

Preparation of silver nanoparticles by pulsed laser ablation in liquid medium

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Abstract: In present work Silver nanoparticles have been prepared by using pulsed laser ablation (Q -switched Nd:YAG) 1064nm pulse duration and(E= 100mJ to 400mJ) of pure Ag metal plate immersed in distilled water and deionized water .The synthesized nanoparticles are characterized using transmittance electron microscopy (TEM) and UV-VIS spectrophotometer . The effect of the pulses energies and number. of shots have been reported .The silver nanoparticles exhibited a surface Plasmon resonance effect with wave length ($\lambda_{spr}=400nm$).The production of pure and spherical Ag with average size of (1-15nm) .All the size measurements have been confirmed by TEM.

Keywords: silver nanoparticles , surface Plasmon resonance , TEM , laser ablation .

Introduction:

NANOPARTICLE IS A RELATIVELY NEW METHOD THAT WAS FIRST INTRODUCED BY (FOJTIK) ET AL IN 1993 AS IS PROMISING TECHNIQUE FOR THE CONTROLLED FABRICATION OF NANOMATERIALS VIA RAPID REACTIVE QUENCHING OF ABLATED SPECIES AT THE INTER FACE BETWEEN THE PLASMA AND LIQUID WITH HIGH -QUALITY NANOPARTICLE FREE FROM CHEMICAL REAGENTS[1]. NOBLE METAL NANOPARTICLES SUCH AS AG NPS HAVE BEEN A SOURCE OF GREAT INTEREST DUE TO THEIR NOVEL ELECTRICAL, OPTICAL, PHYSICAL, CHEMICAL AND MAGNETIC PROPERTIES . COLLOIDAL SILVER NANOPARTICLES ARE WIDELY USED FOR ITS UNIQUE PROPERTIES IN CATALYSIS[1], CHEMICAL SENSING[2], BIOSENSING[3], PHOTONICS[4], AND PHARMACEUTICALS [5], PRODUCTION OF NANOPARTICLES BY LASER ABLATION OF SOLID EITHER IN GAS OR IN VACUUM HAS BEEN EXTENSIVELY EXPLORED DURING TWO LAST DECADE A NEW METHODOLOGY BASED ON PULSED LASER ABLATION ON LIQUIDS MEDIUM (DISTILLED WATER , DIONIZED WATER AND MAGNETIC WATER) DENOTED BY (PLAL) HAS RECEIVED MUCH ATTENTION AS ANOVEL NANOPARTICLES-PRODUCTION TECHNIQUE[6]. THEY WERE VERY ATTRACTIVE FOR BIOPHYSICAL , BIOCHEMICAL AND BIOTECHNOLOGICAL APPLICATION DUE TO THEIR UNUSUAL PHYSICAL PROPERTIES ESPECIALLY DUE TO THEIR SHARP PLASMON ABSORPTION PEAK AT THE VISIBLE REGION[3]. ANOTHER IMPORTANT ADVANTAGE AG NANOPARTICLES PREPARED BY (PLAL) PROCESS WERE STABLE FOR A PERIOD OF MONTHS[4]. THE RESONANCE FREQUENCIES STRONGLY DEPEND ON PARTICLE SHAPE AND SIZE AS WELL AS ON THE OPTICAL PROPERTIES OF MATERIAL WITH IN THE NEAR -FIELD OF THE PARTICLE. THEREFORE

(PLAL) PROCESS HAS RECEIVED MUCH ATTENTION AS ANOVEL NPS PRODUCTION TECHNIQUE[7]. IN GENERAL THERE ARE AN ABILITY TO PREPARE VARIOUS KINDS OF NANOPARTICLE SUCH AS METALS, NOBLE METALS, SEMICONDUCTORS, NANOALLOYS , OXIDES, MAGNETIC, BIAXIAL HETEROSTRUCTURES AND CORE-SHELL NANOSTRUCTURE, MOREOVER THE INTERESTING FEATURE OF THIS TECHNIQUE WHICH DISTINGUISHES IT FROM LASER ABLATION IN GAS OR VACUUM IS THE INFLUENCE OF THE SURROUNDING SOLVENT. IN THE PRESENT WORK WE AIM TO PREPARE PURE SILVER NANOPARTICLES IN EASY , FAST AND ONE STEP METHOD VIA (PLAL) PROCESS. ON-LINE MONITORING TO CONTROLLING ON THE FORMATION PROCESS OF NANOPARTICLES AND FIND THE SMALLEST SIZE OF NANOPARTICLES.

