

PHYSICO-CHEMICAL 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 0.532 μ m), 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 optoelectronic 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 nm 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 recognized 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 \times 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 $^{\circ}$ 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 μ m \times 10 μ 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 measurements are performed over the range between $(400 - 4000) \text{ cm}^{-1}$ 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 length 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 μm , 0.532 μm) 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 caused a developing of intensive plasma plume at solid-liquid interface. The surrounding liquid layer intercept 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.

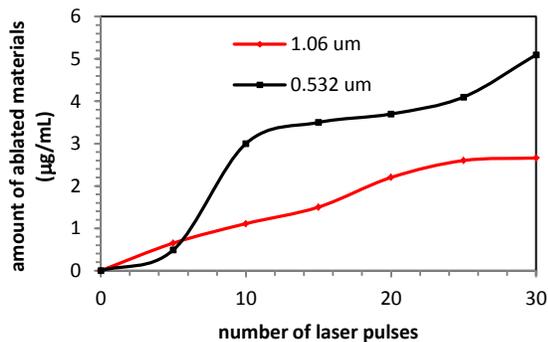
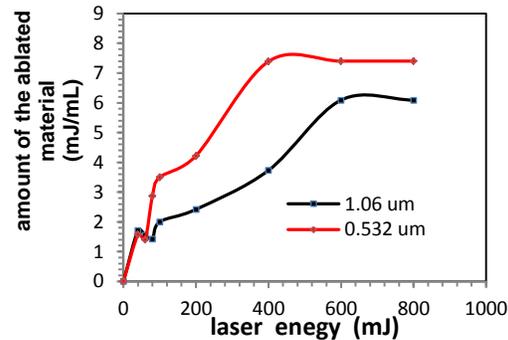


Fig (1) amount of ablated materials as a function of number of pulses for 1.064 μm and 0.532 μm laser pulse wavelengths with constant laser fluency of 71 J/cm^2

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) .

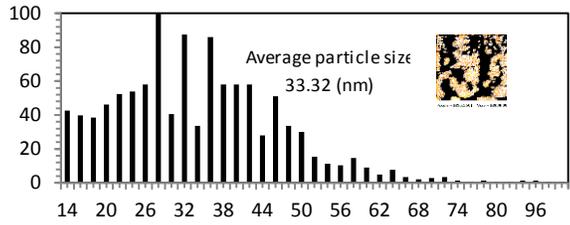
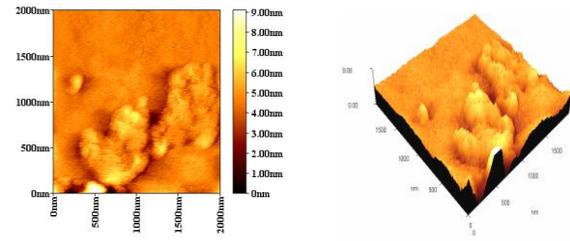
The result give in the plot indicate that there is a certain value of laser power density required for initiation of the laser ablation process. As result of all the above there is direct relation between the attributed size of the nanoparticle and the properties of the laser light. The surface morphology 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° .



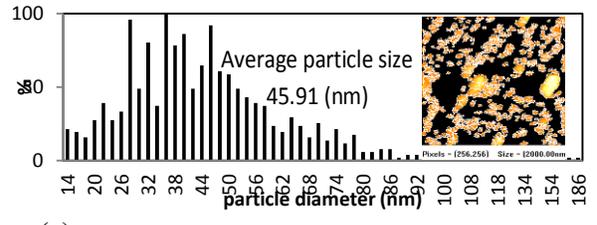
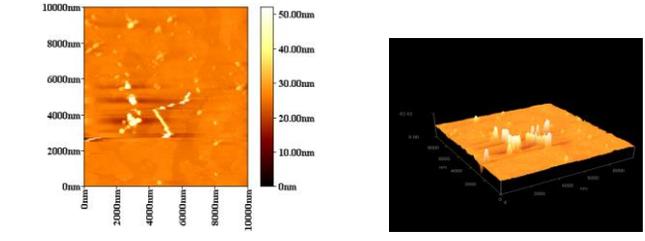
Fig(2) Amount of ablated materials as a function of laser fluency for 1.064 μm and 0.532 μm laser pulse wavelengths with constant number of pulses (20 pulse)

Figure (3 a,b,c) shows the particle size distribution and the nanoparticles topography of drying colloids prepared at different laser fluence (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.

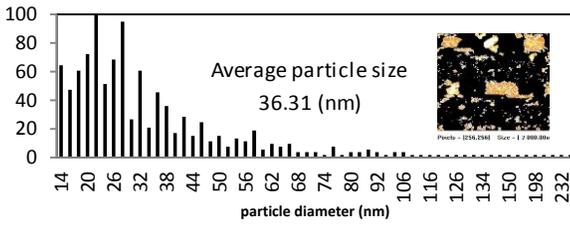
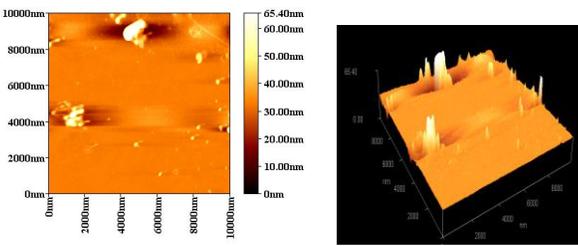
Therefore, in this work, the morphology of the prepared nanoparticles is directly related to the effect of laser energy density on plasma condition, intensity, temperature, pressure and its lifetime. At low laser energy density figure (3a), the weak and low temperature plasma resulted in the formation 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].



