibited good agreement with SPE peak. These

results have two important features. First it is suggested that we obtain coherent result for quantify the PLAL efficiency in terms of SPE peak, as well as the amount of ablated silver nanoparticles. The second feature, one can estimate the amount of silver nanoparticles produced from the spectrophotometer measurements without need to AAS. Under optimum conditions, the rate of particle formation is estimated to be 5200 μg/min in one step, compared with 240 μg/min, was reported by Shekel[18], and 1100 μg/min as reported by Kawasaki et al.[21] in two step (at 10 Hz of laser ablation), attributed to our optimization.

Fig.4 (A and B) shows the concentration of ablated Ag nanoparticles, which was determined by AAS and ablation efficiency, respectively, as a function of laser shots. At high laser shot up to 75 pluses, agglomeration of particles in the form of tiny flakes appearing in the suspension was observed upon prolonged exposure to laser pulses. At first inspection, the change of the spectra could therefore be based on gravitational precipitation of larger particles [22], which would explain the efficiency decrease with increase exposure time.

The Ag nanoparticles having negative surface charge and can demonstrate a highly dispersed state without aggregation because of the electrostatic repulsion between the Ag NPs. However, the repulsive forces are likely to exceed the van der Waals attractive forces leading to coalescence [23], and hence, the nanoparticles are present in a solution without being coalesced even under centrifuge application.

Fig.5: (A and B) shows the TEM images and the corresponding size

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distributions of silver nanoparticles produced by laser ablation of a silver plate immersed in 1 ml of DDDW, at 15 pulses (A) and 90 pulses (B), respectively. The Nd-YAG laser of 1064 nm and energy of 600 mJ. The nanoparticles thus produced were measured to have the average diameters of 14 and 15 nm at 15 and 90 pulses, respectively. The result revealed that the average diameter of nanoparticles increase with an increase of laser shots, because the increase in nanoparticles concentration which enhance the collisions. Moreover, the produced nanoparticles are spherical and homogeneous.

Conclusions

This study has presented easy method for the preparation of silver nanoparticles with well-defined size and shape. No additives, such as solvents, surfactants or reducing agents, are needed in the procedure. Optical measurements of colloidal silver nanoparticles exhibit single maximum optical extinction at 400 nm, which are related to surface plasmon resonance of silver nanoparticles.

There are good agreement in the formation efficiency of PLAL was quantified in term of the SPE peaks as well as of the concentration of ablated silver nanoparticles obtained by AAS. Under optimum conditions, the formation efficiency and rate of particle formation were enhanced.

