Aggregation and Characterization of ZnO Nano Particles Using Laser Ablation Technique in Ethanol

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Abstract

In this work, ZnO nanoparticles were snthyesis using pulse laser ablation of zinc target (purity of 99.99%) immersed in ethanol with wave length of Nd:YAG laser (532 nm) operating at different laser energies (700, 800, 900 mJ) with 1Hz and (2000) pulse. A matching of the observed and standard (hkl) planes confirmed that the product is ZnO having a polycrystalline in nature with hexgonal structure perferention in (101) direction.

FESEM images showed that NPs have different morphologies and not uniform consist of many small irregular nanoparticles. The surface structure, in the energy 700 mJ has been more uniform compared with others energy. [DOI: 10.22401/JNUS.20.4.06]

Keywords**:** ZnO nanoparticles, X-ray diffraction, Morphology, PLA, FESEM.

Introduction

The Pulse laser ablation is typical example of top-down approach to fabricate nanoparticles [1]. The Nanoparticles have great scientific interest as they are effectively a bridge between bulk materials and atomic or molecular structures, at this size, physical, chemical and biological properties of substance are different in compared with properties in the micrometer and larger scales [2]. The characteristitics of new, research have found that they can develop materials, devices and systems that are superior to those in use today, but smaller in size such as laser ablation in liquid and chemical etching [3]. In the period previous, special attention has been devoted to the morphology, as ZnO can form different nanostructures, such as nanobelts, nanoribbons, nanowires, nanotubes, nanohelixes, nanorods and Nanoparticles [4].

Experimental procedure

The zinc target (purity of 99.99%) has been immersed in ethanol and fixed at bottom of glass vessel container with different laser energies (700, 800, 900 mJ). The number of pulse laser which used are (2000) pulses. Nd:YAG laser system (type HUAFEI) providing 532 nm wavelength with pulse duration was 10 ns, repetition rate 1Hz and effective beam diameter 4.8 mm. When ablation of zinc target, ZnO nanoparticles colloidal were formed in liquid. In order to make solution homogeneity the colloidal dispersed with ultrasonically for 15 min and magnetic stirrer for 30 minutes. lather the, solution drop casting on clean glass substrate which put on hot plate stirrer at temperature (85°C) for 45 minute. Fig.(1) shows the experimental setup of pulse laser ablation:

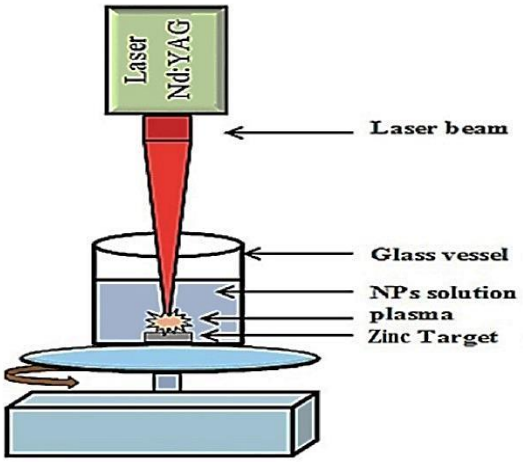

Fig.(1): Experimental setup of noanoparticles synthesis by PLA method.

Results and Discussion

In differaction in Fig.(2). the XRD patterns of ZnO thin film contain five main peaks at diffraction angle 31.77º, 34.32º, 36.32º, 47.06º and 56.56º ,62.52ºcorresponding to (100), (002), (101), (110),(103) and (102) planes. The strong and narrow peaks may be ascribed to the preferential growth along (101) plane of ZnO. The crystal size of the crystalline

material has an important effect in determining the properties of the material and can be of the (FWHM) which is given to (Debye-Scherrer relation):

$$D_g = \frac{0.9\,\lambda}{\beta\, cos\theta_B} \quad \text{..... (1)[5]}$$

Where Dg: is the crystal size, 0.9 is the Scherrer constant, λ: is the X-ray wavelength, β: is the full width ahalf maximum and θ_B: is the Bragg diffraction angle.