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%) placed on the bottom of beaker containing 5ml of deionized water and ethylene glycol . Fig.1 shows The Nd-YAG laser (type RS BPW 21) of 1064 nm at energy set in the range of (100-400 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 6 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 number of laser shots applied for the metal target ranged from 100 to 500 pulses. A transmission electron microscope TEM (CM10 pw6020, Philips-Germany) was employed to study the structure of nanoparticles and to find the size of nanoparticles . UV-VIS spectral analysis has been done using a

double beam spectrophotometer type Metertech SP-8001(Tiwan) and the samples are dispersed in deionized water and kept in quartz cuvette of path length 10 mm.

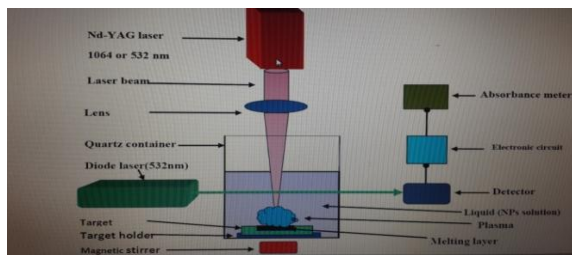


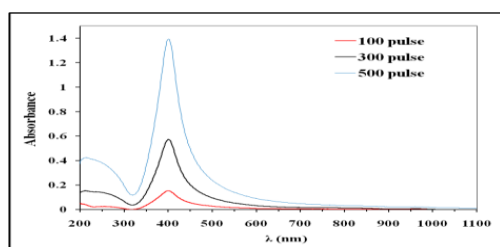
Figure.1 laser system.

Results and Discussion

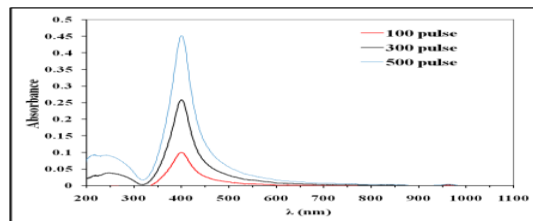
The piece of metal was irradiated by focused energy of 100-400 mJ/pulse and 1064 nm wavelength of Nd: YAG laser. The beam spot diameter at the metal surface was 1.27 mm. UV-VIS absorption spectrophotometer is the commonly used to investigate the SPR. The number of pulses applied for the Ag metal target ranged from 100 to 500 pulses. Fig.2 shows surface plasmon resonance SPR in 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 5ml of deionized water, the height and the width of the SPR peaks were found to be dependent upon the laser shots.

The silver nanoparticles, was faint yellow in color. 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, and hence, the nanoparticles are present in a solution without being coalesced even under centrifuge application. The nanoparticles thus produced were measured to have the average diameters of (2-15nm) at 100 to 500 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.

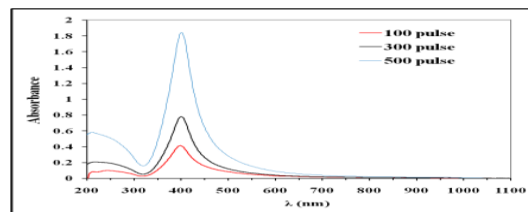
The surface Plasmon resonance in these figures appear at the wave length 400nm. Which are close to the usual SPR wave length of silver.