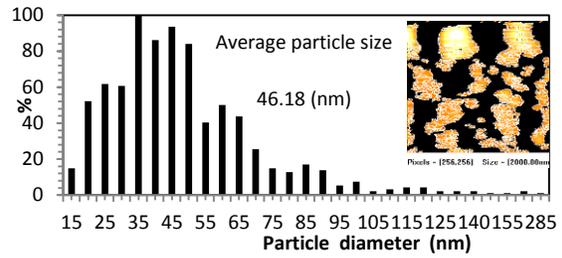
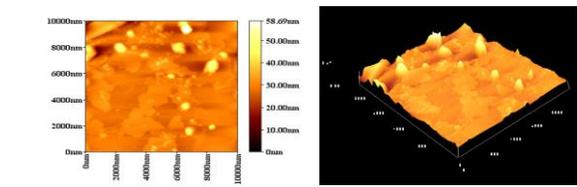
(a)



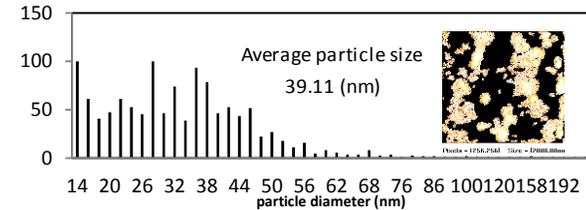
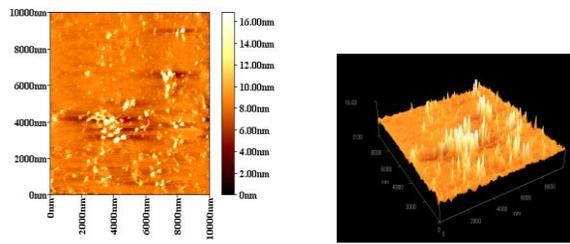
(a)



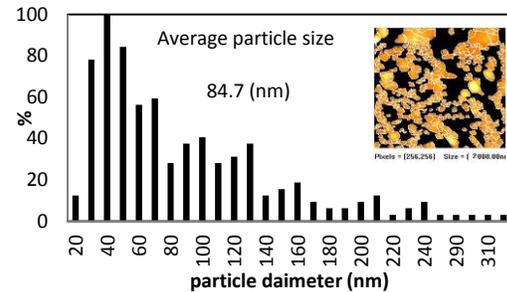
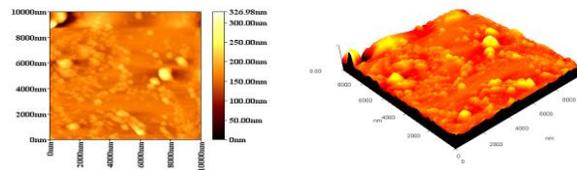
(b)



(b)



(c)



(c)

Figure (3) AFM of ZnO NPs prepared at 1.06 μm laser wavelength and different laser flocnce (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 flocnce (a-248,b-426, c-567) J/cm^2 , and 20 pulses

Further increase in laser fluence from (248-567) J/cm² 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.

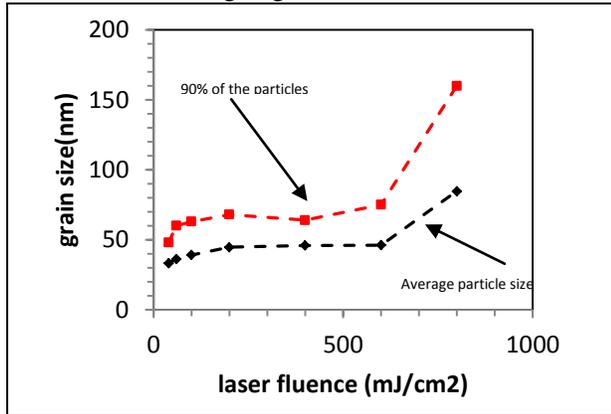


Figure (5) grain size as a function of laser fluence

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.

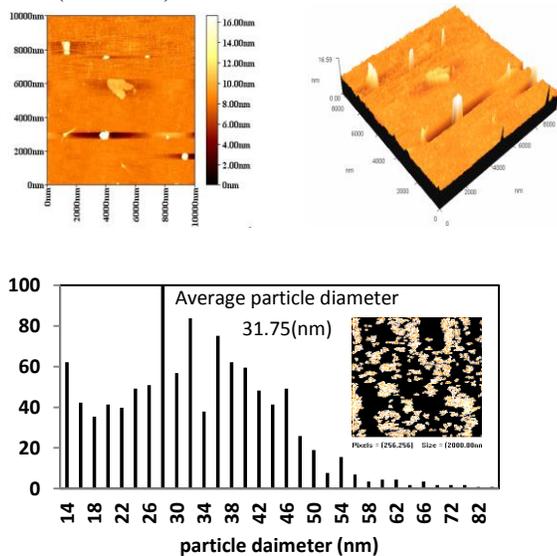


Figure (6) surface morphology of ZnO NPs prepared at 1.06 μm laser wavelength (71) J/cm² and (60) laser pulses

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.