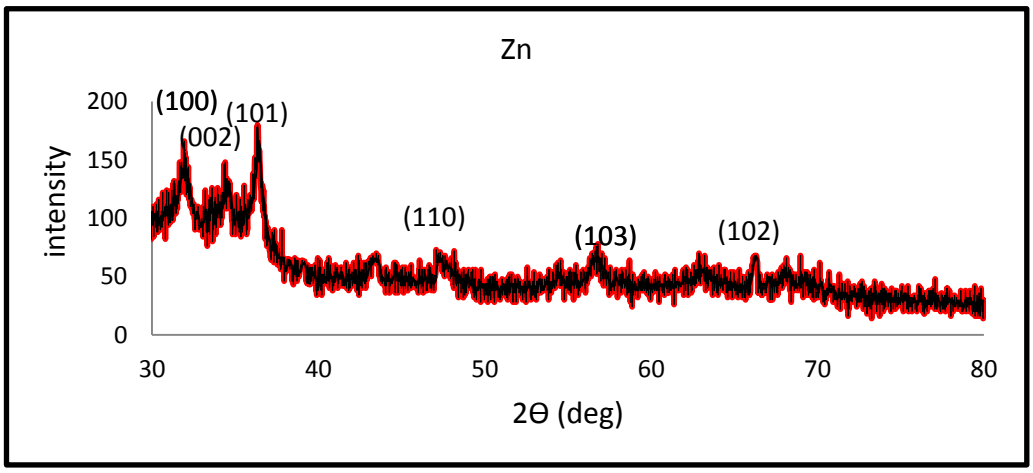

Fig.(2) : XRD pattern of Zn target.

The strong and narrow peaks may be ascribed to the preferential growth along (101) plane of ZnO. The results revealed that the strain and dislocation density are decrease with increasing the grain size. The crystal size of the crystalline material has an important effect in determining the properties of the material. The d-value of nano crystalline ZnO as given in Table (1), crystal size (D) in nm for a knowing X-ray wavelength Θ at a diffraction angle Θ of ZnO nanoparticles is calculated by using Scherrer formula as given in equation (1), the peak width of a strong diffraction plane were calculated and listed in Table (1).

Fig.(3) show that the X-ray differaction obtained through the laser ablation to zinc target in ethanol solution deposition on a glass substrate with energies (700, 800 and 900 mJ) and pulses of laser fixed at 2000 pulses. This figure show that the peakesat diffraction angle (31.82˚,34.6˚2,36˚.62,47.48˚,56.36˚but 62.88˚) at films prepared at 700 mJ bu for at energy films prepare at energy of 800 mJ energy was 800 mJ peak diffraction angle for are 31.14˚,34.22,36˚.22, 47.42˚,56.48˚ and 62.02˚) while in energy 900 mJ the peakes at anglse are a (31.68˚, 34 and 36˚.08), through the diffraction test dispersion (X-ray) found its kind multi gelling by the presence of a number of vectices of acute it the direction (101) as show in Fig.(3).

