

## Fourier Transform Infrared Spectroscopy and Photo Luminance Results for ZnO NPs Prepared at Different Preparation Condition Using LP-PLA Technique

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### ABSTRACT

*This work presents the preparation of Zinc oxide Nanoparticles using straightforward, clean, single step preparation method. Nd-YAG laser pulse at different fluence and laser pulse number was employed to the ablation of pure Zn metal target in the DIW. FTIR results ensure the presence of Zn-O bond related to the ZnO Nps vibrational mode while the PL result shows a blue and redshift depending on laser parameters.*

**Keywords:** ZnO NPs, LP-LPA, FTIR, PL

### 1. INTRODUCTION

ZnO as an old optoelectronic material was attracted massive attention as TCOs with its potential use in optoelectronic devices. Nanostructured ZnO thin films show a distinguished performance in energy conversion, detectors, and photonics application [1-3]. Novel electrical, chemical, optical and mechanical properties are obtained with a reduction in the crystalline size, which are appearing due to quantum QC effects. [4-6] As nanoparticles ZnO exhibit both the semiconducting properties of the ordinary zinc oxide thin films such as large exciton energy of about 60 meV with excellent stability and the novel characteristics of the nanostructure. It is renowned that tiny particles have the large Surface to Volume ratio and surface defect.

ZnO also a fluoresce semiconductor in the visible and ultraviolet regions. The fluorescence peak is directly related to the particle size [7-9]. It's exhibiting red shifts of the UV-Visible absorption peaks for the particles less than 7 nm in size [10, 11]. According to all above properties, ZnO Nanoparticles are employed in a different of applications such as UV detector, antibacterial, photo catalyst, solar energy conversion, gas sensors, luminescent materials, and others [12, 13]. Among different preparation methods for producing nanoparticles, laser ablation technique has been successfully developed and, laser ablation in liquid has been recognize as an essential technique for the fabrication of nanoparticles.

In this work, FTIR analysis of the prepared ZnO nanoparticles at different laser fluence and number of laser pulse was carried out, reaching to the optimum preparation condition.

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## 2. EXPERIMENTAL WORK

(1×1cm) ultra-pure (99.999) Zn metal plate from (Fluke) was fixed at the bottom of an open vessel containing 3 ml DIW. A focused Nd-YAG laser system was used at different laser fluence 28-567 J/cm<sup>2</sup>, laser wavelength 1064nm, 532.5 nm and seven nsec pulse duration. The laser pulse was tightly focused on the ablated target surface using a convex lens with a focal length of (12.5) cm. The position the ablated metal was mechanically and continuously translated using a controlled motor, to ensure fresh surface ablation and to avoid a deep ablation traces or crusts.

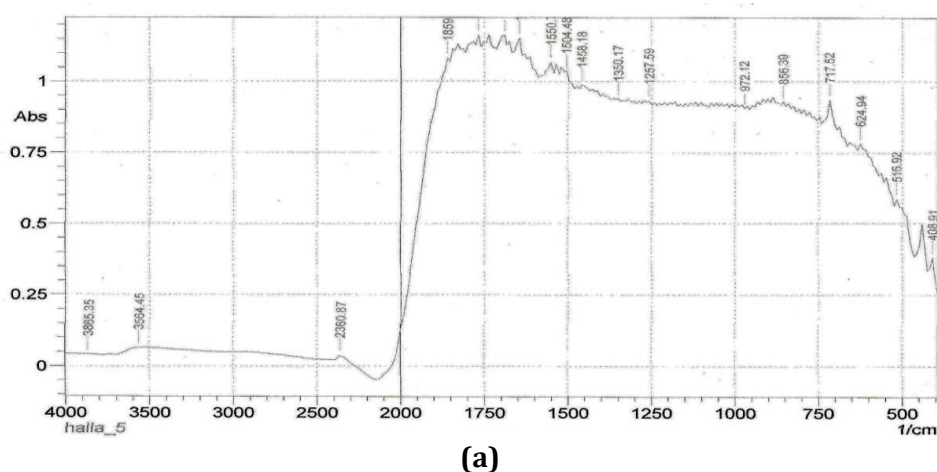
Drop casting method was used to prepared thin film on the glass substrate followed by 60°C heat temperature to convert ZnO nanoparticles colloidal to nanoparticles thin films. Fourier Transform-Infrared Spectroscopy (FTIR) from (SHIMADZU IRAFFINITY) probes the molecular vibrations of molecules for the prepared samples prepared. The scan of the FTIR measurements is performed over the range between (400 – 4000) cm<sup>-1</sup> for the prepared sample.

