Synthesis of ZnO Nanocrystals with Hexagonal (Wurtzite) Structure in Water Using Microwave Irradiation

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Abstract

Nanocrystals of ZnO were prepared by microwave irradiation using Zn (II) acetate and triethanol amin (TEA) as the starting materials and water as solvent. The nanocrystals of ZnO with hexagonal (Wurtzite) structure were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), UV-Vis absorption and FTIR Spectroscopy techniques.

Keywords: Nanocrystals; ZnO; Microwave irradiation

1. Introduction

Transition metal oxides with nano structure have attracted considerable interest in many areas of chemistry, physics and material science [1]. Zinc oxide nanoparticles are used in a variety of applications such as UV absorption, antibacterial treatment [2], catalyst [3], photocatalyst [4] and additive in many industrial products. It is technologically an important material due to its wide range of optical and electrical properties as well as semiconductor crystal with a large binding energy (60 meV) and wide bond gap (3.37 eV). It is also used in the fabrication of solar cells [5], gas sensors [6, 7], luminescent materials [8], transparent conductor, heat mirrors and coatings. Different physical methods such as pulse laser deposition [9,10], vapor phase transparent process [11], chemical vapor deposition [12] and vapor transparent deposition have been developed for the preparation of nano ZnO. Today, sol-gel method is one of the known procedures for the preparation of metal oxide nanoparticles [13] which is based on the hydrolysis of reactive metal precursor. Microwave irradiation as a heating method has found a number of applications in chemistry. The utilization of microwave irradiation in the preparation of nano particles have been reported in recent years [14]. Compared to the conventional methods, the microwave synthesis has the advantages of producing small particle size metal oxides with high purity owing to short reaction time.

In this paper, we report a simple method for the preparation of hexagonal ZnO nanoparticles by using microwave irradiation. It was found that this method is fast, mild, energy-efficient and environmentally friendly rout to produce ZnO nano particles.

2. Experimental

2.1. Materials

All materials were purchased from Merck Chemical Company and used without further purification.

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2.2. Instrumentation

A microwave oven with 1000 W power (Butane) was used. Powder X-ray diffraction (XRD) patterns of prepared ZnO were recorded by diffractometer (SEIFERT PTS 3003) using a Cu Kα radiation ($\lambda = 1.54$ Å). The FTIR spectra were obtained on KBr pellets using a Bruker FTIR spectrometer (Tensor 27). The morphology was examined by a (Philips XL30) scanning electron microscope (SEM). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed with a Philips CM200 at 200 KV electron microscope. A PU-8700 UV-Vis spectrometer was used to record the UV-Visible absorption spectra.

2.3. Preparation of ZnO Nanoparticles

In a typical procedure, 25 ml aqueous solution of 0.2 M Zn (II) acetate was mixed with 25 ml aqueous solution of 0.4 M sodium hydroxide. After stirring for several minutes, 1.2 ml of triethanolamine (TEA) was slowly added to the reaction mixture. It was then stirred for ten more minutes. Finally, the mixture was placed under microwave irradiation (20% power) for 20 minutes. The white solid product was vacuum filtered, washed with distilled water and dried in air at room temperature. It was then calcined at 900°C for 1 h and can be stored for extended period of time.

3. Result and Discussion

3.1. XRD Analysis

Figure 1 shows the XRD pattern of ZnO nanocrystals. The diffraction peaks indicate the nanocrystalline nature (JCPDS card no.0-3-0888). These peaks at scattering angles (2θ) of 31.3670, 34.0270, 35.8596, 47.1635, 56.2572, 62.5384, 67.6356, and 68.7978 correspond to the reflection from: 100, 002, 101, 102, 110, 103, 200, and 112 crystal planes, respectively [15]. The XRD pattern is identical to the hexagonal phase with Wurtzite structure with space group (C6V=P63mc) and unit cell parameters $a = b = 3.248$ Å and $c = 5.2$ Å.