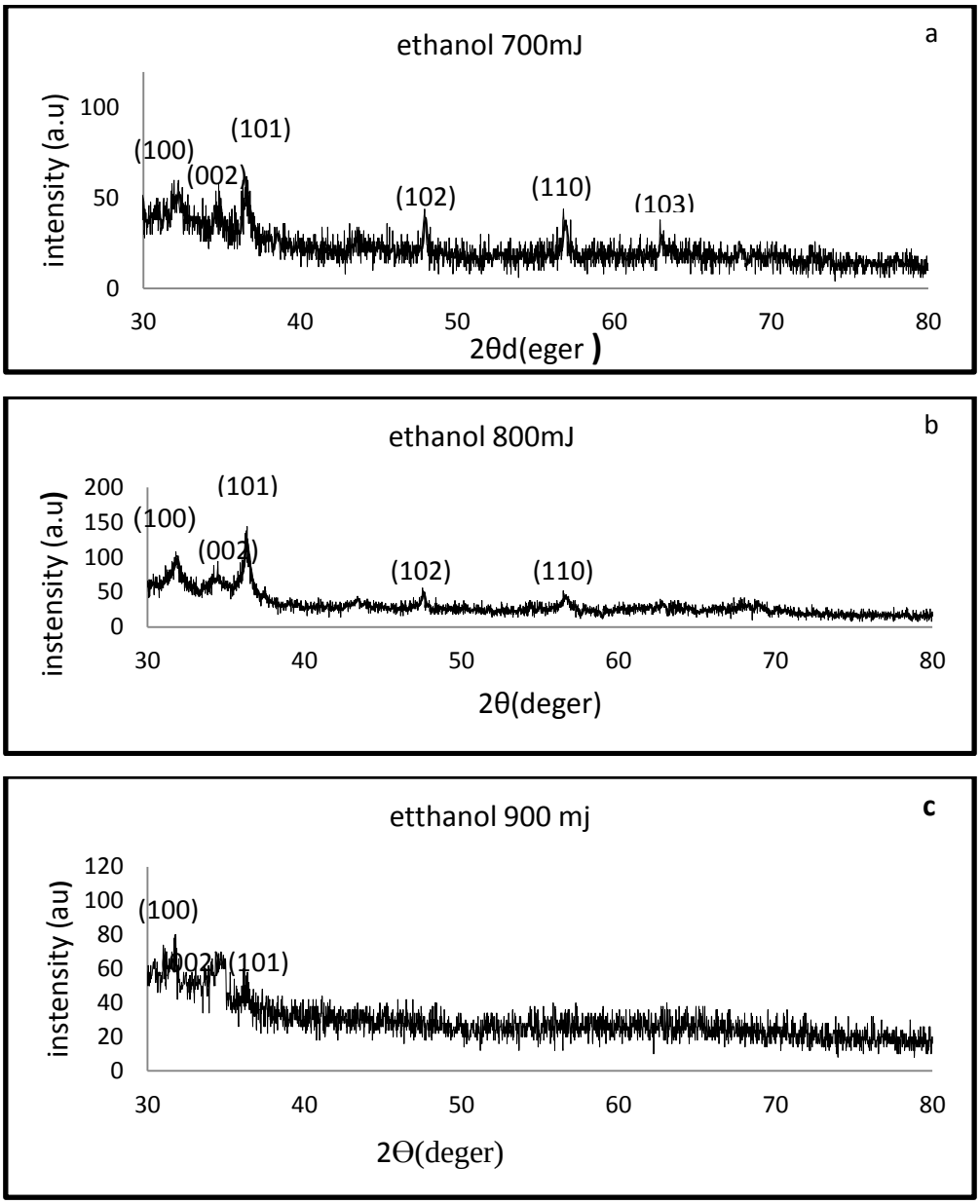

Fig. (3) : XRD pattern of ZnO NPs with different energies (a) 700mJ(b) 800 mJ and (c) 900mJ on glass substrate at 2000 puls.

Table (1)
The obtained results of the XRD of ZnO on glass substrate at different energy (700,800,900 m J) and fixed pulses at 2000.

Ethanol/2000	2θ (deg.)	Plane (hkl)	FWHM (deg.)	Crystal size (D) (nm)	d (A^o)
700 m.J	31.8 34.62 36.62	100 002 101	0.353 0.15 0.376	32.139	321.392
800m.J	31.1 36.137	100 101	0.165 0.15	50.547	505.478
900 m.J	31.02 34.02 36.08	100 002 101	0.165 0.13 0.15	54.058	540

Field emission scanning electron microscope (FESEM)

FESEM images confirmed that these NPs have different morphologies, it can reveal that the morphology of ZnO NPs is not uniform consist of many small irregular NPS.

In Fig.(4) shows SEM images of zinc oxide deposited on the glass substrate at temperature of 85°C, at700 mJ energy the shape is like flowers, But SEM images with energy 800 mJ and 900 mJ the shape seem clusters resembles balls of various sizes. with an average size shown in. Ethanol, in the energy 700 mJ seems the surface more uniform compared with others energies. On other hand, the images in 800 mJ and 900 mJ show irregular, big fragments and homogenous.

