Influence of Laser wavelength on morphological and optical properties of ZnO nanoparticles prepared by laser ablation in water

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Abstract: Nanoparticles (NPs) of Zinc oxide (ZnO) were prepared utilizing pulsed laser ablation of a Zinc metal plate in deionized water without utilizing surfactant. The effect of Laser wavelength on the characterization of ZnO was investigated. The 1064-nm and 532-nm wavelength beams produced from a Q-switched Nd: YAG laser at 10 ns pulse duration were employed. The SEM images displayed that the average diameter of the Zinc oxide NPs generated by the laser wavelength 532-nm are larger than the 1064-nm laser wavelength nanoparticles. Various sizes were observed of round ZnO nanoparticles in the SEM image. As the laser wavelength increased, the density of the nanoparticles in water increased. UV–vis analyses revealed that the absorption peak located at 342 nm (1064nm) and 344 nm (532nm). The nanoparticles formed at 1064 nm exhibited higher absorbance than the nanoparticles formed at 532 nm. The optical band gap is considered to be 3.42 eV for 1064 nm and 3.4 eV for 532 nm.

Keywords: ZnO nanoparticles, Laser ablation, deionized water, Williamsone- Hall method, SEM, absorption peak.

1. Introduction

Study and preparation of semiconductor nanoparticles (NPs) with unique optical, electrical and magnetic properties and their specific applications is particularly important. NPs properties change due to the decreasing size dimension to atomic level [1]. Among this, ZnO nanoparticle is regarded as one of the most novel and promising materials, due to considerable exciton binding energy (60 meV) at ambient temperature, direct bandgap (3.37 eV), low toxicity and high surface energy [2–5]. ZnO NPs have abundant applications in catalysts, arrays sensor and photonics devices [6, 7]. However, practical applications of Zinc Oxide are decided by its properties which can be modified by varying its morphology [8]. Therefore, researchers tried to utilize several methods such as RF-magnetron sputtering [9], physical vapor deposition [10], sol-gel [11], hydrothermal [12], electrodeposition [13], precipitation [6], chemical vapor deposition (CVD) [14] and pulsed laser ablation (PLA) to prepare ZnO nanostructures, including nanoparticles, nanobelts, nanorods, nanotubes, nanowires and other complex morphologies [15, 16]. In recent years the PLA technique of solid target in liquid media has been shown to provide an effective method for preparing different materials at nanoscale [9]. The features of the PLA Method are (1) Well crystallized nanoparticles can be prepare via PLA technique, which are pure without by-products, (2) inexpensive devices for governing the ablation, (3) the size of prepared material can be governed by changing varies factors such as laser fluence, pulse laser duration, laser wavelength, varying the temperature or pH of the solution and adding surfactants. [17-20]. Xi Zhang et al. [21] investigated the effect of Laser power on properties of ZnO nanostructures photoluminescence and
morphology, they found that with the raise of laser power the morphology of the products varied from nanoflakes to nanoparticles then to short nanorods. Correspondingly, the relative intensity of green emission increased and that of violet emission decreased. M. Moradi et al. [19] prepared ZnO nanoparticles in four aqueous environment by laser ablation method involve SDS (0.1 molar), acetone, CTAB (0.01 molar), and distilled water. NP prepared in SDS and CTAB is higher in degree of crystallinity than the two other samples. SEM image points to that the morphology of ZnO nanoparticles in SDS, water and acetone was spherical while in CTAB was spindle-like. S. Abdi et al. [7] studied the influence of CTAB molarity on optical properties and size of ZnO NPs which were produced via PLA method. Their results confirm that higher CTAB molarity promoted the degree of crystallinity in nanoparticle. Increasing molarity of CTAB leaded to increase the size of produced nanoparticles and thus caused reduction of the samples' absorption. This work is dedicated to the preparation of nanoparticles (NPs) of zinc oxide (ZnO) from a zinc solid plate immersed in an de-ionized water using the laser Q-switched Nd:YAG working at 1064 nm and 532nm wavelengths. The research objective is to study the influence of laser wavelength on the formed nanoparticles properties optical and morphological.

2. Synthesized of Zinc oxide (ZnO) nanoparticles

In deionized water, zinc oxide was prepared by the method of pulsed laser ablation of the zinc plate (99.9 %). The plates were cut to pieces with dimensions of (10×10) mm. The Zn plate was cleaned ultrasonically in ethanol and deionized water before the experiment. On the bottom of immaculate glass vessel full of with 5 ml of deionized water, the target was kept. Laser ablation was carried out with a Q-switched Nd: YAG laser kind (HUAFEI). ZnO nanoparticles were prepared utilizing the 1064nm and 532nm (frequency doubled) wavelength at energy 0.70 J, width of the pulse is 10 ns, the diameter of the effective beam of 5 mm and the rate of repetition is 1 Hz, to achieve high laser fluence a convex lens was used with (100 mm) focal length.

