Effect of Laser Wavelengths on the Silver Nanoparticles Size Prepared by PLAL

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ABSTRACT
In this present study, Pulsed Laser Ablation in Liquid (PLAL) experiment setup for synthesis colloidal solution of silver-NPs. The laser system was used in this study, a (Nd-YAG) nanosecond laser system with optimal pulse duration of 10 ns and repetition rate 1-6 Hz. The Laser wavelengths were: 1064 nm, 532 nm and 355 nm. The spot size of the laser beam on the surface of metal plate was varied in the range of 1.4-1.5 mm in diameter by changing the distance between the focusing lens and the metal plate. The ablation process was typically done for 1 minute. The average particle size has been characterized by TEM, SEM and UV-Vis investigation. From morphology results for colloidal silver nanoparticles images were spherical shape and average size of the particles is 55-60 nm at wavelength (λ =1064 nm), average size of the particles is 35-40 nm at (λ =532 nm) and average size of the particles is 28 nm at (λ =355 nm).
Keywords: silver nanoparticles, PLAL, Nd:YAG laser, SHG, THG.

INTRODUCTION
In the last two decades, the term of nanoscience has inserted into the scientific vocabulary such as nanomaterial, nanoparticle, nanostructure, nanocolloids and nanocluster [1]. Nanomaterials are defined as a solid material characterized by at least one dimension in the nanometer range can be classified into nanocrystalline materials and nanoparticles. The term "Nanoparticle" (NP) refers to a particle with dimensions in nanometer scale. Nanoparticle contains a small number of constituent atoms or molecules that differ from the inherent properties in their bulk counterparts, exists in diverse shapes such as spherical, triangular, cubical, pentagonal, rod-shaped, shells, ellipsoidal and so forth [2]. The term Nanocolloid has a stable liquid phase containing particles in different sizes ranging from nanometers to several hundreds of micrometers, many colloidal particles can be detected by scatter light [3]. The term Nanocluster or "Cluster" usually refers to small nanoparticles that have well-defined composition and surface structure as finite aggregation of atoms or molecules which are bound by forces of metallic, covalent, ionic, hydrogen bonded or van der Waals [4,5].

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The pulsed laser ablation in liquids PLAL (of a metallic target immersed in solvents employed for nanoparticle synthesis) has become an increasingly popular top-down approach [6] for producing nanoparticles. It's a relatively new method that was first introduced by Fojtik et al. in 1993 [7], Neddersen et al. 1993 [8] it is a promising technique for the controlled fabrication of nanomaterials via rapid reactive quenching of ablated species at the interface between the plasma and liquid with high-quality nanoparticles free from chemical reagents. Opposed to chemical reduction, the laser ablation method requires less time and the nanoparticles can be obtained in a pure solvent, without any additives that can contaminate their surface; reducing as well, the toxicity issues during the synthesis of nanoparticles. Therefore, PLAL process has received much attention as a novel NPs production technique [9-11].

In this work, preparation of colloidal solution of Ag-NPs by PLAL and study the effect of laser wavelengths on size and shape of silver nanoparticles.

Experimental work

Figure (1) shows the schematic diagram of PLAL experiment setup for synthesis colloidal solution of silver-NPs. The laser system was used in this study, a (Nd-YAG) nanosecond laser system with optimal pulse duration of 10 ns and repletion rate 1-6 Hz. The Laser wavelengths were: 1064 nm "fundamental harmonic generation", 532 nm "second harmonic generation SHG" used KDP crystal (K. potassium, D. deuterium, P. phosphate) and 355 nm "third harmonic generation THG" used KTP crystal. The laser beam was focused by using a lens onto a piece of silver metal plates (ounces: 5mm x 5mm x 0.5mm, Nilaco 99.999%) placed on the bottom of quartz vessel containing 10 ml of DDDW. The pointer laser (He-Ne) using the light for pointing and a focusing on the surface of the plate using a quartz lens (f=130 mm). The Ag metallic target was fixed by a fixture inside the flask and immersed at 12 mm depth in the solution inside the flask; the ablation process was typically done at room temperature. The spot size of the laser beam on the surface of metal plate was varied in the range of 1.4-1.5 mm in diameter by changing the distance between the focusing lens and the metal plate. The ablation process was typically done for 1 minute.