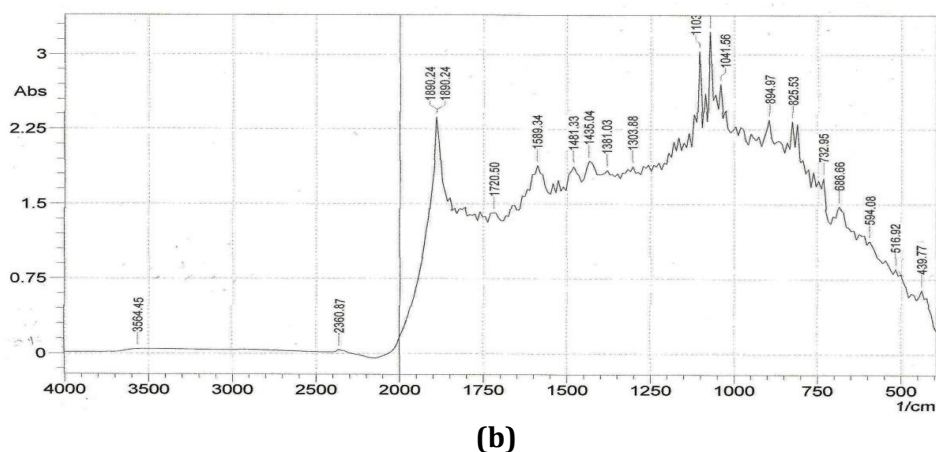
The photoluminous (PL) measurements were measured using LABRM-HR spectrometer using (He-Cd) laser as an excitation source.

## 3. RESULTS AND DISCUSSION

Figure (1 a, and b) gives the FTIR result for ZnO NPs prepared at a different number of pulses (30, 50 pulses) with constant laser fluency of (71J/cm<sup>2</sup>).

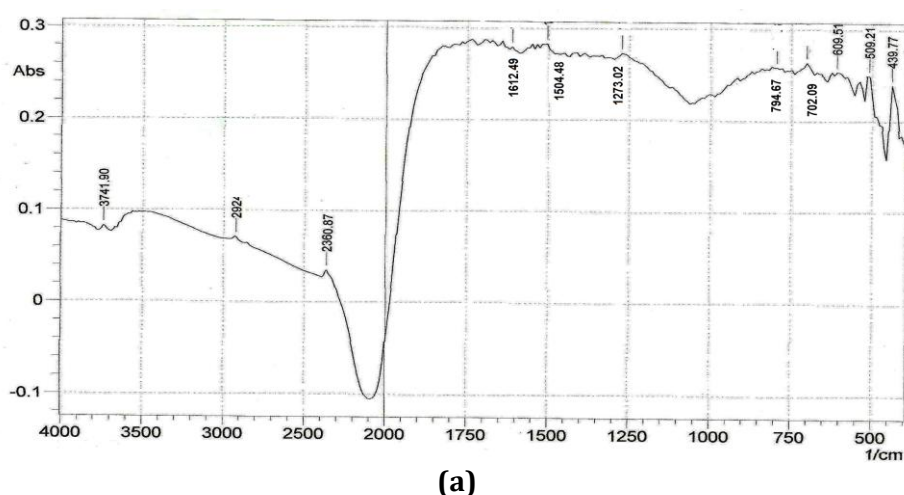
In these figures we could recognize the absorption peaks at (439.77, 516.92, 594.08, 408.19 and 516.92) cm<sup>-1</sup> wave number which related to the stretching vibrations mode of the Zn-O band [14], at the same time we could notes the increase in the intensity of the absorption peak by increasing the number of laser pulses which related to the larger amount of the ablated material from the target surface that takes place mainly during the arising part of each laser pulse, and then increase in the concentration of ZnO NPs at higher number of laser pulse. Absorption peaks at (3564.45, 3865.35, 2360.87 and 1481.33) cm<sup>-1</sup> are related to the harmonics of H-OH stretching modes, while those at (1435.04, 1458.18) cm<sup>-1</sup> are related to the C-O vibration modes refers to the little contribution of CO<sub>2</sub> dissolution from air contain.