The particle size was calculated using the Scherer formula. The lattice strain and crystalline size was calculated from the following equation: [15]

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{\varepsilon} + \frac{\tau \sin \theta}{\lambda}$$

where $\beta$ is the measured FWHM (full-width at half maximum), $\theta$ is the Bragg peak angle of the peak, $\lambda$ is the X-ray diffraction wavelength (in this case, it is 1.59 Å), $\varepsilon$ is the effective particle size and $\tau$ is the effective strain.

The average particle size can be estimated from the extrapolation of the plot shown in Figure 2 and the crystalline size was obtained 35 nm based on the intercept inverse, i.e., $1/\varepsilon = 0.28 \times 10^8$, which yields $\varepsilon = 35 \times 10^{-9}$ m or 35 nm.

3.2. EDX Analysis

The EDX elemental analysis is shown in Figure 3. This result indicates that calcined ZnO nanoparticles contains 100% ZnO void of template.

3.3. SEM and TEM Characterization

The SEM of ZnO nanocrystalline particles produced by microwave irradiation is shown in Figure 4. As seen, single phase primary particle is spherical in shape with the average diameter of about 50 nm.

![Figure 1. The XRD pattern for the nano ZnO.](image1)

![Figure 2. $\beta \cos \theta/\lambda$ vs. Sin$\theta/\lambda$ for ZnO nanocrystals.](image2)
The size and morphology of ZnO particles analyzed by TEM is represented in Figure 5. This image reveals that the product consist of spherical particles with the average size of 35-45 nm which is in good agreement with that estimated by Scherer formula based on the XRD pattern.

![Figure 5. The TEM image of ZnO nano crystalline.](image)

Figure 6 shows the selected area electron diffraction (SAED) pattern of ZnO nanoparticle. The diffraction rings composed of dots show that the particles are well crystallized and can be indexed to (100), (002), (101), (102), (110), and (103), respectively which is in accordance with similar peaks in the XRD pattern.

### 3.4. FTIR Spectroscopy

The FTIR spectrum of ZnO in KBr matrix is shown in Figure 7. There is a broad band with very low intensity at 3493 cm\(^{-1}\) corresponding to the vibration mode of water OH group indicating the presence of small amount of water adsorbed on the ZnO nanocrystal surface. The band at 1628 cm\(^{-1}\) is due to the OH bending of water. A strong band at 500 cm\(^{-1}\) is attributed to the Zn-O stretching band which is consistent with that reported before [16].

### 3.5. Optical Properties

Optical properties of ZnO nanoparticles were characterized based on photoluminescence (PL) and UV absorption shown in Figure 8.

![Figure 6. The SAED pattern of nano ZnO.](image)

![Figure 7. FTIR Spectrum of ZnO nanocrystal.](image)
3.5.1. UV-Vis Spectroscopy

The absorption spectrum of ZnO nanostructures dispersed in ethanol solution is shown in Figure 8. The band position at 375 nm corresponds to ZnO nanoparticles. Compared with bulk ZnO, the blue shift observed in the ZnO nanostructures, is due to size effect. This band is also attributed to the semiconductor of ZnO nanoparticles band gap [17].

3.5.2. P.L. Spectroscopy

The green band emission is attributed to the radiative recombination of photogenerated hole with an electron belonging to a singly ionized vacancy in the surface and subsurface. The observation of strong green band emission relative to bulk ZnO indicates the existence of oxygen vacancies concentrated on nanoparticles surface. These results are in agreement with those reported before [11].

4. Conclusion

Compared to the other methods, ZnO nanoparticles were prepared using microwave irradiation as an easy and very fast method. XRD results showed that the obtained ZnO nanoparticles were composed of hexagonal wurtzite phase with very good crystallinity. The particle size obtained as 35-45 nm using Scherer formula was in good agreement with TEM results. The PL and UV absorption spectra showed a broad green band emission and a relatively narrow absorption band at 550 and 375 nm respectively. Due to the wide application of ZnO in various fields, scaling up of the process toward ZnO nanoparticles with high purity and excellent yield seems efficient.

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References