Ablation of ZnO in liquid by Nanosecond Laser

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Abstract. Zinc oxide (ZnO) was synthesized by laser ablation in liquid. The preparation steps included immersing ZnO bulk pellet in ethanol and then ablating by Nd-Yag laser. The used laser has a wavelength ranging from 1064 nm to 532 nm with 140 mJ pulse intensity. Structural, morphological and optical properties of the prepared material were investigated by X-ray diffraction, scanning electron microscopy and UV-Vis spectroscopy, respectively. The XRD results revealed the formation of hexagonal ZnO structure with (101) as dominant peak. The SEM studies demonstrated the formation of spherical ZnO nanoparticles which agglomerated to form nanocluster. Typical exciton absorption was observed at 376 nm in the absorption spectrum of UV-Vis spectroscopy at room temperature and the energy gap was equal to (3.48 eV).

1. Introduction

Recently, nanotechnology has involved many potential investigations due to their unique chemical, physical, electrical and mechanical properties [1]. Thus nanomaterials revealed improvements in many fields, such as medicine [2], chemical sensors [3], gas sensing [4], solar cells [5], water treatment [6, 7], light emitting diodes [8] and other applications. In recent years, domestic wastewater, industrial waste, dyes and other sources have been major sources of water pollution [9]. The pollution can be treated using complex and traditional methods including thrombosis, adsorption on activated carbon, carbon nanotubes [10], chemical deposition and separation. Recently, metal oxide nanomaterials such as WO2, Fe2O3, ZnS, TiO2, ZnO have been used as photocatalysts in water treatment due to high efficiency, low cost, high stability and non-toxicity [11, 14].

There are many techniques to synthesis nanomaterials such as sol-gel [15], hydrothermal [16, 17], physical and chemical vapor deposition [18] microwave method [19, 20] and other techniques. These techniques can be classified according to their working principle into two different approaches, top-down and bottom-up [21]. The bottom-up approach is to gather materials atom by atom or molecule by molecule. The top-down approach is to cut material into small pieces to obtain nanoparticles. For example, laser ablation is a typical top-down technique for preparation nanoparticles [22]. Laser ablation (LA) technology is a simple and effective technique for producing nanomaterials. This technique also works when the laser beam is focusing on the target that immersed in liquid which is called laser ablation in liquid (LAL) to produce nanoparticles [23]. The importance of this technique increased due to the absence of secondary products as well as it considered as simple, economy and environmentally friend method [24].

Metals and semiconductors nanoparticles have strong size-dependent properties [25]. Thus, at the moment, preparation these materials in liquid medium are carefully considered for their prospective
development in many fields. ZnO is a highly used substance because it has a large energy gap (3.37 eV) and high exciton binding energy (60 meV). Other properties of ZnO nanoparticles such as non-toxic, high sensitivity to various gases, easy to manufacture and inexpensive made it widely used materials [26]. Thus, in this work the control of particle size is the key factor in the synthesis of ZnO colloids, which were prepared by nanosecond laser ablation. The purpose of preparation ZnO nanoparticles is to use as a photocatalyst material for water treatment.

2. Experimental

ZnO bulk powder of purity (99%) was purchased from Fluka chemicals. Using hydraulic system, 3 grams of ZnO powder was pressed into pellet form with dimensions of (2.5 cm diameter and 0.2 cm thickness). In order to remove the inner stresses and to make the material more durable and homogeneous, the pellets were annealed at temperature of (400 °C). The used laser source is Nd-YAG with 1064-532 nm wave length, power of (160-1000 mJ) and frequency of (1-6 Hz). A (30 cm) lens was used to focus the laser beam on the sample. The prepared pellet was located in the bottom of a 100 mL baker contained 4 mL ethanol. The ZnO pellet was removed from the reactor after (200) laser pulses. The color of the prepared liquid was changed to gray due to the ZnO nanofluid formation. The preparation setup is shown in Figure (1).

The structural properties of as prepared sample were examined using X-ray diffractometer (XRD). The used instrument was (6000 Shimadzu - Japan) X-ray diffractometer of Cu-Kα radiation with wavelength of (λ= 1.5406 Å). The system voltage, current and scan speed is 40.0 kV, 30.0 mA, and 8.0000 (deg/min) respectively. The morphology of the sample was monitored by scanning electron microscopy (SEM) model (Inspect S50). The optical properties were measured using UV/Vis spectroscopy model (CECIL 7200 - Korea) with wavelength range from (190-1100 nm).

Calculation the energy gap experimentally using UV/Vis spectrum can be done according to the equation below [27]:

$$E_g = \frac{hc}{\lambda_c} = \frac{1240}{\lambda_c}$$  \hspace{1cm} (1)

where $E_g$ represented the energy gap of the sample, $h$ is the planck's constant = 6.626070040×10^{-34}, $c$ is the light speed in vacuum = 3×10^{8} m/s and $\lambda_c$ = cutoff wavelength of the photon which can be determined from the UV/Vis spectrum.

The energy gap of nanosize semiconductor can be also calculated using Kubelka-Munk function and Tauc plots .

$$(ahv)^{1/n}=k(hv-Eg)$$  \hspace{1cm} (2)

where $h$ is Planck's constant, $v$ the frequency of vibration, $a$ represents the absorption coefficient, $E_g$ is the band gap and $k$ is the proportional constant. The value of the exponent $n$ denotes the nature of the sample transition and it is $n = \frac{1}{2}$ for direct allowed transition.