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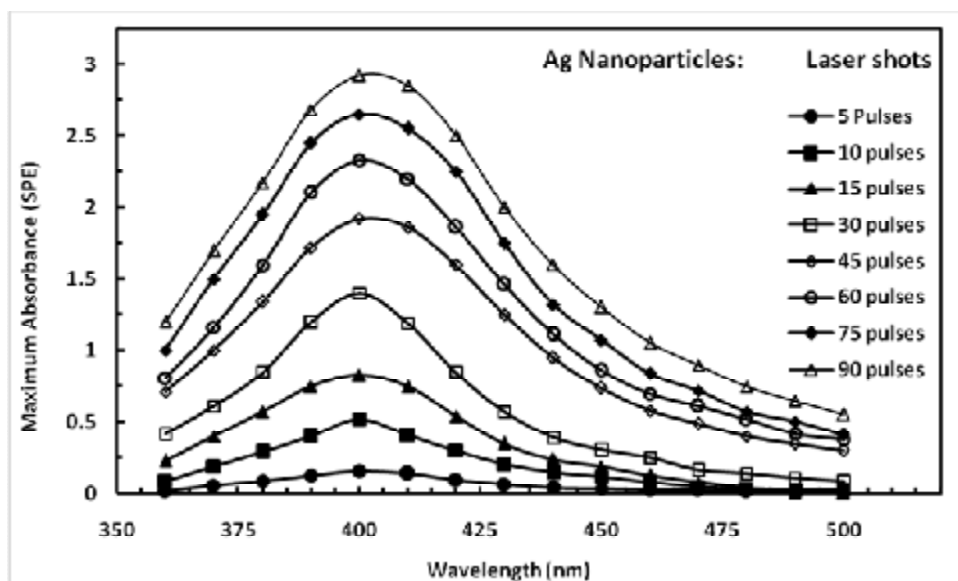
**Figure (1): UV-vis absorption spectra of the plasmon band of silver
nanoparticles, obtained by laser ablation in DDDW with laser shots of 5 to 90
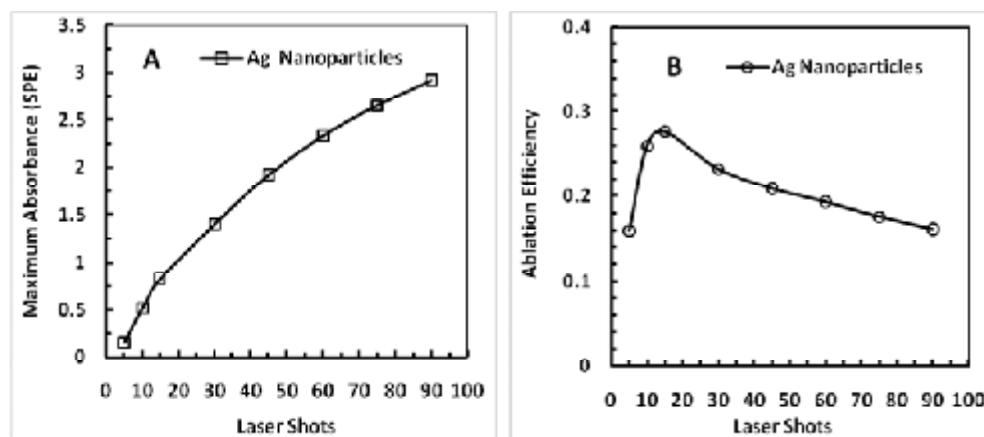pulses and 600 mJ at λ=1064 nm.**

**Figure (2): Intensity of the SPE peaks as a function of number of laser shots,
of silver nanoparticles (A) and, PLAL efficiency as a function of laser shots for
silver nanoparticles (B), obtained by laser ablation in DDDW with an energy
of 600 mJ at λ=1064 nm.**

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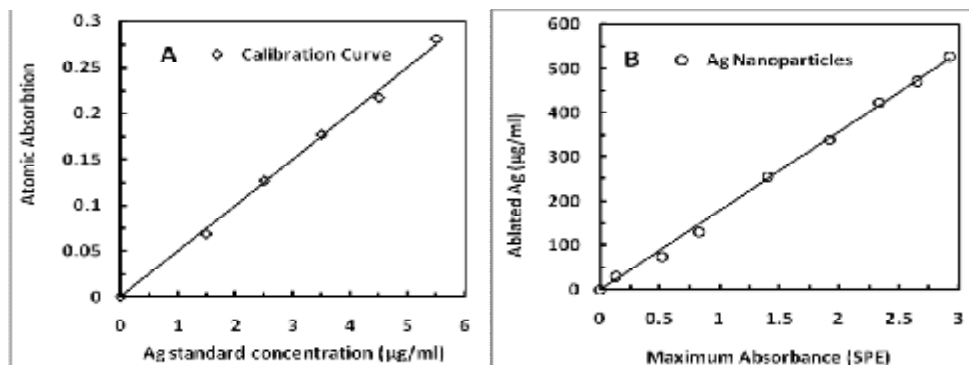Pulsed Laser Ablation in Liquid Medium

