PHYSICOCHEMICAL PROPERTIES OF ZnO NANOPARTICLES PREPARED USING LOW ENERGY LOW REPETITION RATE LASER SYSTEM

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ABSTRACT: *Simple, cheap and single step method for the preparation of oxide Nanoparticles with no need for any complex and expensive further step was presented. Also, this work shows a long period of stability, less aggregation, non toxic and contamination colloidal Nanoparticles. It provides a controlled method to prepare Nanoparticles with a specific property depended on the preparation condition and laser parameters. In the present work, ZnO Nanoparticles was fabricated using LP-PLA system at which ablation of pure Zn metal target in DIW was done using 7 nsec Q-switching Nd:YAG laser , (tattoo removal system) ,at a different laser wavelength (1.06 and 0.532μm), laser fluence and number of the laser pulse. The effect of these parameters on surface morphology has been carried out. The Grain size of the obtained NPs is found to be increased with laser fluence and decreased with number of laser pulses.*

Keywords: ZnO NPs, LP-LPA, surface morphology, AFM , laser parameter, FTIR

1. INTRODUCTION

Zinc oxide has attracted attention as transparent conducting oxide and potential use in optoelectric devices, [1-4]. Nanostructured ZnO materials have received broad attention due to their distinguished performance in electronics, optics and Photonics. With a reduction in size, novel electrical, mechanical, chemical and optical properties are introduced, which are largely believed to be the result of the surface and quantum confinement effects.

It is also a semiconductor and fluoresces in both the UV and visible regions. The peak in fluorescence shifts as a function of particle size, It's exhibiting red shifts of the UV-Visible absorption peaks for the particles less than 7 mm in size [4,5]. Thus Zinc oxide Nanoparticles are used in a variety of applications such as UV absorption, antibacterial treatment, catalyst, photo catalyst, biochemical engineering, It is also used in the fabrication of solar cells, gas sensors, luminescent materials, transparent conductor, heat mirrors and coatings [6,10]. Among different preparation methods for producing nanoparticles, The laser ablation technique has been successfully developed and laser ablation in liquid has been recognizance as an important technique for the fabrication of nanoparticles[11-14].

Most importantly, LP-PLA (Liquid Phase –Pulsed laser Ablation) was presented as a highly controllable method, at which size and thus, all related physical properties, could be justified by changing specific parameters such as, laser parameter and varying the environmental parameter such as pH and temperature of the solution.One of the most important laser parameters which has been no yet extensively studied is the laser wavelength. It was found that Nanoparticles prepared by infrared laser give a perfect spherical morphology with high production rate, compared with those produced using UV laser undergo fragmental shapes and lower production rate. [1, 15-17]

This work present effect of different parameter on the surface morphology, particle distribution and size of ZnO nanoparticles prepared using LP-PLA technique.

2. EXPERIMENTAL DETILES

High purity (1×1cm) (99.99) Zn plate frame (Fluke) was used as a target, so it fixed at the bottom of open a plastic cell containing (3 ml DIW,). The pure metal target was irradiated with the focused Nd-YAG laser pulse at different laser fluency (28-567 J/cm2), wavelength (1064nm, 532.5 nm) and (7 nsec) pulse duration. The laser pulse was tightly focused on the target surface using a convex lens with a focal length of (12.5) cm to create a spark or a breakdown in the sample. The position of metal plate was continually translated mechanically using a controlled motor so that each laser pulse falls on the fresh surface and ablates the target surface homogeneously also to avoid a deep ablation trace or crusts. The colloidal solution vibrated for 10 min by ultrasonic vibrator in order to get homogeneity for the product, and then dropped on the glass substrate; dried in an oven at 60^{o}C temperature in order to convert ZnO nanoparticles colloidal to nanoparticles thin films, this method was depended on other work [18]. Efficiency of LA process was quantified in terms of the amount of ablated as determined by atomic absorption spectroscopy (AAS) for the prepared samples using AAS spectrometer model GBS 933, where the test was carried in Baghdad university.