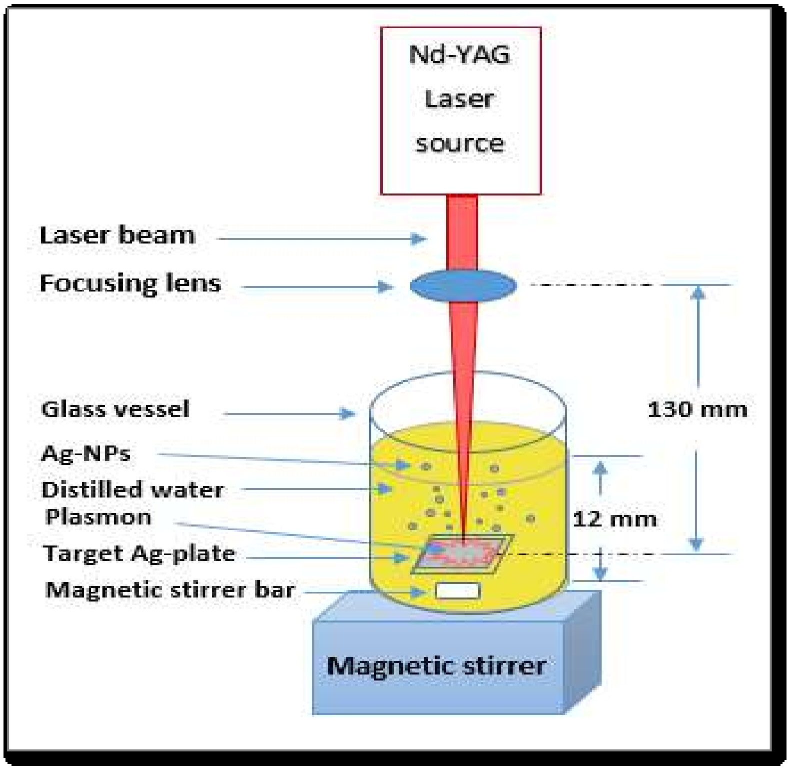


Figure (1) shows Experimental set up for nanoparticles synthesis, by pulse laser ablation in liquid PLAL technique.

The laser influence was varied in a range from 4.77 to 13.6 J/cm^2. The pulse energy was/were varied in the range (100-1000 mJ). The pulse duration and the repetition rate of the laser pulse were 10 ns and 1 Hz respectively.

Result and Discussion

Recently researches found the effect of many parameters such as height of the column of the liquid above the target, angle of the incidence of the laser beam on the target, the effect of number of the laser pulses which are important parameter for the ablation process. At which, the absorption spectrum as a function of wavelength was studied for different laser pulses ranging from (500 to 1000). This ablation process was carried out with three different laser wavelength (1064, 532 and 355) nm at fixed energy 800 mJ

Figures (2, 3 and 4) illustrates the relationship between the ABS as a function of wavelength (for a fixed laser pulse energy 800 mJ for wavelengths (1064, 532 and 355) nm and different pulses numbers. From these figures it is a clear that the peaks of increased with increasing the number of pulses and this refers to the fact that the increasing of the pulses lead to increase the density (concentration) of silver nanoparticles in the colloidal solation. Additionally, the peak of will shift toward the short wavelengths (blue shifting). This shifting may due to the decreasing of silver nanoparticles size.

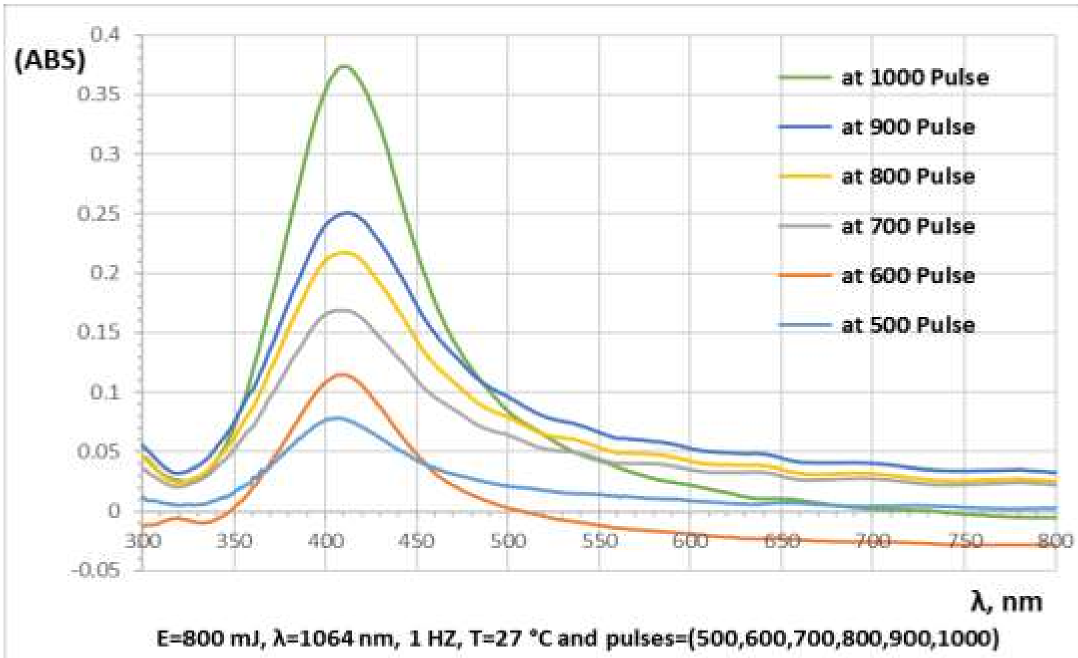


Figure (2) Shows the UV–Vis absorption spectra for silver nanoparticles prepared using PLAL synthesis at E= 800 mJ, λ=1064 nm, 1 HZ, T= 27 ℃ and different pulses numbers.