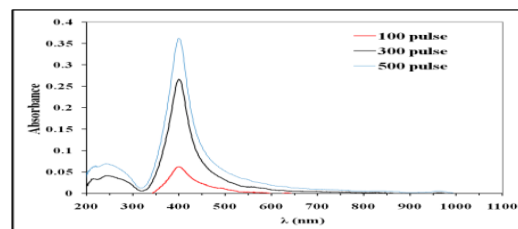
"a"



"b"



"c"

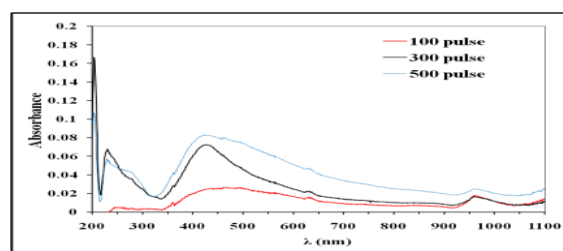


"d"

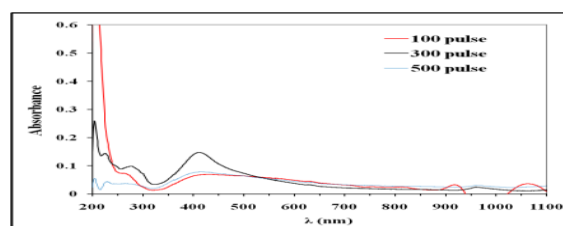
Figure .2: UV-VIS absorption spectra of silver nanoparticles solution at 100,300,500pulses with constant energy "A"100mJ "B"200mJ"C"300mJ"D"400mJd in deionize water.

Moreover, the produced nanoparticles are spherical and homogenous. silver nanostructure exhibits interesting optical properties directly related to surface Plasmon resonance (SPR), which highly dependent on the preparation condition, UV-VIS absorption spectrophotometer is the commonly used to investigate the SPR.

Fig.3 shows the SPE spectra of silver nanoparticles produced by laser ablation of a silver plate immersed in neat water or in ethelenglycol aqueous solutions at various concentrations of (1:4,2:3,3:2,4:1,5 ml). It have been using different concentrations for ethelenglycol to get the best result The SPE peaks are sensitive by ethelenglycol concentration.



"a"



"b"

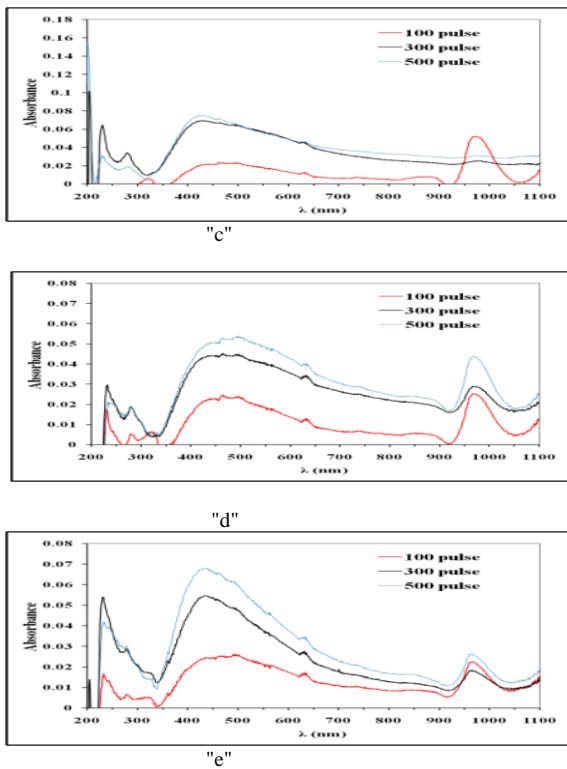


Figure.3: SPE spectra of silver nanoparticles prepared by laser ablation of a silver plate immersed in Dionized water and ethelenglycol solutions at various concentrations "A"1:4,"B"2:3,"C"3:2,"D"4:1,"E"5. The laser energy is 300 mJ, laser wavelength is 1064 nm and laser shots of 100,300,500 pulses.

The plasmon absorption peak at rang (410) nm is the characteristic plasmon absorption peak of silver nanoparticles but when we used 1ml ethelenglycol to 4ml dionized water , The position of the Plasmon shift to longer wavelength (red shift) Absorption peak depends on the particle size , shape and the adsorption of surfactant to the particle surface. It was noticed that the plasmon absorption peak shifts toward longer wavelengths (red shift) as we increased ethelenglycol concentration, usually is associated with an increase in particle size .

Fig.4 shows electron micrographs and corresponding size distributions of silver nanoparticles, produced by laser ablation of silver plate immersed in the deionized water. The laser wavelength is 1064 nm and energy 300 mJ and 500 pulses. The nanoparticles thus produced were calculated to have the average diameters of (2-10 nm) .