Figure (3): Calibration curve of atomic absorbance as a function of Ag standard concentration (A) and ablated Ag nanoparticles as a function of maximum absorbance (B), obtained by laser ablation in DDDW with an energy of 600 mJ, at λ=1064 nm.
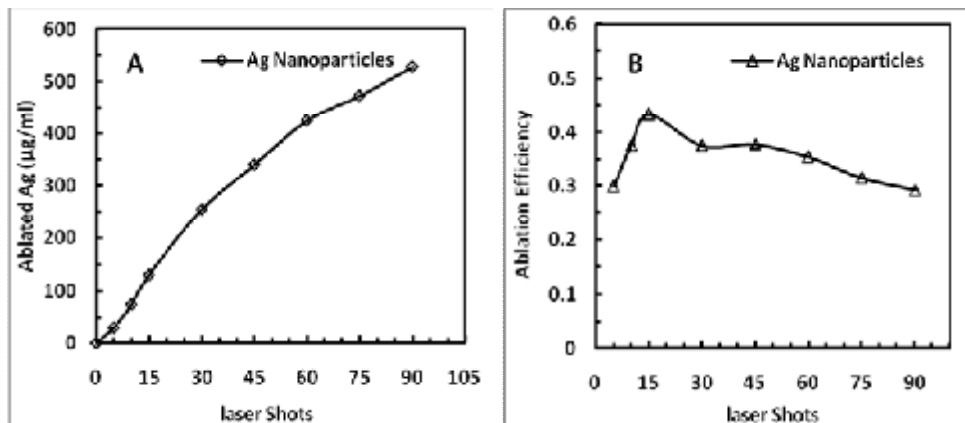

Figure (4): Amount of ablated Ag nanoparticles (A) and ablation efficiency in terms of the amount of ablated Ag nanoparticles (B), as a function of laser shots.
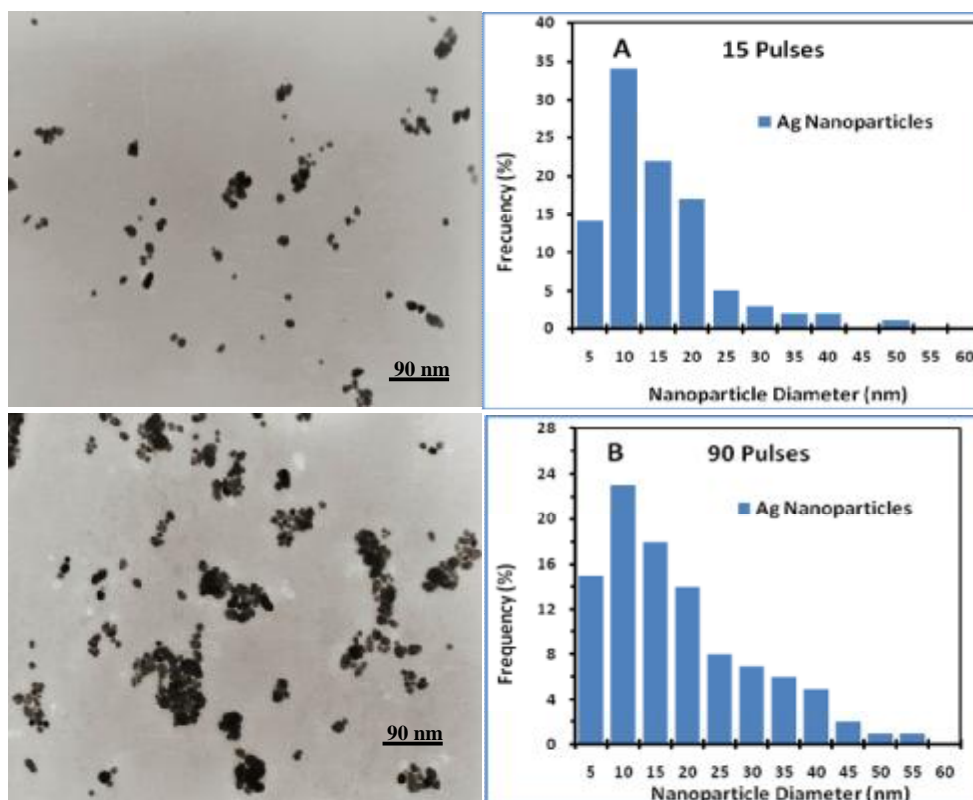
Figure (5): Electron micrograph and size distribution of silver nanoparticles produced by 1064-nm laser ablation (600 mJ/pulse) in 1ml of DDDW. The laser shots set of 15 pulses (A) and 90 pulses (B), respectively.

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