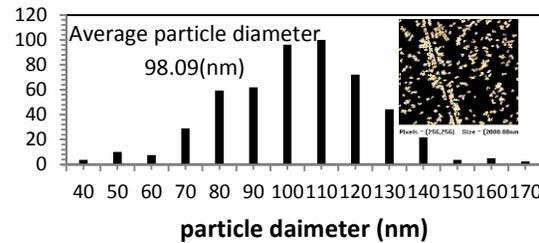
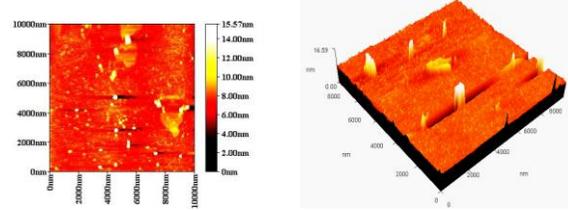


Figure (7) surface morphology of ZnO NPs prepared in 0.532μm laser wavelength (2030) J/cm² and (20) laser pulses

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 μm laser wavelength with (28) J/cm² 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 roughness of spraying a thin film are about (0.214nm) which reflect a high quality thin film. Such result open a new gate toward introducing such colloidal in to optoelectronic application, e.g fabrication of thin films solar cell detectors, and others.

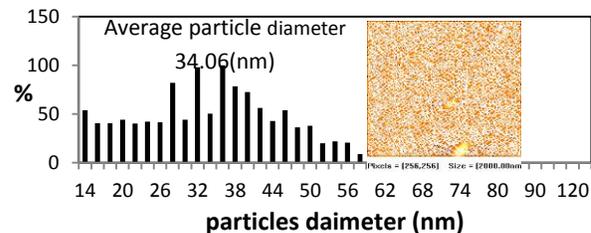
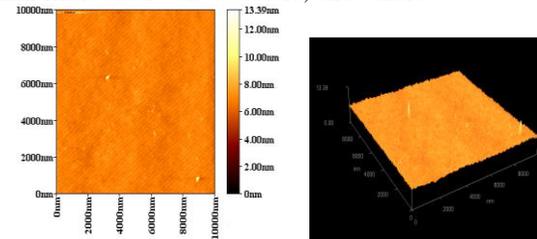
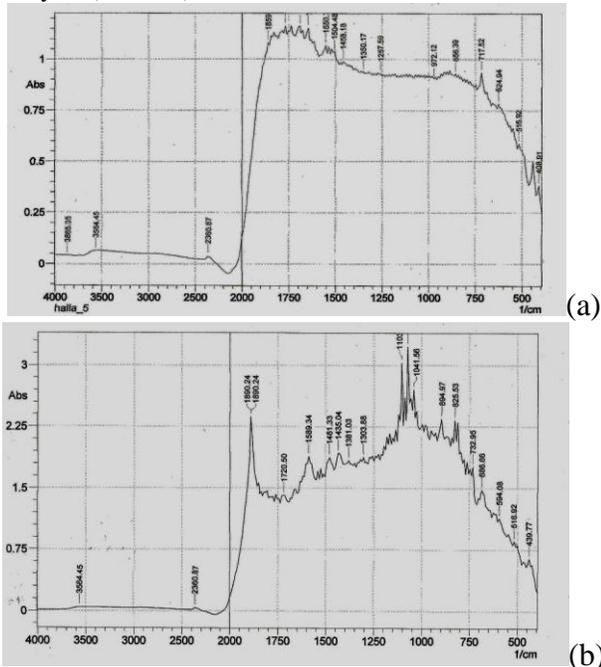


Figure (8) surface morphology of ZnO NPs thin film prepared by direct spraying using 1.06μm laser (28) J/cm², and (20) laser pulses

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 ($71\text{J}/\text{cm}^2$).



Fig(9) Fourier transform infrared spectrum of ZnO nanoparticles in DIW as a thin film on the glass substrate prepared with constant laser fluency ($71\text{ J}/\text{cm}^2$) (a) 30 pulses (b) 50 pulses

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 ($1435.04, 1458.18\text{ cm}^{-1}$) are related to the C-O vibration modes refers to little contribution of CO_2 dissolution from air contain.

4. CONCLUSIONS

Efficiency of laser ablation and hence the concentration of ZnO NPs 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 $0.532\mu\text{m}$ laser wavelength greater than that with $1.06\mu\text{m}$ 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 frounce, 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 $0.532\mu\text{m}$ laser wavelength is larger than that those prepared with $1.06\mu\text{m}$ 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.

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