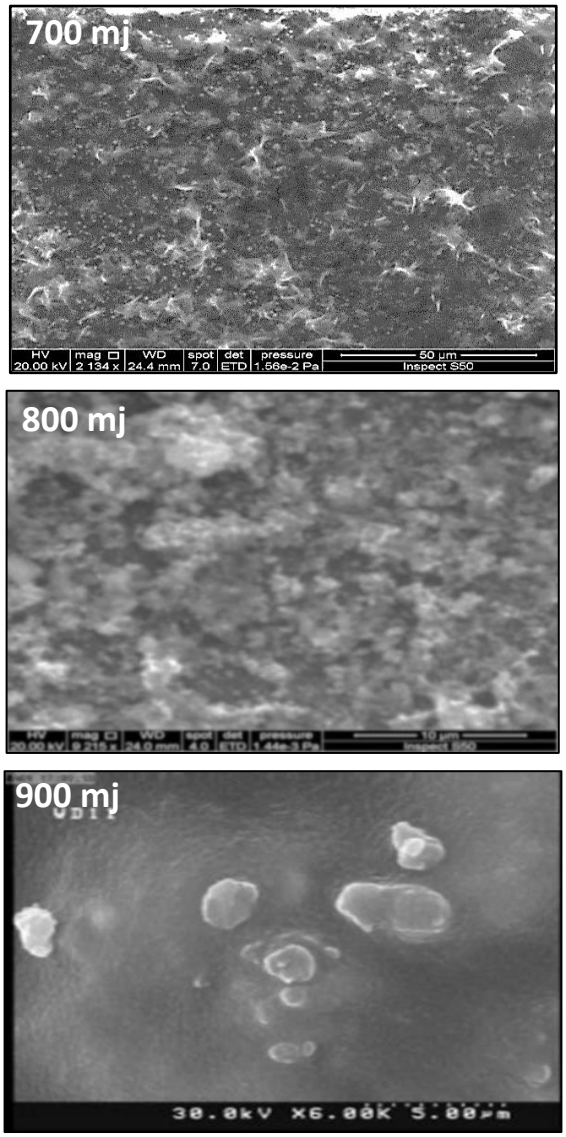

Fig.(4): FESEM images of ZnO NPs prepared by pulsed laser ablation in ethanol with different energyies (700, 800, 900 m.J) and pulses fixed (2000).

Energy-dispersive X-ray spectroscopy

Fig.(5) represent EDX spectra of the films contain the elements (Zn and O) indicating formation of the ZnO films with high purity. The elements (Au and Si) reveal the material in substrates, (silicon and glass).