The crystallite size of the studied material could be estimated from the full width at half maximum (FWHM) of the most intense diffraction line by Debye Scherrer's formula as follows.

$$D_S = \frac{k\lambda}{\beta \cos \theta}$$ \hspace{1cm} (3)

where, $D_S$ is crystallite size, $k=0.94$ is the shape factor and $\beta$ is (FWHM) in radians. The X-ray diffraction data can also be used to determine the dimension of the unit cell [28].
3. Result and Discussion

3.1. Structure characterization by XRD

Primarily, to identify the prepared material, the as prepared sample was examined by XRD as shown in Figure (2). The qualitative investigation was performed by comparing the diffraction peaks of as prepared sample with the ICDD PDF database. This analysis indicated that the sample can be indexed to the wurtzite phase of ZnO (hexagonal, $P6_3mc$) with lattice constants of $a = 0.325 \text{ nm}$ and $c = 0.520 \text{ nm}$, which match well with the standard XRD data file of ZnO (JCPDS 00-36-1451).

In addition, the strong relative intensity of the (101) line reveals a preferred orientation. Subsequently, the search was extended to another two peaks that not matching with the ZnO. The result revealed that the unidentified peaks were matched by a mineral Zn (Card-00-004-0831). This result indicates that during the ablation process ZnO was redox into Zn. The reduction of oxygen concentration is due to the reaction of atomic oxygen with ethanol which become much faster in the presences of ultrafast laser pulse [29]. The appearance of Zn peaks in the XRD patterns is attributed to the fact that the post annealing process was not used in this study. Further study will be conducted on effects of annealing on the structure in our next manuscript. Table (1) shows angles, Miller coefficients, the inter planer spacing ($d$) and full width at half maximum (FWHM). The experimental values of ($d$) are matching well with that of standards with error of 1% as listed in Table (1). It is obvious that $d$ decreased with increasing the diffraction angle which followed the Bragg law ($n\lambda=2dsin\theta$). From the figure it is clear that the prevailing peak is (101) at angle equals to $36^\circ$ with FWHM = 0.1730. This indicates that the crystal size of the sample is very small which was calculated by equation (3). The average crystal size is equal to 50 nm. These results were compared with previous studies of ZnO prepared using laser ablation where Zn were also found [30].
Figure 2. The XRD spectrum of ZnO prepared by LAL ethanol

Table 1. Experimental and standards value of d- spacing of as-prepared sample using LAL method.

| 2θ (deg) | hkl  | I/I₀ | FWHM (deg) | d (Å) Experimental | d (Å) standards | Rate error | Crystal size (nm) |
|----------|------|------|------------|--------------------|-----------------|------------|-------------------|
| 31.5996  | 100  | 85   | 0.1698     | 2.8291             | 2.814           | 0.0151     | 50.82             |
| 34.2711  | 002  | 40   | 0.1691     | 2.6144             | 2.603           | 0.0114     | 51.39             |
| 36.0914  | 101  | 100  | 0.1730     | 2.4866             | 2.475           | 0.0116     | 50.48             |
| 47.3990  | 102  | 17   | 0.1490     | 1.9164             | 1.911           | 0.0053     | 60.86             |
| 56.4449  | 110  | 31   | 0.1853     | 1.6289             | 1.6247          | 0.0042     | 50.86             |
| 62.8624  | 103  | 18   | 0.1600     | 1.4805             | 1.4771          | 0.0034     | 60.82             |

3.2 SEM studies

SEM is one of the instruments that used to monitor the surface morphology as shown in Figure (3). The sample was monitored under different high magnification namely (1000 and 10000X). The micrographs demonstrated the formation of spherical ZnO nanoparticles which agglomerated to form nanocluster. The dimensions of nanoparticles range from 219.7 nm to 330 nm.
3.3. Optical properties by UV-Vis spectroscopy

In this study, UV-Vis spectroscopy was used to determine the optical properties of the sample. The spectrum in Figure (4) revealed that the highest absorption of as prepared sample was at 199 nm due to the natural absorption of ZnO. The absorption reduced as the wavelength increased. Typical exciton absorption at 376 nm was observed in the absorption spectrum at room temperature, which is considered blue shifted compared to the bulk ZnO. The blue shift in UV spectrum is caused by the reduction in size of the nanoparticle. The appearance of this strong peak in the absorption edge is due to the quantum size effect. The energy gap was experimentally calculated from equation (1), which is equal to 3.3 eV. These results were compared with previous ones of ZnO which were equivalent to 3.3 eV for average value of crystallite size of (40-60 nm) [31].
Figure 4. The absorption spectrum of the as prepared sample in ethanol by LAL.

Figure (5) shows the energy gap of ZnO which is equal to (3.48 eV). These results are consistent with the results of the previous studies (3.49 eV) [32].

Figure 5. The energy gap spectrum of the as prepared sample in ethanol by LAL.
4. Conclusion

ZnO nanoparticles were prepared by laser ablation in liquid (ethanol). The used laser energy was 140 mJ with 300 pulses. The XRD spectrum revealed that ZnO was successfully prepared using LAL method. The SEM images showed the growth of spherical nanoparticles. The appearance of ZnO absorption peaks in the ultraviolet portion of light spectrum (376.7 nm) with energy gap to equal (3.48eV) which make it good candidate for photocatalyst applications

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