Surface morphology and particle size was analysed using atomic force microscope (AFM). The surface morphological studies of the nano ZnO were conducted by tapping mode atomic force microscopy (AFM) from (AA3000). The sample surface was probed with resolution 0.26 NM lateral and 0.1mm vertical. The scan area was 10□m×10□m, and the scan rate was 0.1~100 Hz.

In order to explain the structural properties, the nature and the crystal growth of the dried films at different preparation conditions, The Fourier Transform-Infrared Spectroscopy (FTIR) from (SHIMADZO IRAFFINITY) probes the molecular vibrations of molecules for prepared samples. Light of different energies (or frequencies) represented by wavenumbers in the spectrum above is directed through a sample. When a particular energy (or frequency) of light matches a vibrational frequency of the molecule, the molecule absorbs the light and vibrates. Peaks in an infrared spectrum are upsidedown compared to other forms of spectroscopy to convey that the peak is a decreased intensity, or absorbance of light. The scan of the FTIR measurments are performed over the range between (400 – 4000) cm^{-1} for prepared sample .

3. RESULTS AND DISCUSSION

The amount of the ablated materials as a function of the laser pulse number and laser fluency for two laser wave lengths are studied and discussed as below. The effect number of pulses on the concentration of ZnO NPs at same laser energy (100 mJ) and different fluency (71, 338) J/cm^2 related to different laser wavelength (1.06 um, 0.532um) could be shown in figure (1)

It has been found that by increase the number of laser pulses, the amount of the ablated NPs increase. The focused laser light on to the solid target coused a developing of intensive plasma plume at solid-liquid interface. The surrounding liquid layer intercepts the expansion of plasma. Due to this imprisonment effect, the plasma reaches a non equilibrium state and gain high pressure and temperature. The individual excited species of plasma not only reacts with liquid at solid-liquid interface but also at plasma-liquid interface. The excessive physical status of the plasma results into ionization of embracing liquid molecules advocate non equilibrium bonding of target species with ionized molecules from the liquid. The process take place as an onset of nucleation process to form metal oxide Nanoparticles. So that there is a specific number of laser pulse beyond which the the amount of the ablated material become constant since the increase in the number of laser pulse lead to the formation of dense plasma that itself prevent the laser pulse to reach the target or limited the energy that reach the target surface.

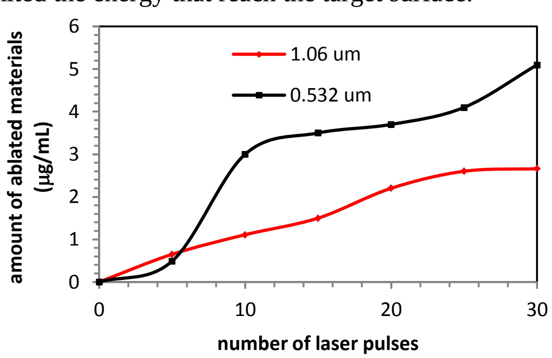
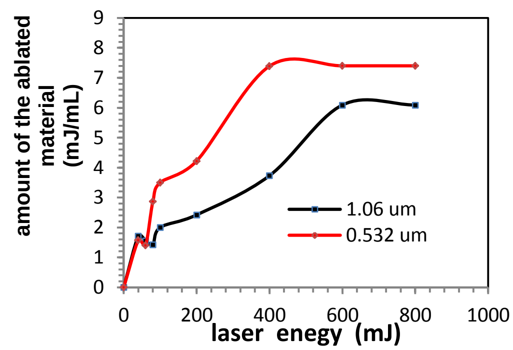


Fig (1) amount of ablated materials as a function of number of pulses for 1.064 µm and 0.532 µm laser pulse wavelengths with constant laser fluency of (71J/cm^2)

So that performance of laser ablation can be justified both by the amount of Zn convey from the Zn target into the liquid medium, and convert to ZnO NPs, amount of ZnO NPs can be varied at given wavelength by factors depend on the value of laser fluency and number of pulses. The effect of laser power on LA at wavelength (1.06 and 0.532 µm) as shown in figure (2).

The result give in the plot indicate that there is a certain value of laser power density required for initiation of the laser ablaition process. As result of all the above there is dirct relation between the attributed size of the nanoparticle and the properties of the laser light. The surface morphology of ZnO Nanoparticles colloidal prepared by LP-PLA at different condition was obtained using Atomic force microscopic images. Multi- drop of the colloidal suspension was drying on glass substrate at 60 C^o.