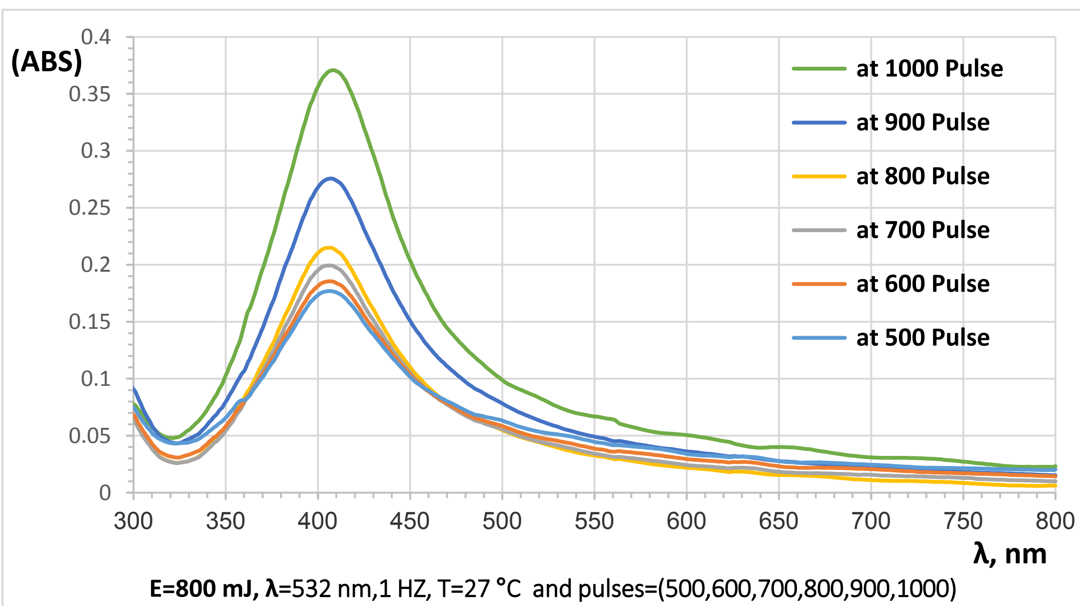


Figure (3): Shows the UV–Vis absorption spectra for silver nanoparticles prepared using PLAL synthesis at E= 8400 mJ, λ=532 nm, 1 HZ, T= 27 ℃ and different pulses numbers.

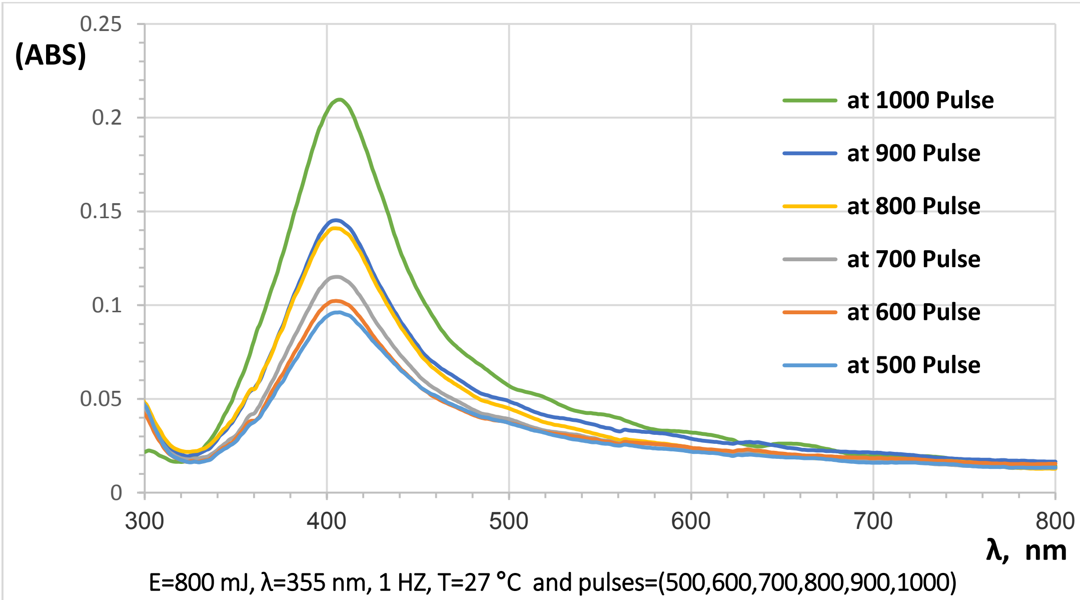


Figure (4): Shows the UV–Vis absorption spectra for silver nanoparticles prepared using PLAL synthesis at E= 800 mJ, λ=355 nm, 1 HZ, T= 27 ℃ and different pulses numbers.

