Crystal structure analyses of ZnO nanoparticles growth by simple wet chemical method

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Abstract. We have synthesized ZnO nanoparticles by using simple wet chemical method at calcination temperature of 400°C for 2 hours. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were performed to analyse morphology and crystal structure of ZnO nanoparticles, respectively. Morphologically, ZnO nanoparticles aggregated formed larger particles. Then, according to the International Center for Diffraction Data (ICDD) number #98-002-9272, the XRD spectra confirmed that the ZnO nanoparticles have polycrystalline hexagonal structure with prefer orientation of (002) and crystallite size in the range 21 nm.

1. Introduction

ZnO as II-VI semiconductor material with wide band gap energy of 3.34 eV and large exciton binding energy (60 mV) at room temperature is a potential material for optoelectronic applications [1,2]. In the last two decades, ZnO nanostructures have been studied theoretically and experimentally [3–5]. Scientist and engineer believed that the specific form ZnO nanostructure has a different application [3,6]. Compared with other nanostructures, ZnO nanoparticles with the range of 100 nm have a large specific surface area and small size effect [7]. Furthermore, ZnO nanoparticles have paid considerable attention due to quantum confinement effects which control optical properties of ZnO [7,8].

There are many methods to synthesize ZnO nanoparticles such as wet chemical [9], thermal decomposition, hydrolysis, hydrothermal, vapor transport, etc [10,11]. Among of these methods, wet chemical offers low-cost and has been used to synthesized different ZnO nanostructure [12].

In small concentrations, ZnO nanoparticles strongly inhibit the action of pathogenic microbes [13]. It also possesses antibacterial and antifungal activities [7]. Interestingly, ZnO nanoparticles have used to enhance electrochemiluminescence of luminol which used cancer biomarker detection [14]. Recently, ZnO nanoparticles are believed have a potential application as photocatalyst [11]. Even though, synthesized and characterization of ZnO nanoparticles still become major interest due to abundant their potential applications.

In this paper, we report structure analysis of ZnO nanoparticles which synthesized with simple wet chemical method. The morphology of powder ZnO nanoparticles have been observed by scanning electron microscopy (SEM) JEOL JSM-6510, X-ray diffraction (XRD) measurement with CuKα radiation (PAN-analytical), and compositions of precursors have been observed by energy dispersive X-ray.
2. Experimental
Zinc Chloride (ZnCl2) and Sodium Hydroxide (NaOH) were used as Zn precursor and for controlling pH in solution. Each of ZnCl2 and NaOH was dissolved in de-ionized (DI) water to obtain various molarities. The NaOH solution was added into ZnCl2 solution drop by drop under vigorous stirring without any heat treatment until a white suspension formed. ZnCl2 the molarities of ZnCl2/NaOH are 0.4/0.8 (ZnO-A), 0.4/0.4 (ZnO-B), and 0.8/0.4 (ZnO-C). Then, each of the suspension solutions was centrifuged to obtain precipitated of Zn(OH)2. Finally, the precipitation of Zn(OH)2 was calcined at the temperature of 400°C to obtain powder ZnO nanoparticles.

3. Results and discussion
Figure 1 (a)-(c) show SEM images of powder ZnO nanoparticles various compositions of ZnCl2/NaOH ratios. It can be observed that the ZnO nanoparticle aggregate tremendously. More clearly images of the aggregation can be confirmed in figure 1 (a). As seen from the figure 1(b) and (c), the aggregation of nanoparticles quite large. The aggregation of ZnO nanoparticles are predicted due to high surface energy of ZnO nanoparticles during calcination [15].

We further investigated the composition of powder ZnO particles by energy dispersive X-ray (EDAX). In can be seen from the table 1 that the ZnCl2/NaOH ratio of 0.4:0.8 yield the optimum composition ratio to synthesized ZnO nanoparticles.