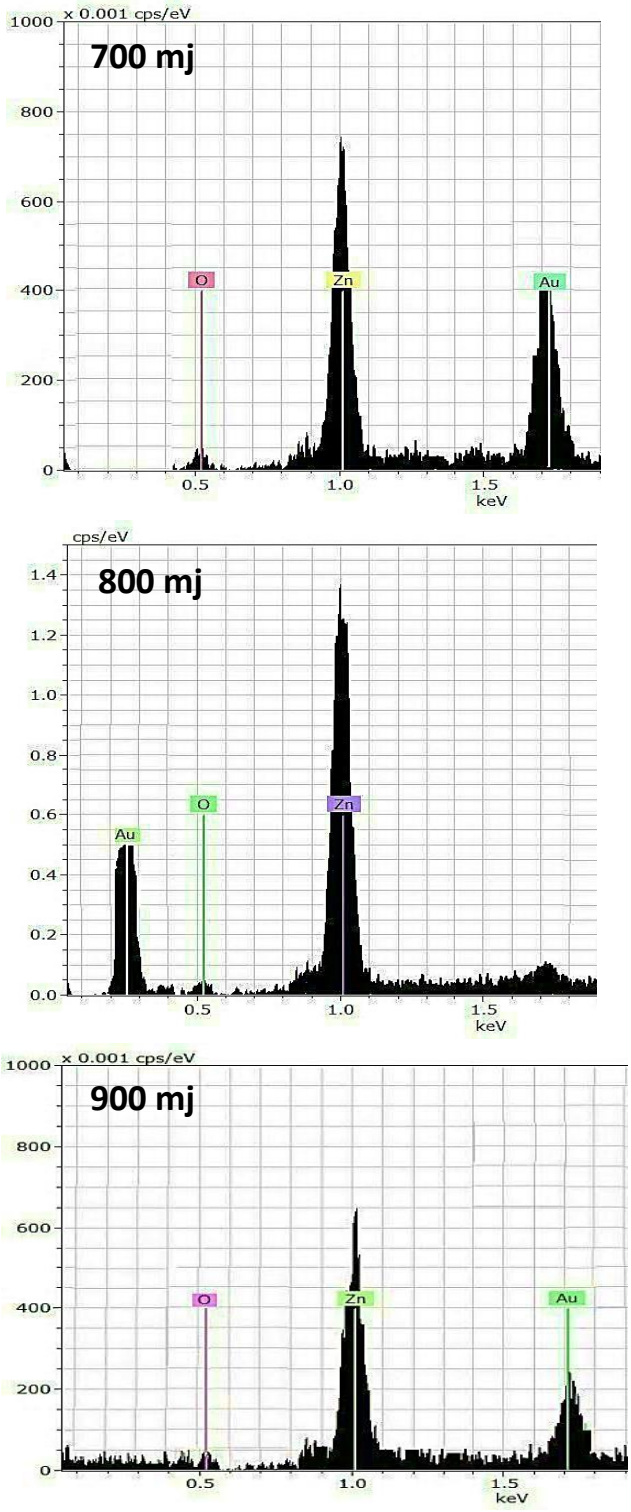

Fig.(5): EDX of ZnO thin films deposited on a glss substrate at 85 C for ethanol with different laser energies (700, 800 and 900 mJ).

Absorption

The laser pulses parameters having an important effect on the formation of ZnO NPs show in Fig.(6) which tested by uv-vis at room temperature in the range (300 nm to 900 nm). For all the films, it is observed that the optical absorption increases due to increase in roughness with increasing the number of laser pulses, increased energy lead to increased absorpance thus will increased surface roughness. It is obvious that colors of liquids were changed differently within the process, it showed the fine bubbles formed in front of target after first 12 min of ablation. These bubbles apparently prohibited the laser energy to be absorbed by target. the maximum values observe at (375,370 and 365 nm) of values of tion exponential as follows power 700mJ was energies 700,800 and 900 mJ respectively.

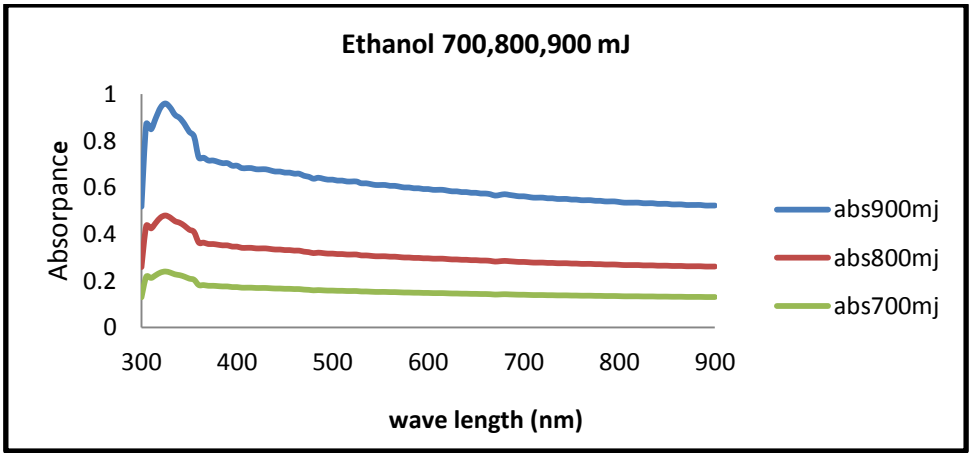

Fig.(6): Optical absorption as a function of wavelength for ZnO prepared on glass substrate with laser pulses of 2000 at different laser energies of (700 ,800 ,900 mJ).

Optical energy gap

The optical band gap decreases with increasing laser pulses, as showen in Fig.(7) ,The curves show shifts in the value of the band gap towards lower energy when increasing the laser pulses. This attributed to the increases in the crystal size with increasing laser energy. Where in the quantum confinement range, the band gap of the particle decreases as the crystal size increases, this behavior can be explained by the quantum confinement model [6]. This decrease in energy gap can be due to the prohibited impurities that led to the formation of donor levels with energy gap near the conduction band, which is in accordance with the findings of other workers [7]. At lower laser energy, a low number of ZnO NPs are ablated from the target as show in Table (2). The band gap reaches 3.25 eV at 700 mJ, 3.40 eV at 800 mJ and 2.95 eV at 900 mJ.