In this work, we have focused here on the effect of the wavelength of the laser on the ablation process as follows:

The effect of the wavelength of the laser

The values of particle cross section for absorption of light of different wavelengths, σ_{abs}^{λ}, can be calculated for spherical silver particles by classic Mie theory [3, 12, 13]. The results of such calculations are shown in figure (5) for fundamental harmonic generation (FHG) at wavelength λ= 1064 nm, second harmonic generation (SHG) at λ = 532 nm, and third harmonic generation (THG) at λ= 355 nm of Nd:YAG laser. It can be seen that from Figure (5), the absorption of this cross sections are strongly depends on particle size for different wavelengths. When particle cross sections of light absorption are known, the “soft” and “hard” laser fluences can be calculated the different particles sizes for different laser wavelengths.

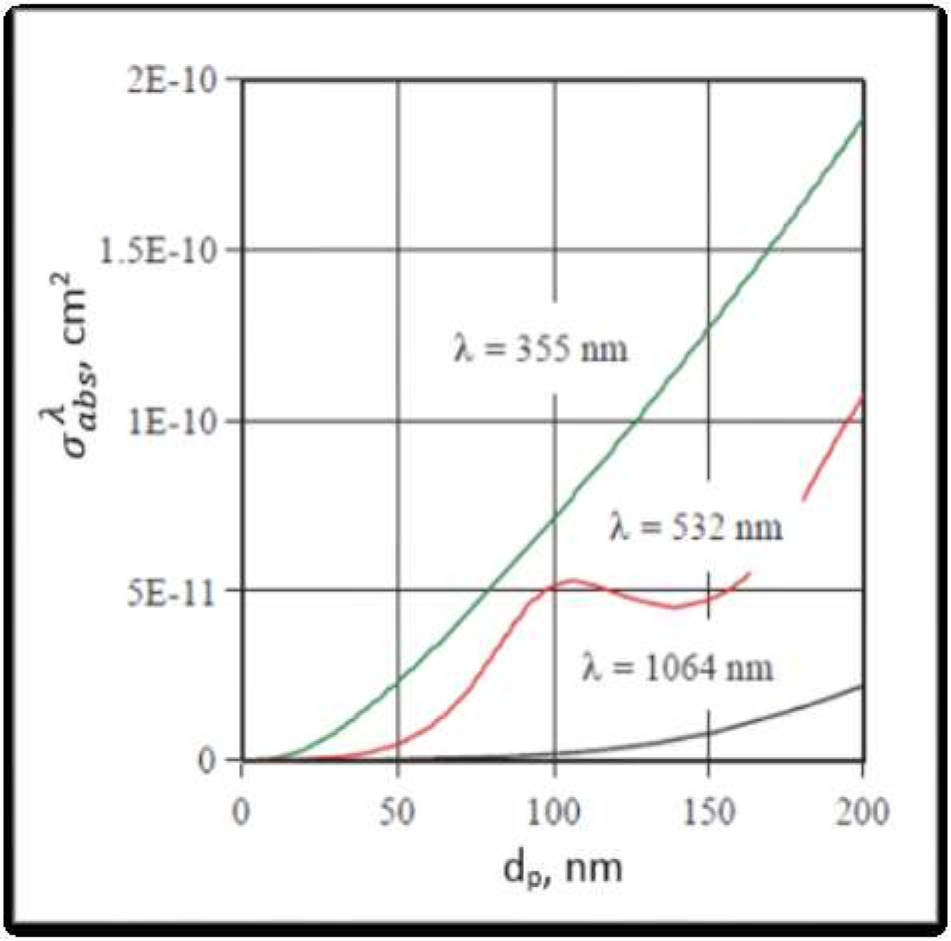


Figure (5): Absorption cross sections,σ^{λ}_{abs}, for spherical silver nanoparticles calculated as a function of particle diameter, d_p, with Mie theory [12,13] for three characteristic wavelengths of Nd:YAG laser.