Fig(2) Amount of ablated materials as a function of laser fluency for 1.064 µm and 0.532 µm laser pulse wavelengths with constant number of pulses (20 pulse)

Figure (3 a,b,c) shows the particle size distribution and the nanoparticles topography of drying colloids prepared at different laser flounce (28,43,71 J/cm^2) the surface morphology and hens particle size distribution could be recognized. It's clearly the obvious increase in the particle size with increasing the laser fluence, this attributed to the effect of laser power on the states of the plasma during the laser ablation process in liquid. This is related to the overall process of the oxide nanostructure formation by LP-PLA mechanism. In general, there are three processes controlled the formation of nanoparticles depend on the state of plasma briefly, are the instantaneous initiation, short lifetime Plasma with rapid annihilation, second one is the nucleation and growth of the particle during annihilating period and after it, and finally oxidation in aqueous environments and rapid cooling of the formed clusters.

Therefore, in this work, the morphology of the prepared nanoparticls is directly related to the effect of laser energy density on plasma condition, intensity, temperature, pressure and its lifetime. At low laser energy density figure (3a), the weak and low temperature plasma resulted in the formation of small ZnO Nanoparticles, which its size begins to increase as the laser fluence increase and thus inversely, at high laser fluence figures (3c), the plasma is intense with longer lifetime and higher temperature, the grain size increase and its shape close to a helical like shape. The plasma at a medium laser energy density, figure (3b) would be moderate between the two cases above which result in moderate grain size and resulted in spherical nanoparticles, this result is in consistence with other work [2,1].