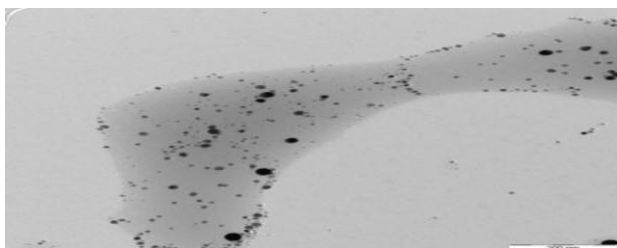


Figure:4 TEM images of silver nanoparticles at energy 300mJ at laser shots of 500 pulse in deionized water.

Fig.5 shows a typical TEM images and the particle size distributions of silver nanoparticles produced by laser ablation ($\lambda=1064$ nm and laser energy of 300mJ/pulse) of a silver plate

immersed in ethelenglycol aqueous solution. The Ag nanoparticles have an average diameter of (15 – 30) nm were produced in 1:4 ethelenglycol aqueous solution. The silver nanoparticles prepared in ethelenglycol solutions were more dispersed on the TEM grids than those prepared in neat water and the particle size was clearly increased by addition of ethelenglycol compared with pure water. It was found that, the size distribution increased by addition of ethelenglycol. The products are composed of the particles with nearly spherical shape. For the samples prepared in ethelenglycol solution, the particles are covered with surfactant (especially for high ethelenglycol concentration). It can be seen that with the ethelenglycol concentration increasing, the size distribution increased. According to our result the optimum size was obtained when 1:4 concentration .

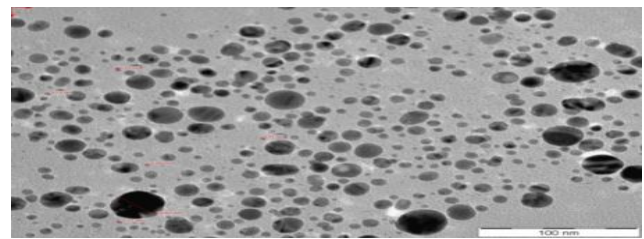


Fig. 5: TEM images and size distributions of the silver nanoparticles produced by laser ablation of silver plate immersed in ethelenglycol aqueous solution have the concentration of 1:4. The laser parameters are (E=300 mJ, $\lambda=1064$ nm and laser shots is 500 pulses).

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 peakes. The TEM of samples reveal that the average diameter for deionized water is 2-10 nm and the average diameter for the ethelenglycol is 15-30 nm.

References

- [1] Q. Xia, S. Y. Chou (Applications of excimer laser in nanofabrication) *Appl Phys A*, 98 9–59, (2010).
- [2] X. Huang, M. A. El-Sayed (Gold nanoparticles: Optical properties and implementations in cancer diagnosis and photothermal therapy) *Journal of Advanced Research* 1, 13–28, (2010).
- [3] H. Cui, P. Liu and G. W. Yang (Noble metal nanoparticle patterning deposition using pulsed-laser deposition in liquid for surface enhanced Raman scattering) *applied physics letters* 89 153124, (2006).
- [4] A. V. Kabashin, M. Meunier, C. Kingston, J. T. Luong (Fabrication and Characterization of Gold Nanoparticles by Femtosecond Laser Ablation in an Aqueous Solution of Cyclodextrins) *J. Phys. Chem.* 107, 4527-4531(2003).
- [5] A. Pyatenko, M. Yamaguchi, and M. Suzuki (Mechanisms of Size Reduction of Colloidal Silver and Gold Nanoparticles Irradiated by Nd:YAG Laser) *J. Phys. Chem. C* 113, 9078–9085.(2011).

[6]S.Petersen, J. Jakobi and S. Barcikowski (In situ bioconjugation- Novel laser based approach to pure nanoparticleconjugates) App. Surface Science 255, 5435 5438.(2012).

[7]K.Sivaranjani and M.Meenakshisundaram (silver nanoparticles using ocimum basillicum le af extract and their antimicrobial activity)issn 2230 –8407.(2013).

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