2.1 Reaction mechanism

According to the previous researches [7, 19, 20], the generation of ZnO nanostructure prepared by liquid-phase laser ablation occurs in three steps, 1. Zinc plasma is produced with high pressure and high temperature on the liquid-solid interface, directly after laser beam is ablated onto the surface of the zinc, 2. Zinc clusters are formed after the refrigeration of the region of zinc plume.

\[
\text{Zn} \xrightarrow{\text{target}} \text{Zn}^+_{(\text{plasma})} + 2e^- \quad (1)
\]

\[
\text{Zn}^+_{(\text{plasma})} + 2e^- \xrightarrow{} \text{Zn}^{(\text{clusters})} \quad (2)
\]

3. Chemical reactions results from Zinc cluster interaction with surrounding water molecules. The very strong oxidation reactions for zinc clusters occur due to the rise in temperature, leading to the formation of the initial oxidation product zinc hydroxide, Zn (OH)₂.

\[
\text{Zn}^{(\text{clusters})} + 2\text{H}_2\text{O} \xrightarrow{} \text{Zn(OH)}_2 + \text{H}_2 \quad (3)
\]

Due to thermal effects Zn (OH)₂ will decompose to produce ZnO.

\[
\text{Zn(OH)}_2 \xrightarrow{} \text{ZnO} + \text{H}_2\text{O} \quad (4)
\]
2.2 Characterization

For the characterization of the samples, assortment of analytical techniques was utilized. The crystal structural of ZnO NPs was investigated by X-ray diffraction with Cu Ka radiation source (\(\lambda=0.15406\) nm), utilizing XRD device type (Bruker Axs) made in Germany model (D8 Advanced). The samples morphology was examined with (SEM) scanning electron microscopy type INCA Penta FET, made in England, model 17426. The optical properties of the nanoparticle solution were measured by UV–vis double beam spectrophotometer, (Lambda 750, Perkin Elmer).

![Figure 1: Schematic diagram of used apparatus.](image)

3. Results and discussion

The spectrum of the XRD reveals the crystalline structure of the different peaks of the nanoparticles of ZnO and Zn. The x-ray diffraction spectrum of the nanoparticles of ZnO formed by 1064 nm wavelength laser beam in deionized water displays that they were crystalline with hexagonal wurtzite structure as shown in Fig.2. The \(2\theta\) peaks were at 30.6989, 34.6883, 36.4073, 47.4683, 56.5363, 62.7395 and 72.5549 which corresponding to the crystal planes (100) (002) (101) (102) (110) (103) and (004), the results matched the standard XRD JCPDS data: 036-1451. The peak of (101) located at \(2\theta =43.2^o\) was the characteristic of Zn phase. The sample contain Zn NPs in addition to the ZnO which may be because the incomplete oxidation of the few large Zinc particle prepared in step2, resulting in formation core/shell structured of Zn/ZnO NPs. XRD results are consistent with previous reports on ZnO NPs synthesized by PLA method [19, 22]. No peak observed in the spectrum of the sample formed with the 532 nm laser pulse wavelength as shown in Fig. 2. Small amount of NPs in crystalline structure may be the reason, this result is in agreement with that of previous studies [17]. The crystallite size (D) was computed by utilizing the Scherrer equation using the (FWHM) full width at half maximum of the (001) diffraction peak of ZnO.

\[
D = \frac{k\lambda}{\beta\cos\theta}
\] (5)
K is constant ($0.89 < k > 1$), $\lambda = 1.5406$ Å, $\theta$ is diffraction angle and $\beta =$ full width at half maximum of the diffraction peak [23-25].

There are two hexagonal unit cell lattice constants, referred to as 'a' and 'c', which can be estimated from the XRD sample spectrum by the upcoming equation [23].

$$\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + k^2 + hk}{a^2} \right) + \frac{l^2}{c^2}$$

(6)

Where, k, h, and l, represents the Miller indices. Table 1 presents the lattice constant of the unit cell of the sample.

**Table 1:** The structure parameters of ZnO NPs

| Wavelength laser beam (nm) | Crystal structure | Lattice constants (Å) | Volume of unit cell ($\text{Å}^3$) |
|---------------------------|-------------------|-----------------------|----------------------------------|
|                           |                   | a=b                  | C                                | c/a   |                             |
|                           |                   |                      |                                  |       |
| 1064                      | Hexagonal         | 3.2568               | 5.170                            | 1.5874| 47.49                        |
| Standard                  | JCPDS card no. 036 - 1451 | 3.24982               | 5.20661                          | 1.602 | 47.62                        |

Williamsone- Hall method was used for evaluate lattice microstrain and also crystallite size by using X-ray peak profile analysis of nanoparticles of ZnO. In all crystallographic directions, the strain was called uniform, thus confirming the isotropic existence of the crystal, where all the properties of the materials are independent of the direction in which they were investigated. As displayed in Fig.3, the plot was drawn between $4\sin \theta$ and $\beta \cos \theta$. The strain and the crystallite size evaluated from the slope and the intercept of the fitted line sequentially as shown in Table (2). It can be observed that the values of crystallite size from W-H plot were larger than that calculated using Scherrers relation. The two varies methods presume that size and strain broadening were additive components of the total integral breadth of a Bragg peak. The plot displayed a negative
strain for the ZnO-NPs. From the estimation of lattice parameters it was noticed that this strain may be due to the shrinkage of the lattice [26, 27].