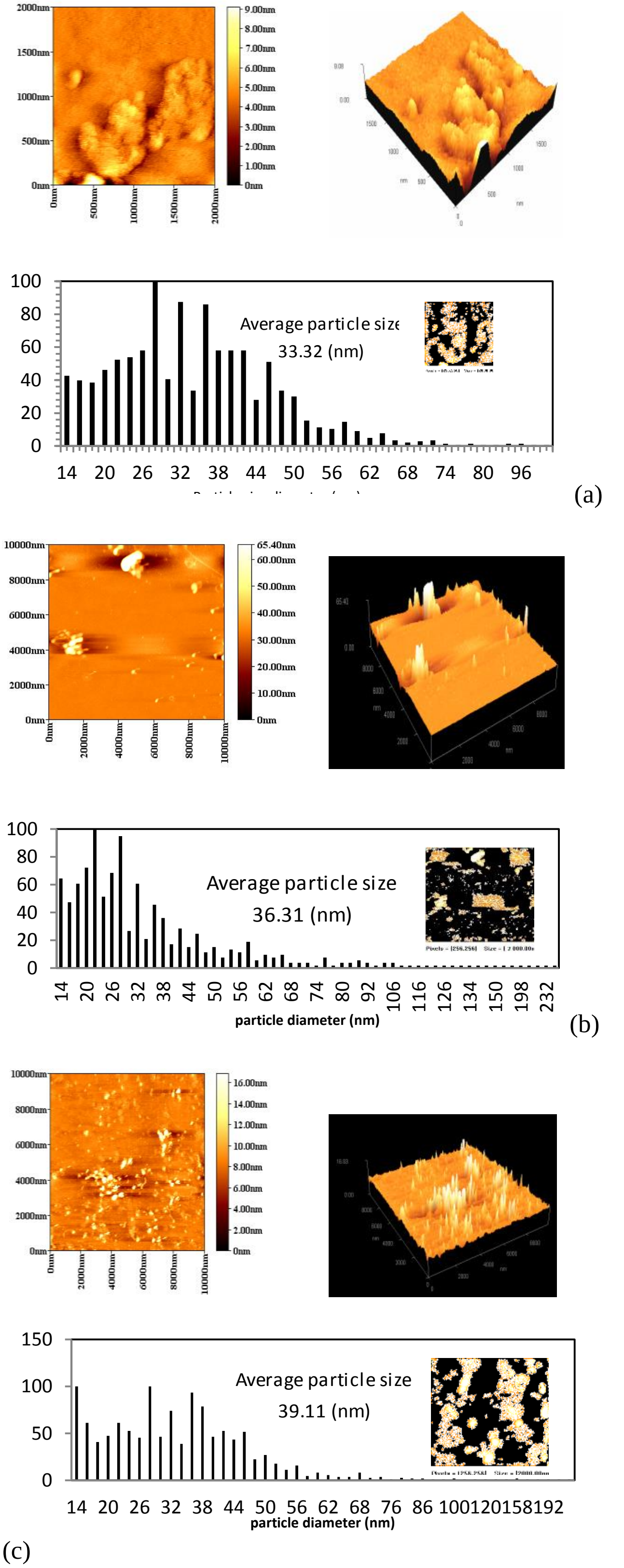


Figure (3) AFM of ZnO NPs prepared at 1.06 μm laser wavelength and different laser flounce (a-28, b-43 and c-71) J/cm^2 and 20 pulses

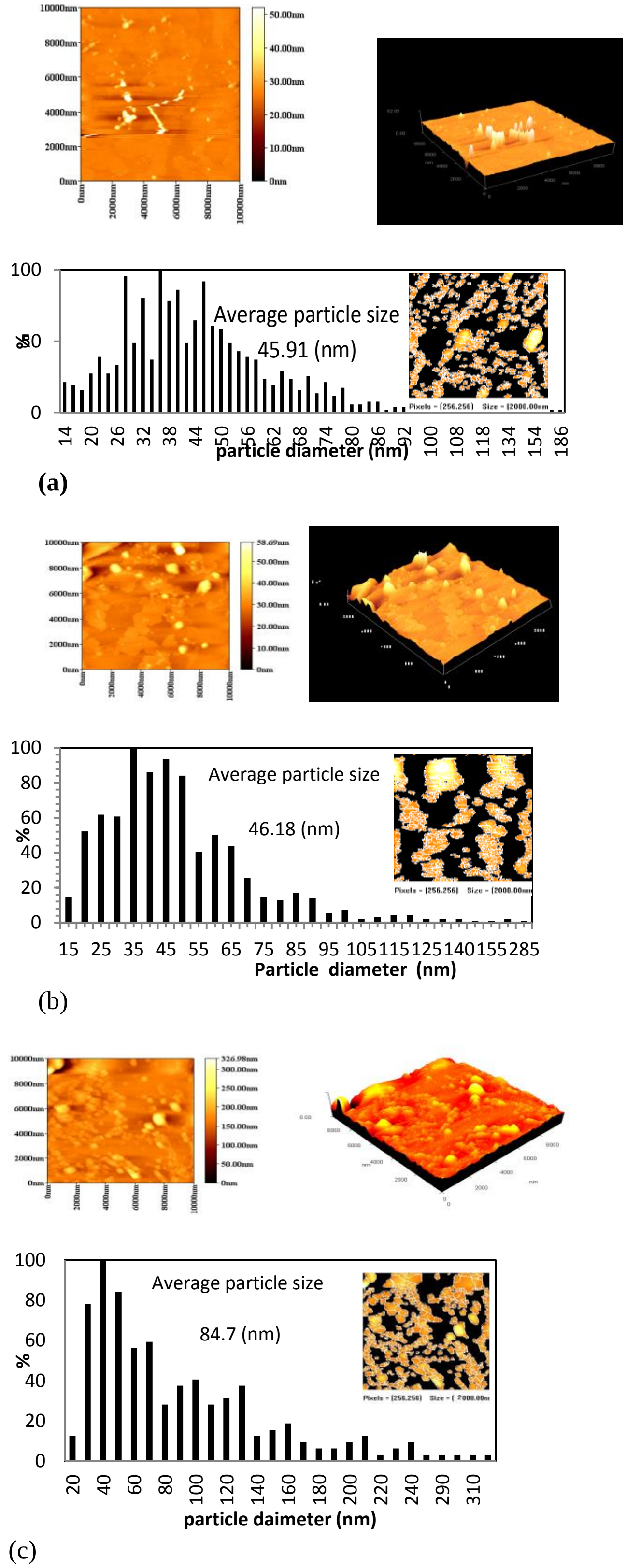


Figure (4) AFM results of ZnO NPs prepared at 1.06 μm laser wavelength and different laser flounce (a-248,b-426, c-567) J/cm^2, and 20pulses

Further increase in laser fluence from (248-567)J/cm^2 figure (4 a,b,c) larger particle size could recognize with a lot of particles with a symmetrical shape resulted from the laser sublimation at high laser fluence and also may be a result of the uneven intensity distribution of the laser spatial profile.