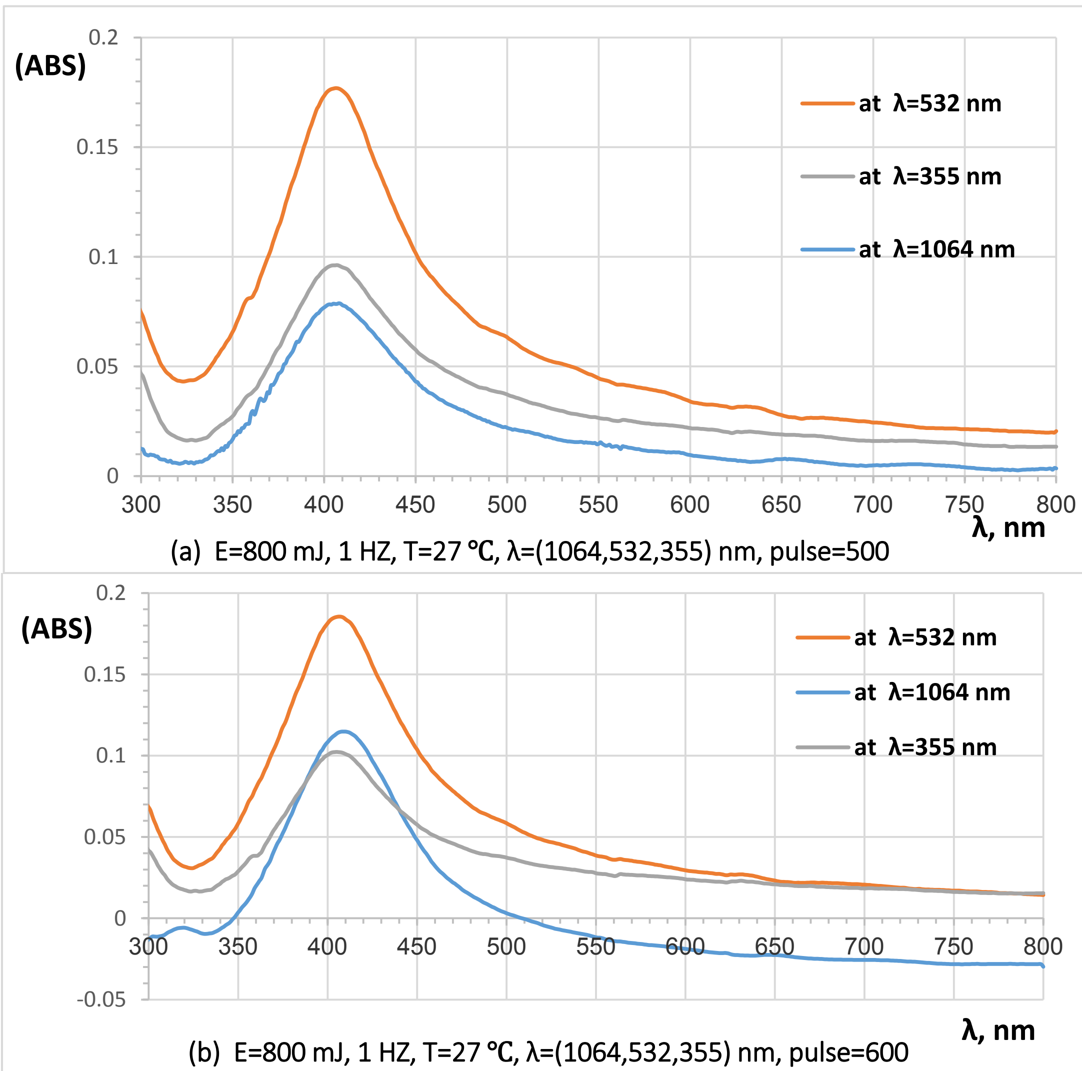
Therefore, the wavelength of laser plays a great role in the ablation efficiency and strongly depends on it [4,14].

Figure (6) shows the UV–Vis absorption spectra for silver nanoparticles prepared using PLAL synthesis for ABS as a function of the wavelength, for laser wavelengths (1064 nm, 532 nm and 355 nm) it is clear that increasing peaks of the absorbance with decreasing the wavelength of laser. However, at case 355 nm, it was rare as normal with 1064 nm and 532 nm, the absorbance peak reduces due to the energy of generating the third harmonic generation (THG) or we can say the number of photons would be less in this case.

It has presented the results, UV-Vis obtained measurements for the wavelengths (1064 nm, 532 nm and 355 nm), through which it is possible to predict or estimate the size and the diameter of the nanoparticle size depending on the reference standard measurements as tabulated in table (1).

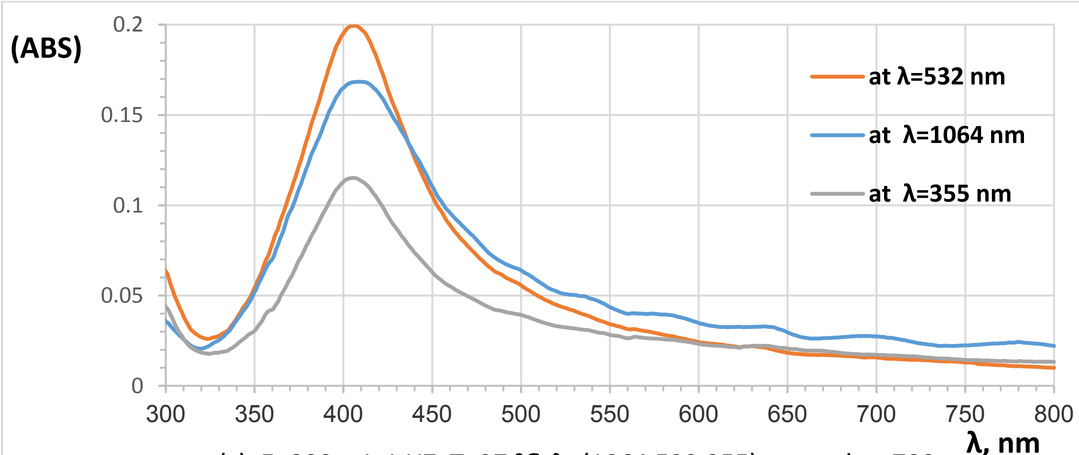
Table (1): Shows a comparison between the results of the UV-Vis earned the previous ways and compared with the standard results of previous studies for the expected diameter.