![SEM images of powder ZnO nanoparticles various compositions of ZnCl2/NaOH ratios. The atomic percentage of Zn and O are 48.24% and 51.76%, respectively.](image)

Figure 1. SEM images of powder ZnO nanoparticles various compositions of ZnCl2/NaOH ratios. The atomic percentage of Zn and O are 48.24% and 51.76%, respectively.
Table 1. Elements composition of ZnCl$_2$/NaOH ratio.

| Sample | Precursor (Molaritas) | EDAX Analysis (At.%) |
|--------|-----------------------|----------------------|
|        | ZnCl$_2$  | NaOH | Zn | O | Cl |
| ZnO-A  | 0.4 | 0.8 | 48.24 | 51.76 | - |
| ZnO-B  | 0.4 | 0.4 | 26.12 | 72.70 | 01.17 |
| ZnO-C  | 0.8 | 0.4 | 29.59 | 58.16 | 12.25 |

Figure 2 show XRD pattern of ZnO nanoparticles with various compositions of ZnCl$_2$/NaOH ratios. According to the XRD pattern, we confirm that the sample ZnO-A with ZnCl$_2$/NaOH ratio of 0.4:0.8 have only one phase ZnO. Meanwhile, ZnO-B and ZnO-C have other phases such as Zn(OH)$_2$.

According the XRD pattern of ZnO-A as shown in fig. 2, we observed eleven peaks with the hkl are (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202). Among of these peaks, the peaks belongs to hkl (100), (002), and (101) are more intense compared with others.

Figure 2. XRD pattern of ZnO nanoparticles with various compositions of ZnCl$_2$/NaOH ratios.

Refer to the International Center for Diffraction Data (ICDD) number #98-002-9272, the powder ZnO nanoparticles have a hexagonal wurtzite structure.

Table 2. The data of full width at half maximum (FWHM), crystallite size, and lattice strain of ZnO nanoparticle structure at hkl of (002).

| No. | 2 theta | hkl | FWHM | Crystallite size (nm) | Lattice Strain (%) |
|-----|---------|-----|------|----------------------|-------------------|
| 1   | 31.837  | 100 | 0.307| 21.672               | 0.650             |
| 2   | 34.502  | 002 | 0.316| 21.586               | 0.600             |
| 3   | 36.334  | 101 | 0.322| 21.342               | 0.580             |
A crystallite size and lattice strain have been calculated by using Scherer’s and Stokes-Wilson’s equation, respectively [16]. Table 2 is the data of full width at half maximum (FWHM), crystallite size, and lattice strain of ZnO nanoparticle structure at hkl of (002). As seen in table 2, the FWHM for three peaks (100), (002), (101) are 0.307, 0.316, 0.322. Meanwhile, for the peaks orientation of (100), (002), (101) the crystallite size and lattice strain are 21.672 nm, 21.586 nm, 21.342 nm and 0.650 %, 0.600 %, 0.580 %. Raou reported that the crystallite size of ZnO nanoparticle (101) which was synthesized at the temperature of 450 °C and 550 °C are 19.810 nm and 27.590 nm, respectively [17]. The crystallite size increase by increasing annealing temperature. According to our results, we believe that our calcination temperature of 400 °C is optimum temperature to obtain ZnO nanoparticles with ZnCl₂/NaOH ratio of 0.4:0.8.

![Figure 3. Coefficient of texture of ZnO nanoparticles with ZnCl₂/NaOH ratios of 0.4:0.8.](image)

In order to confirm prefer orientation, we calculated quantitavely coefficient of texture by using this equation [18],

\[
T_{hkl} = \frac{I(hkl)}{1/n \sum I(hkl)/I_0(hkl)}
\]  

(1)

I (hkl) is the measured relative intensity of the reflection from the (hkl) plane, I₀(hkl) is that from the same plane in a standard reference sample, and n is the total number of reflection peaks from the sample. Figure 3 show coefficient of texture from XRD pattern of ZnO nanoparticles. It can be confirmed that the hkl of (002) is prefer orientation.

4. Conclusions
In conclusions, ZnO nanoparticles have been synthesized by using simple wet chemical method at calcination temperature of 400 °C for 2 hours. Morphologically, ZnO nanoparticles aggregated formed larger particles. Then, according to the International Center for Diffraction Data (ICDD) number #98-002-9272, the XRD spectra confirmed that the ZnO nanoparticles have polycrystalline hexagonal structure with prefer orientation of (002) and crystallite size in the range 21 nm.

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