Figure (5) represents the grain size as a function of laser fluence where two curves could recognize the first is the average grain size and the second is the grain size of (90%) of the particles which conclude the result of the figure above and show the increasing of grain size with laser.

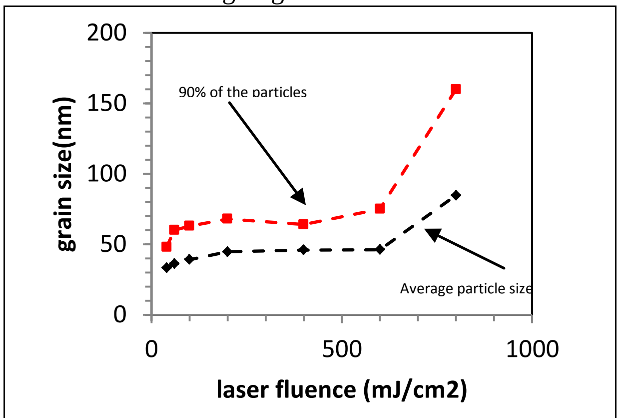


Figure (5) grain size as a function of laser flounce

Larger pulse number lead to a smaller particle size due to the fragmentation effect as shown in the following figure (6) where (60) laser pulse was used to prepare ZnO NPs at (71) J/cm2 laser fluence average particle diameter found to be about (31.75 nm) as shown below.

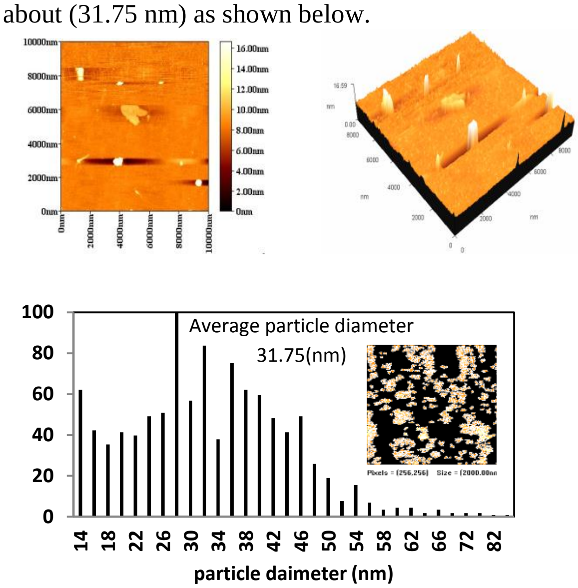


Figure (6) surface morphology of ZnO NPs prepared at 1.06 µm laser wavelength (71) J/cm^2 and (60) laser pulses

The effect of laser wavelength could be shown in figure (7) where the sample prepared using SHG Nd-YAG laser of (532.5) nm wavelength at laser fluence (2030) J/cm2. It's clear that the obtained particle size is much higher comparing with that at the same laser energy (600 mJ) for the first wavelength (1.06) nm , it's value found to be about (98.09nm). The variation in the size distribution of Nanoparticles may be due to the different absorption coefficient of the solvent for the ablation laser light and higher fluency.