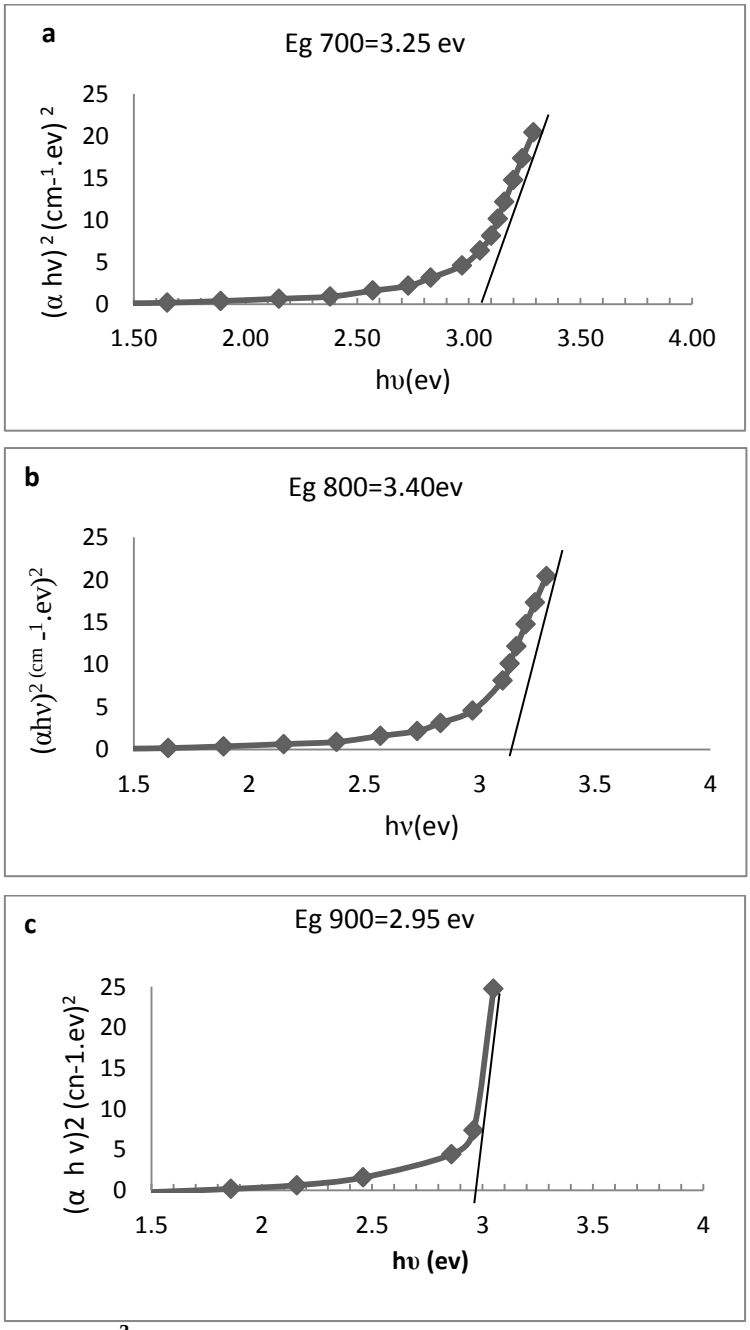

Fig.(7): Plot $(\alpha h\upsilon)^2$ versus hυ of ZnO NPs prepare at different laser energies (a) 700 (b)800 (c) 900mJ.

Table (2)

Values of optical band gap as function of laser energy for ZnO NPs deponided on glass substrate.

Solvent	No. of Pulses	Energies (mJ)	E_g (eV)	Wave length(nm)
Ethanol	2000	700	3.25	325
		800	3.40	
		900	2.95	

Photoluminescence (PL)

PL emission spectra of ZnO with different laser energies have been recorded at room temperature at excitations source of wave length of 325 nm as s shown in Fig.(8). The PL spectrum of the pure ZnO exhibits stronge near-band-edge (NBE) emission at 382 nm and green luminescence band centered at about 492 nm. The UV-emission typically results from the recombination of force of bound

excitation indicating high crystal quality of the material wihle the green emission band originates from the recombination of photo-generated hole with a singly ionized defect. When using energy (700 mJ) and strikes in 2000 pulses there will be an increase in the spectrum of fluorescence to be(368 nm), while in the second form, which has been using the energy (800 mJ) it note a decrease fluorination in range (371nm). But in energy (900 mj) it note an increase in the spectrum of fluorescence value to be (377) nm.