Method name		Range of λ_{max} (nm) at ABS	Typical Range of λ_{max} (nm)	Typical Diameter (nm)	Diameter (nm) expected
PLAL	λ =1064 nm	402-409	400-410	30	6-30
	λ =532 nm	402-405	390-405	10	6-10
	λ =355 nm	403-407	400-410	30	7-25

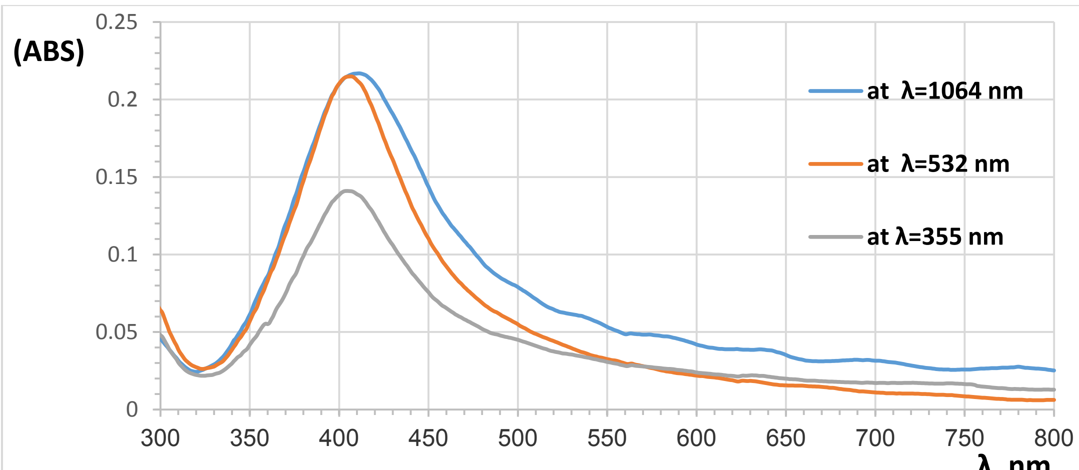


(a) E=800 mJ, 1 HZ, T=27 ℃, λ=(1064,532,355) nm, pulse=500

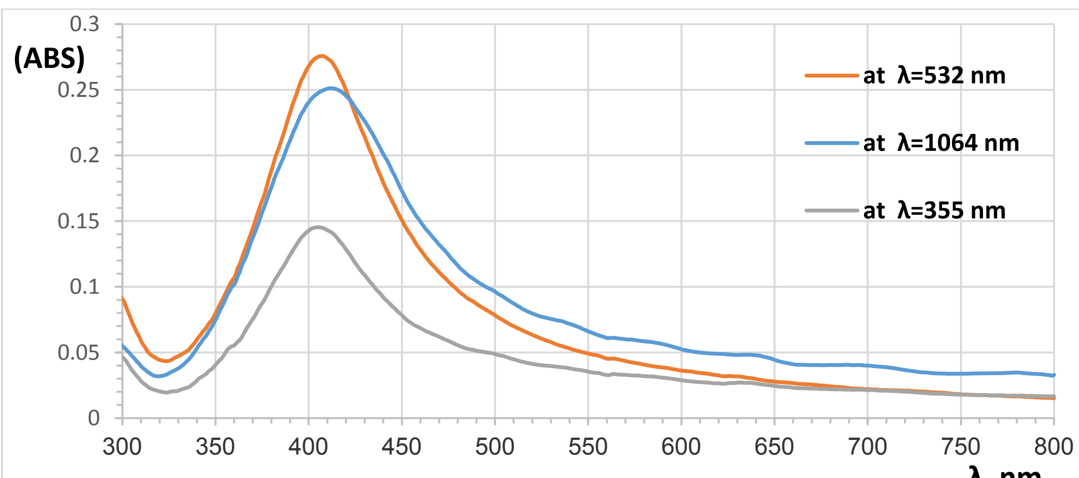
(b) E=800 mJ, 1 HZ, T=27 ℃, λ=(1064,532,355) nm, pulse=600