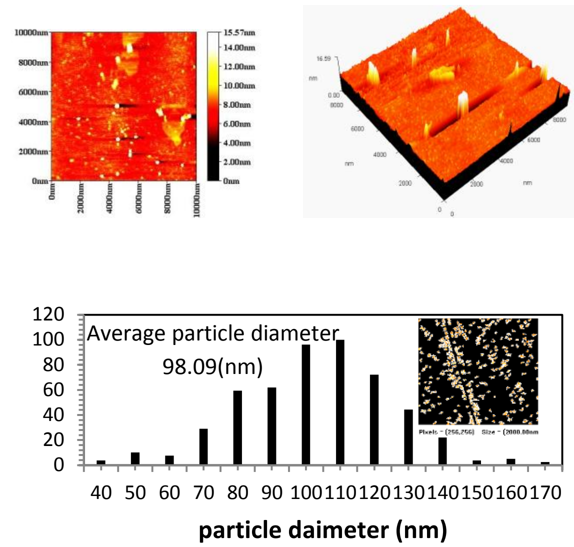


Figure (7) surface morphology of ZnO NPs prepared in 0.532µm laser wavelength (2030) J/cm^2 and (20) laser pulses

Figure (8) shows the surface morphology of direct spraying ZnO nanoparticle colloidal on glass substrate at (60 Co) resulted in highly uniform ZnO Nanoparticles thin film. In this case 1.06□m laser wavelength with (28)J/cm^2 laser fluency was used for the preparation of ZnO colloidal suspension with an average grain size of about (34.06) nm which are very close to the value of the grain size of samples prepared at same laser fluency and its drop drying on glass substrate figure(1). Surface roughnesses of spraying a thin film are about (0.214nm) which reflect a high quality thin film. Such result opens a new gate toward introducing such colloidal in to optoelectronic application, e.g fabrication of thin films solar cell detectors, and others.

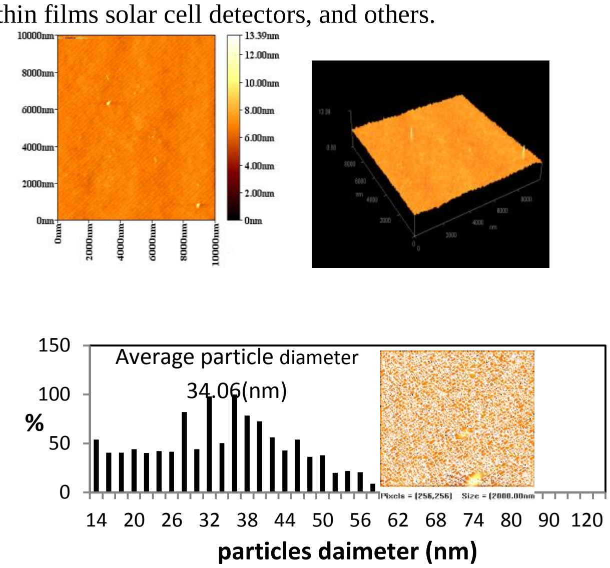
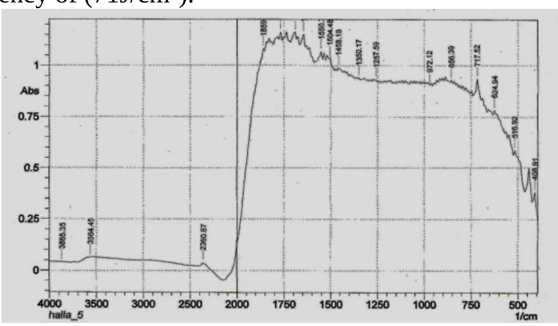


Figure (8) surface morphology of ZnO NPs thin film prepared by direct spraying using 1.06µm laser (28) J/cm^2, and (20) laser pulses

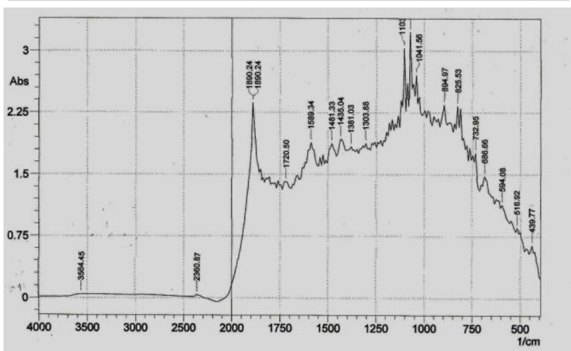
The Fourier Transform Infrared spectroscopy (FTIR) is a technique based on the vibrations of the atoms within a molecule. An infrared (IR) spectrum is obtained by passing IR radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy.