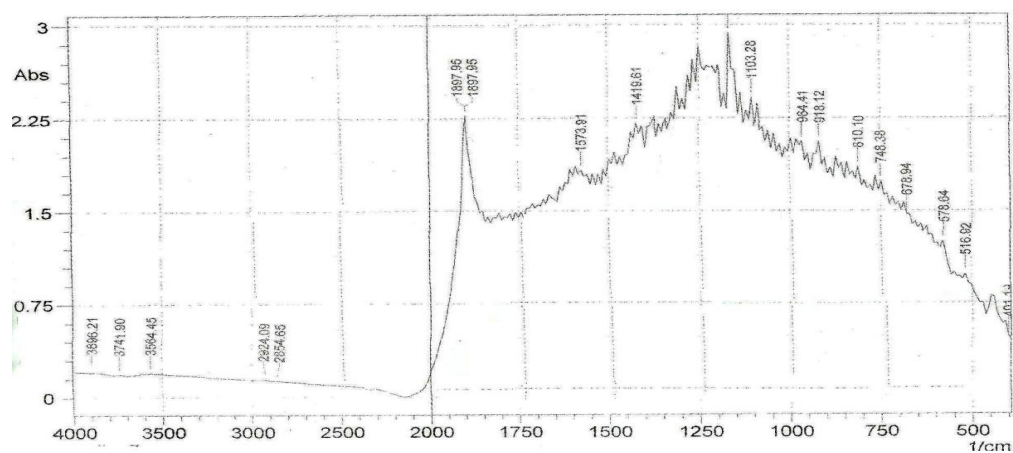




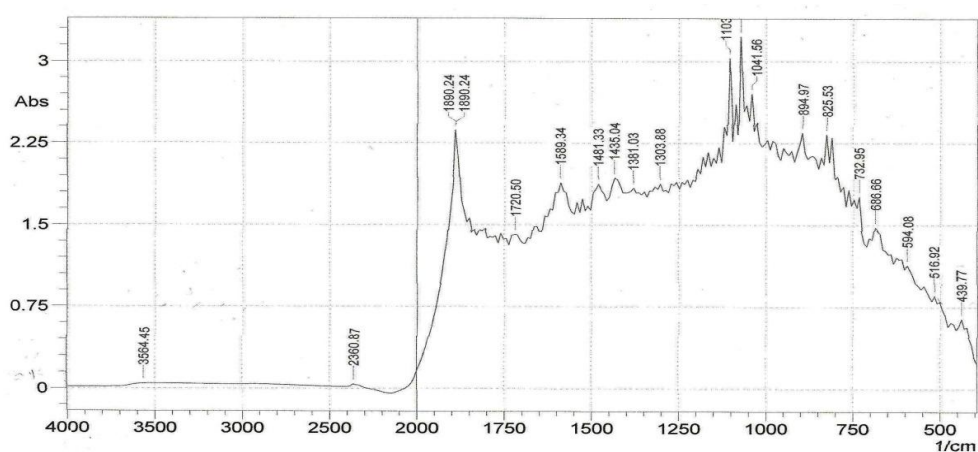
**Figure 1.** Fourier transform infrared spectrum of ZnO nanoparticles in DIW as a thin film on the glass substrate prepared with constant laser fluency (71) J/cm<sup>2</sup> (a) 30 pulses (b) 50 pulses.

Effect of laser power density with a constant number of pulses (20 pulses) could be shown in Figure (2 a, b, c, d, and e). In These figures all the absorption peaks at (439.77, 424.34, 401.19, 509.21, 516.92, 578.64, 447.49, 501.49, 594.08, 532.35, 462.92, and 547.78) cm<sup>-1</sup> are related to the stretching vibrations mode of Zn-O bonds. This figure indicated that when increasing laser power density, the absorption peak appears with larger intensity due to increase in the ablated material and as a result the concentration of ZnO NPs increase except in case of figure (e) due to the limitation in the ablated material because of the saturation effect at high laser fluence. The absorption peaks at (1504.48, 1612.49, 1419.61, 1481.33, 1573.91, 1612.49, 1450.47, 1550.77, 1597.06) cm<sup>-1</sup> wave number are corresponding to the stretching mode of the carboxyl group (C=O) While Absorption peaks at (3741.9, 3564.45, 3896.21, 3610.74, 3896.21, 385.63) cm<sup>-1</sup> are related to the stretching modes of the H-OH band. In all the above FTIR spectrum a lot of peaks appear at (717.52, 972.12, 825.53, 894.97, 856.39) cm<sup>-1</sup> and (686.66, 624.94) cm<sup>-1</sup> wave number are related to the symmetrical stretching mode and bending mode of the C-H-H bands respectively, this consistent with other work [15].