(c) E=800 mJ, 1 HZ, T=27 ℃, λ=(1064,532,355) nm, pulse=700



(d) E=800 mJ, 1 HZ, T=27 ℃, λ=(1064,532,355) nm, pulse=800



(e) E=800 mJ, 1 HZ, T=27 ℃, λ=(1064,532,355) nm, pulse=900

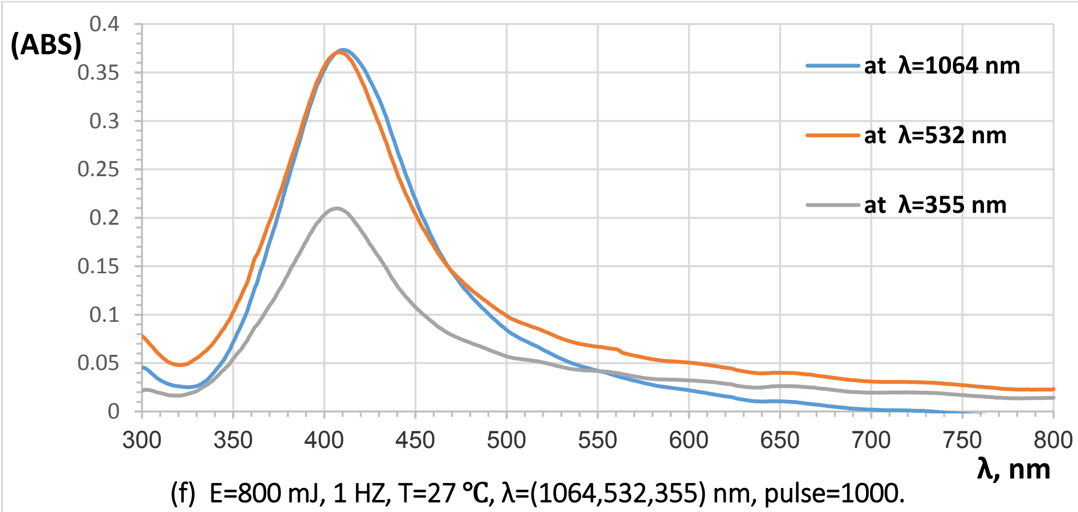


Figure (6): shows the UV–Vis absorption spectra for silver nanoparticles prepared using PLAL synthesis at E= 800 mJ, λ= (1064, 532, 355) nm, 1 HZ, T= 27 ℃ and pulses numbers (a) 500, (b) 600, (c) 700, (d) 800, (e) 900, (f) 1000.

SEM Measurements:

To identify the morphology and the structures of the particles in addition to measure the grain size for samples prepared in PLAL method, a set of Scanning Electron Microscopy (SEM) images have been taken for different samples with different wavelengths (1064 and 532) nm as shown in figure (7).

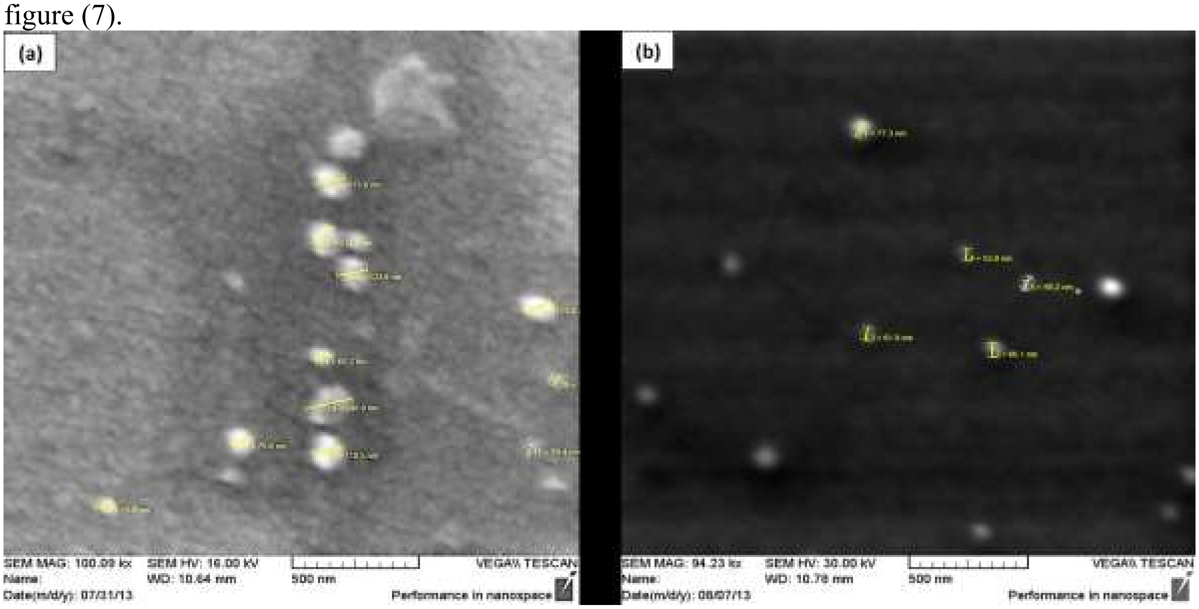


Figure (7): SEM images of colloidal silver-NPs by PLAL method prepared at 1000 pulses, T=27 ℃ and different wavelengths (a) 1064 nm and (b) 532 nm.

TEM Measurements:

Transmission electron microscopy (TEM) investigation of silver nano-composite nanoparticles is a direct and effective approach to determine the particle size and morphology of the nanoparticles, as well as the dispersion uniformity.