The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule. Moreover, chemical bonds in different environments will absorb varying intensities and at varying frequencies[19].

Figure (9 a,b) gives the FTIR result for ZnO NPs prepared at different number of pulses (30, 50 pulse) with constant laser fluency of (71J/cm^2).



(a)



(b)

Fig(9)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^2 (a) 30 pulses (b)50pulses

In these figures we could recognize the absorption peaks at (439.77, 516.92, 94.08,408.19 and 516.92)cm^{-1} wave number which related to the stretching vibrations mode of the Zn-O band as present in other work [20], 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 (3000, 3564.45, 3865.35 and 1481.33) cm^{-1} are related to the harmonics of H–OH stretching modes, while those at (1435.04, 1458.18) cm^{-1} are related to the C-O vibration modes refers to little contribution of CO_2 dissolution from air contain [21-27].

4. CONCLUSIONS

Efficiency of laser ablation and hence the concentration of ZnO NPs found to be increased with the increase of the number of laser pulses, and laser fluency. In other hand the amount of ablated material associated with 0.532μm laser wavelength greater than that with 1.06 μm at same number of pulse and laser energy.Particles size and surface morphology of ZnO nanoparticle were completely related to the properties of laser light. It could be highly controlled by comprising laser flounce, laser wavelength as well as the number of pulses. Results showed that the particle size increases with increasing the laser fluence, and decreases with number of laser pulses,also the obtained results insure that the grain size of particles prepared with 0.532μm laser wavelength is larger than that those prepared with 1.06 μm laser wavelength. 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.

5. REFERANCE

[1] Gondal, M. A., Drmosh, Q. A., Yamani, Z. H., Saleh, T. A., "Synthesis of ZnO2 nanoparticles by laser ablation in liquid and their annealing transformation into ZnO nanoparticles" *Applied Surface Science*, **256**: 298-304(2009).

[2] Evan T. Salim, Raid A. Ismail, Makram A. Fakhri, Yushamdan Yusof " Reactive PLD of ZnO thin film for optoelectronic application" *Int. J. Nanoelectronics and Materials*, **9**: 111-122 (2016).

[3] Yang, G. W., " Laser ablation in liquids: Applications in the synthesis of nanocrystal"*progress in materials science*, **52**:648-698(2007).

[4] Z. T Salim, U Hashim, MKM Arshad, MA Fakhri, ET Salim " Zinc oxide flakes-corolla lobes like nano combined structure for SAW applications" *Materials Research Bulletin* **86**: 215-219 (2017)

[5] John, N., George, C. and Therese, M. C.," Laser Ablation of Metals: A New Method for Preparing SERS Active Colloids"*Applied Spectroscopy*,**47**(12): 1959-1964(1993)

[6] Makram. A. Fakhri, Y. Al-Douri, Uda. Hashim, Evan. T. Salim "Annealing Temperature Effects on Morphological and Optical Studies of Nano and Micro Photonics Lithium Niobate using for Optical Waveguide Applications " *Australian Journal of Basic and Applied Sciences*, **9**: 128-133 (2015).

[7] Siegel, R.W., Hu, E. and Roco, M.C., "Nanostructure Science and Technology A Worldwide Study" *National Science and Technology Council (NSTC) Committee on Technology* (1999).

[8] Stephan, B. and Giuseppe, C.,"Advanced nanoparticle generation and excitation by lasers in liquids"*Phys. Chem. Chem. Phys.*, **15:**3022-3026 (2013).

[9] Evan T Salim, Marwa S Al Wazny, Makram A Fakhry" Glancing Angle Reactive Pulsed Laser Deposition (GRPLD) FOR Bi_2O_3/Si Hetrostructure" *Modern Physics Letters B*, **27**: 1350122-7- 1350122-1 (2013).

[10] Usui, H., Shimizu, Y., Sasaki, T. and Koshizaki, N.,"Photoluminescence of ZnO nanoparticles prepared by laser ablation in different surfactant solutions"*J Phys Chem B.*, **109**(1):120-4(2005).