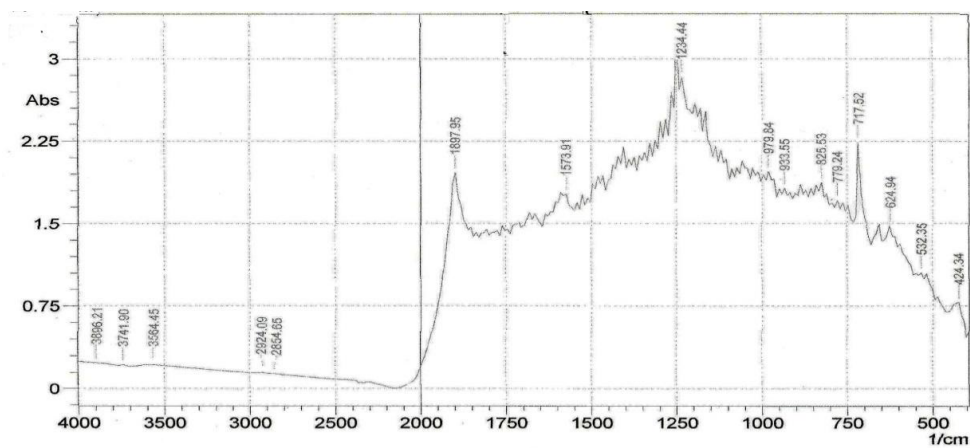




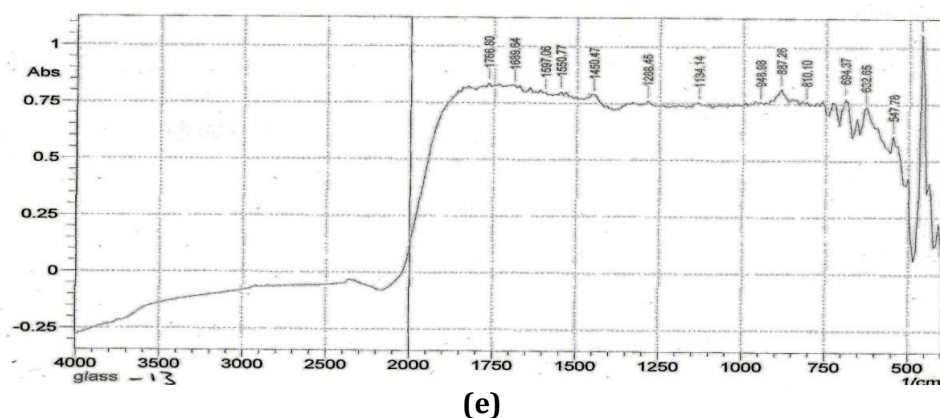
(b)



(c)

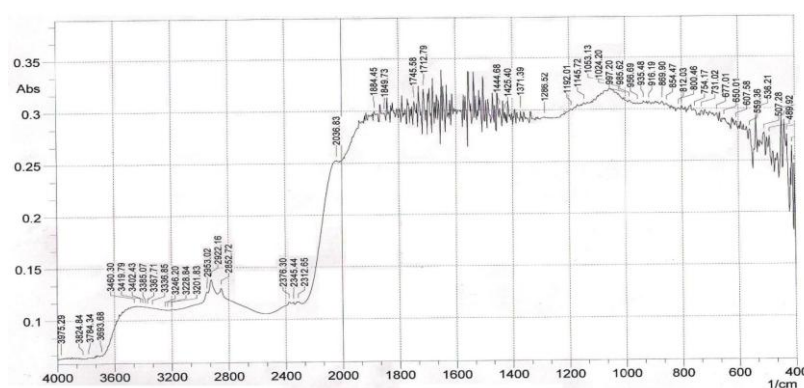


(d)



**Figure 2.** Fourier transform infrared spectrum of ZnO nanoparticles in DIW as a thin film on the glass substrate prepared with constant laser pulse (a) 28 J/cm<sup>2</sup> (b) 43 J/cm<sup>2</sup>, (c) 71 J/cm<sup>2</sup>, (d) 142 J/cm<sup>2</sup>, (e) 567 J/cm<sup>2</sup>.