The size and morphology of the silver was studied via transmission electron microscopy (TEM) (Philips CM-10). The microscope was operating at an accelerating voltage of 80 kV. The silver samples an aliquot (20 µL) was applied onto a carbon coated grid. The solution was then left for 1 minute, and the excess was removed from the grid by blotting with a filter paper .The grids were placed in the grid box for two hours to dry before imaging. The images are shown in figure (8).

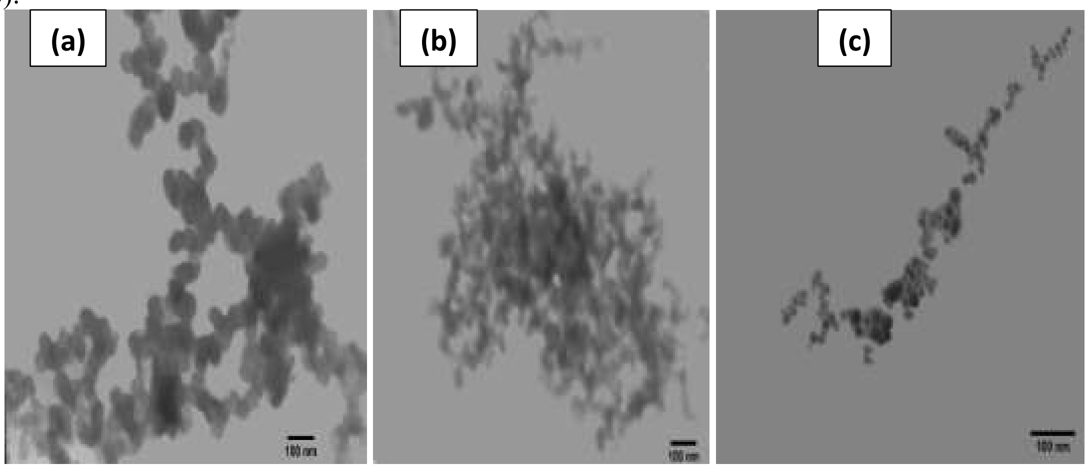


Figure (8): Shows TEM image for colloidal silver nanoparticles prepared by PLAL, at E= 800 mJ, 1 HZ, T= 27 ℃, 1000 pulse and (a) at λ =1064 nm, average size of the particles is (55-60) nm, (b) at λ =532 nm, average size of the particles is 35-40 nm, (c) at λ =355 nm, average size of the particles is 28 nm.

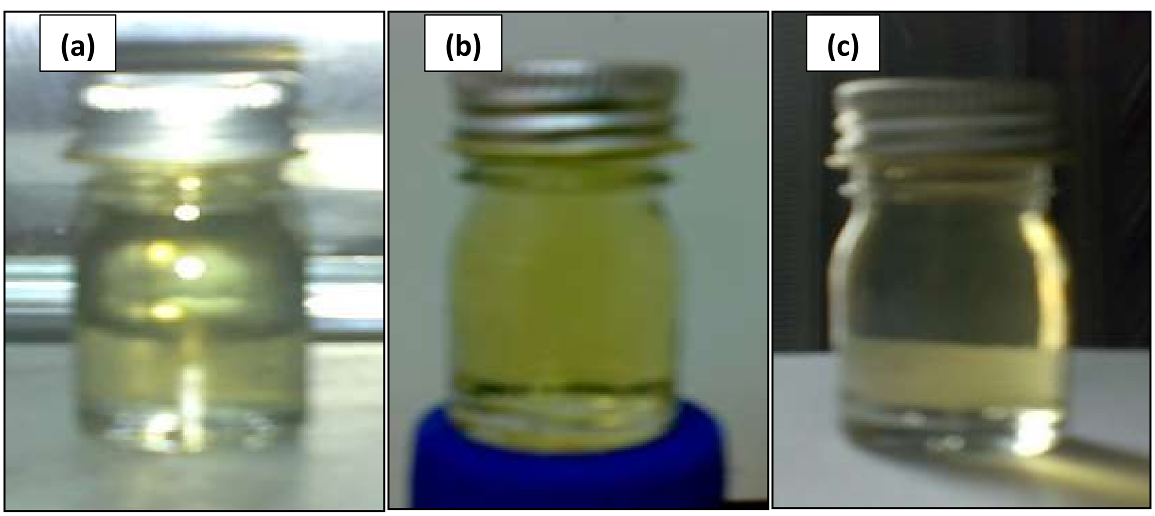


Figure (9): shows images of colloidal silver nanoparticles obtained by PLAL at 1000 pulse and (a) λ= 1064 nm, (b) λ= 532 nm, (c) λ= 355 nm.

CONCLUSION

Efficiency of laser ablation increased with short wavelength at higher laser energies, vice versa. Particles size could be controlled by laser wavelength parameter.

The optimum results of morphology for colloidal silver nanoparticles images were spherical shaped and the average size of the particles is ranged 55-60 nm at wavelength of λ =1064 nm, the average size of the particles is about 35-40 nm at wavelength of λ =532 nm and average size of the particles is 28 nm at wavelength of λ =355 nm.

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