[11] Makram A Fakhri, Y Al-Douri, Uda Hashim, Evan T Salim" XRD Analysis and Morphological Studies of

Spin Coated $LiNbO_3$ Nano Photonic Crystal Prepared for Optical Waveguide Application" *Advanced Materials Research*, **1133**: 457-461 (2016).

[12] Takeshi, S., Yoshiki, S. and Naoto, K., "Preparation of metal oxide-based nanomaterials using nanosecond pulsed laser ablation in liquids" *Journal of Photochemistry and Photobiology A: Chemistry*,**182**(3): 335–341(2006).

[13] Makram A. Fakhri, Y. Al-Douri, U. Hashim, Evan T. Salim, Deo Prakash, K. D. Verma" Optical investigation of nanophotonic lithium niobate-based optical waveguide" *Applied Physics B*, **121**: 107–116 (2015)

[14]Evan T. Salem,Ibrahim R. Agool,Marwa Abdul Muhsien " Construction of $SnO_2/SiO_2/Si$ Hetrojunction and its Lineup using I–V and C–V Measurements" *International Journal of Modern Physics B*, **25**: 3863-3869 (2011)

[15] Said, A., Sajti, L., Giorgio, S. and Marine, W.,"Synthesis of nanohybrid materials by femtosecond laser ablation in liquid medium"*IOP Publishing Journal of Physics: Conference Series*,**59**: 259-265 (2007).

[16] Xi, Z., Haibo, Z. and Weiping, C., " Laser power effect on morphology and photoluminescence of ZnO nanostructures by laser ablation in water"*Materials Letters*,**63**: 191 -193(2009).

[17] Abdulhadi Kadhim, Evan T. Salim, Saeed M. Fayadh, Ahmed A. Al-Amiery,Abdul Amir H. Kadhum, and Abu Bakar Mohamad" Effect of Multipath Laser Shock Processing on Microhardness, Surface Roughness, and Wear Resistance of 2024-T3 Al Alloy" *The Scientific World Journal* , Article ID 490951, 6 page (2014)

[18] Ngqondo, S. T.," Hydrothermally grown Pb2+ doped ZnOnanorods for hydrogen and acetylene ga sensing"*Department of Physics*, *University of Zululand Institutional Reprsetory* (2008).

[19] Evan T. Salim" Optoelectronic properties of Fe_2O_3/Si heterojunction prepared by rapid thermal oxidation method" *Indian Journal of Physics*, **87**: 349–353 (2013)

[20] Li, L., Deng, J., Deng, H., Liu, Z. and Xin, L., "Synthesis and characterization of chitosan/ZnO nanoparticle composite Membranes"*Carbohydrate Research*, **345**: 994–998(2010).

[21] Makram A Fakhri, Y Al-Douri, U Hashim, Evan T Salim" Optical investigations of photonics lithium niobate" *Solar Energy*, **120**: 381-388(2015).

[22] Evan T. Salim" Rapid thermal oxidation of silicon nanocrystal based Solar cell" *International Journal of Nanoelectronics and Materials*, **5**: 95-100 (2012)

[23]Marwa Abdul Muhsien,Evan T. Salem, brahim R. Agool, Haidar Hamed Hamdan" Gas sensing of Au/n-SnO2/p-PSi/c-Si heterojunction devices prepared by rapid thermal oxidation" *Applied Nanoscience*, **4**: 719–732 (2014)

[24]Ibrahim R. Agool,Evan T. Salem,Marwa Abdul Muhsien " Optical and Electrical Properties of SnO_2 Thin Film Prepared Using RTO Method" *International Journal of Modern Physics B*, **25**: 1081-1089 (2011)

[26] Evan T. Salem" Surface Morphology and X-RAY Diraction Analysis for Silicon Nanocrystal Based Hetrostructures" *Surface Review and Letters*, **20:** 1350046-1-1350046-6 (2013)

[27] Makram A. Fakhri, U. Hashim, Evan T. Salim, Zaid T. Salim" Preparation and charactrization of photonic $LiNbO_3$ generated from mixing of new raw materials using spry pyrolysis method" *J Mater Sci: Mater Electron* 27:13105–13112 (2016)

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