![Graph showing β cos θ vs 4 sin θ with a linear fit equation y = -0.0007x + 0.0018]

**Figure 3:** The W–H analysis of Zinc Oxide nanoparticles.

**Table 2:** Crystallite size and lattice microstrain values of ZnO NPs.

| wavelength laser beam (nm) | Gs (nm) | Gs (nm) | Microstrain (Ɛ) |
|---------------------------|---------|---------|----------------|
|                           | Scherer method | W-H method |               |
| 1064                      | 72       | 80.38   | -0.0007        |

Fig. 4 displays the SEM images of ZnO NPs in deionized water synthesized by laser ablation. The density of NPs in water increased as the laser pulse wavelength increased. The particles of both samples were spherical and having granular nature [4]. The agglomeration of particles was observed in the higher resolution SEM images. The average diameter of the NPs prepared by 1064 nm wavelength laser beam was about 26 nm and the average diameter of the NPs prepared by 532 nm wavelength laser beams was about 43 nm. Various sizes were observed round ZnO nanoparticles in the SEM images. E. Y. Salih et al. [28] reported the formation of mesoporous ZnO/ZnAl₂O₄ mixed metal oxide by utilizing co-precipitation and thermal reduction technique. The FE- scanning electron micrograph reveals that after thermal treatment of 300 and 400 °C the samples showed sheet-like morphology while when the researches utilizing doctor blade technique and thermal oxidation treatment, an ordered mesoporous film created and some nanoparticles merged and synthesized a continuous film [29].
ZnO nanoparticles were generated at the two wavelengths mentioned above by the nanosecond laser. It can be noticed from Fig. 5a, the spectra of the optical absorption of the two samples were similar. The nanoparticles formed at 1064 nm exhibited higher absorbance than the NPs prepared with 532 nm laser wavelength. According to Beer–Lambert equation [30]:

\[ A = \varepsilon cl \]  

(7)

A represents the absorbance, \( \varepsilon \) represents molar extinction coefficient, c represents concentration, and l represent path length. Since A is directly proportional to c, where \( \varepsilon \) and l are constant, higher nanoparticles concentration is obtained from solution produced by laser wavelength of 1064 nm. The absorption peak located at 342 nm and 344 nm for the wavelength 1064 nm and 532 nm, respectively. A blue shift in the spectrum of the absorption was due to the decreasing in the average diameters of nanoparticles in the products. In this method the measurements of the absorption supply a qualitative allusion of the crystal size distribution [19].

**Figure 4**: SEM images (high and low magnification) of ZnO nanoparticles formed with different wavelength (a-c) 532nm, (d-f) 1064nm.

**Figure 5**: a) Absorbance vs. wavelength plot of ZnO NPs for various wavelength. b) Plot of \((\alpha h\nu)^2\) vs. \(h\nu\) of the two samples.
The directly allowed optical band gap, was calculated by based on the upcoming expression [23]:

\[ a\nu = \text{constant} \left( \nu - E_g \right)^{1/2} \]

Where \( a \) represents the absorption coefficient, photon energy represents by \( \nu \) and \( E_g \) is the band gap. Figure 5b reveals the plot of \( (a\nu)^2 \) vs. \( (\nu) \) and it was utilized for compute \( E_g \). The optical band gap was computed to be 3.42 eV for 1064nm and 3.4 eV for 532 nm, which had almost conformity with the reported experimental magnitudes [3]. \( E_g \) of nanoparticles depends on their size and decreases as their sizes increases. Number of atoms in NPs decreases with reducing the size of nanoparticles, resulting to generation of defect levels of smaller number so, the energy gap rises with reducing the size of nanoparticles [31].

**Conclusion**

This study displayed that zinc oxide nanoparticles were successfully produced using Q-switched Nd: YAG laser ablation of a Zinc plate (99.9 %) in deionized water. In conclusion, the diameter and the density of ZnO nanoparticles were clearly dependent on the laser wavelength as revealed by SEM images. We found that the average diameter of the NPs formed by 532 nm wavelength laser beams was about 43 nm while that the average diameter of the NPs formed by 1064 nm wavelength laser beams was about 26 nm. As the laser wavelength increased, the density of the nanoparticles in water increased. The absorption peak located at 342 nm and 344 nm for the wavelength 1064 nm and 532 nm, sequentially. The energy band gap of the two samples was computed to be 3.42 eV (1064nm) and 3.4 eV (532nm).

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