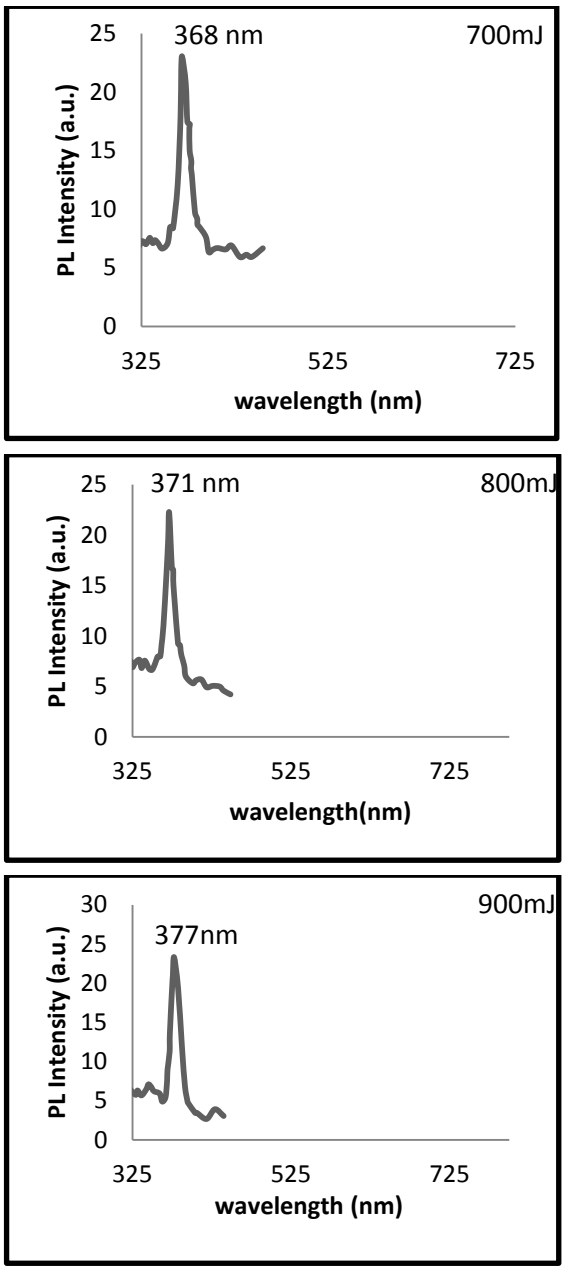

Fig.(8): PL spectra of ZnO NPs prepared at differences laser energies.

Table (3)
The photoluminescence measurements.

PL Intensity (a.u.)	*Eg (ev)*	*Emission wavelength (nm)*	*energy (mJ)*
304.22	3.2	368	700
305.87	3.4	371	800
305.88	2.9	377	900

Conclusions

Laser ablation in liquid provides a simple, flexible, controllable process and less expensive way for fabrication of ZnO nanoparticles. From the X-ray characteristics for as prepared sample showed that amorphous structure of ZnO NPs films, but after annealing film 300 º C show that is polycrystalline with hexoganal structure without any trace of an extra phase with preferential orientation in the (101) direction because the multiplicity of vertices of acte the direction. From SEM technique the formation rate ZnO nanoparticles suspensions, mean particle size could be controlled by proper selection of the laser parameters and liquid media. The NPs in liquids----have an almost perfect different shape, different flowers irregular shapes agglomerated and some presented chains of welded particles.

- Optical absorption spectra of -the sample prepared in ethanol at varying energy strong features in the UV range but have low absorption in visible region.
- The estimated band gap energy changes from (3.25 eVto 3.40 eV and 2.95 eV) for nanoparticles suspension which is large and small than the bulk (3.4eV) and is found to be decreased with increase in average crystal size of the prepared Nanoparticles.

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