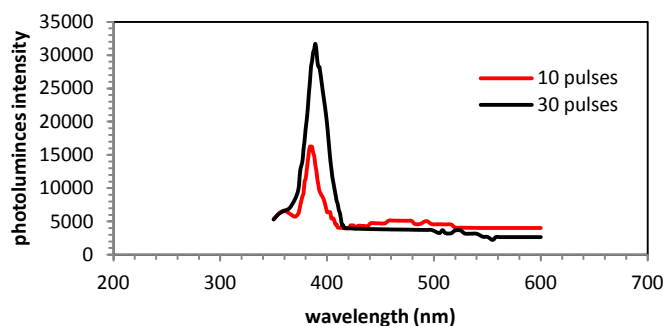
The FTIR results for sample prepared at different wavelength 0.532  $\mu\text{m}$  and laser power could be shown in figure (3), In this figure we could recognize the absorption peaks at (489.92, 507.28, 536.21 and 559.21)  $\text{cm}^{-1}$  wave number which related to the stretching vibrations mode of the Zn-O band, at the same time we could notes the increase in the intensity of the absorption peak in the sample prepared at 0.5328  $\mu\text{m}$  rather than at 1.06  $\mu\text{m}$ , because of the increasing the amount of the ablated material from the target surface that, and then increase in the concentration of ZnO NPs at 0.5328  $\mu\text{m}$  rather than 1.06  $\mu\text{m}$ , this result similar to that obtained with other work [16]. In the FTIR spectrum, a lot of peaks appear at (731.02, 754.17, 800.46, 812.03, 854.47 and 869.90)  $\text{cm}^{-1}$  and (607.58, 650.01 and 677.01)  $\text{cm}^{-1}$  wave number are related to the symmetrical stretching mode and bending mode of the C-H-H bands respectively. The absorption peaks (3201.83, 3228.84, 3336.85, 3367.71, 3402.43, 3693.68, 3784.34, 3824.84 and 3975.29)  $\text{cm}^{-1}$  is related to the stretching modes of the H -OH band, the similar result has been obtained by other workers [21].



**Figure 3.** FTIR spectrum of ZnO Nanoparticles in DIW as a thin film on the glass substrate prepared at 0.532  $\mu\text{m}$  with laser power 60 mJ (203 J/cm<sup>2</sup>) laser fluency and 50 laser pulses.

Photoluminescence results of the Nanoparticles colloidal could be shown in Figure (4). This figure indicates that photoluminescence intensity of the UV near band edge emission peaks located at 381, 384 nm increases with the increase of the number of pulses, while the broad small band at the green region, presumably associated with the intrinsic defects in ZnO and with oxygen vacancies on the surface of Nanoparticles. The shift in of PL peak position may attribute variation in the grain size of nanoparticles due to the quantum-confinement effect.

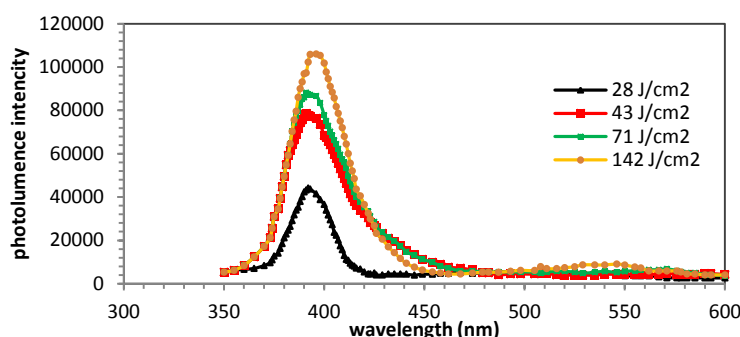




**Figure 4.** PL spectra of ZnO nanoparticle solutions prepared at different number of pulses. The laser power was 100 mJ/pulse and laser fluency 71 J/cm<sup>2</sup>.

Effect of laser fluence on the PL properties of the ZnO nanoparticles could be shown in figure (5). Blue shifts could be recognized at the near band edge emission as the laser fluence decreases, which related to the decrease in the particle size with decrease laser power density [6, 17-20], the increase in the optical transition energy indicating a blue shift toward shorter wavelength.

Beside that the reduction in the grain size means high surface to volume ratio resulting in large active sites surface of the chemical reaction and hence of the photon absorption. Also, the weak green emission peaks located at (500-590) nm resulted from intrinsic defects in ZnO and with oxygen vacancies. The green emission intensity grows as a function in the laser power densities.



**Figure 5.** PL spectra of ZnO nanoparticle solutions prepared at 1.06 μm with various ablation laser powers (28,43,71 and 142 J/cm<sup>2</sup>) laser fluency.

#### 4. CONCLUSION

The FTIR spectrum indicated that the intensity of the absorption peak related to the Zn-O vibrational mode insure that all the ablated Zn metal transferred to its oxide. The photoluminescence spectra at RT revealed that UV near band edge shifts to blue region when the laser fluence and number of pulses decreases while the weak green emission related to very small amount of defects due to oxygen vacancies.

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