Morphological and Structural Studies of ZnO Micro-Nanorod Structures Synthesized Using a Low-Cost Hydrothermal Method

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Abstract

Micro-nanorod structures of zinc oxide (ZnO) have been successfully synthesized via a simple and low-cost hydrothermal method. ZnO solutions with different concentrations of 0.05 and 0.1 M were prepared using zinc nitrate tetrahydrate and hexamethylenetetramine precursors. They were dissolved in aquades and stirred before the hydrothermal process at 95 °C for 4 hours in an oven. Extensive characterizations using scanning electron microscope (SEM) and X-ray diffraction (XRD) were conducted on ZnO powder samples. SEM results showed that hexagonally shaped ZnO micro-nanorods were formed with diameters ranging from hundreds of nanometers to several micrometers. The ZnO sample synthesized at 0.05 M was observed to have a better surface morphological structure than the 0.1 M sample. In addition, XRD measurements confirmed that samples exhibited a hexagonal crystal structure of ZnO. Moreover, the calculated crystallite sizes of ZnO using the Debye-Scherrer equation using the full-width half maxima of the XRD peaks were 25.153 nm for the 0.05 M sample and 28.707 nm for the 0.1 M sample. The most prominent growth of ZnO had 101 plane orientation or nonpolar a-plane followed by nonpolar 100 m-plane and 002 polar c-plane orientations. This study offers a simple and low-cost route to produce high-quality ZnO micro-nanorods for use in various electrical and optical devices.

Abstrak

Kajian Morfologi dan Struktural Batang Mikro-nano ZnO Disintesis Menggunakan Metode Hidrotermal dengan Biaya Rendah. Struktur batang mikro-nano seng oksida (ZnO) berhasil disintesis menggunakan metode hidrotermal sederhana dan dengan biaya yang rendah. Larutan ZnO dengan konsentrasi berbeda yaitu 0,05 dan 0,1 M diisapkan menggunakan prekursor seng nitrat tetrahidrat dan heksamethylenetetramin. Prekursor tersebut dilarutkan di dalam akuades dan diaduk sebelum proses hidrotermal berlangsung pada suhu 95 °C selama 4 jam di dalam oven. Sampel serbuk ZnO dikarakterisasi secara ekstensif menggunakan mikroskop elektron (SEM) dan difraksi sinar-x (XRD). Hasil analisis SEM menunjukkan bahwa batang mikro-nano ZnO berbentuk heksagonal dihasilkan dengan rentang diameter dari ratusan nanometer hingga beberapa mikrometer. Sampel ZnO yang disintesis dengan konsentrasi 0,05 M terama memiliki struktur morfologi yang lebih baik dibandingkan sampel 0,1 M. Pengukuran XRD mengkonfirmasi bahwa sampel sesuai dengan ZnO dengan struktur kristal heksagonal. Lebih lanjut, perhitungan estimasi rata-rata ukuran kristal ZnO menggunakan persamaan Debye-Scherrer dengan puncak XRD lebar penuh pada setengah maksimum didapat yaitu sebesar 25,153 nm untuk sampel 0,05 M dan 28,707 nm untuk sampel 0,1 M. Pertumbuhan ZnO paling dominan yaitu pada orientasi bidang 101 atau bidang nonpolar a diikuti orientasi bidang nonpolar m 100 dan bidang polar c 002. Kajian ini menawarkan metode yang simpel dan dengan biaya rendah untuk menghasilkan batang mikro-nano ZnO yang memiliki potensi untuk diaplikasikan dalam berbagai peralatan elektronik dan optik.

Keywords: electron microscope, hydrothermal, nanorod, X-ray Diffraction, zinc oxide
**Introduction**

The rapid progress of research in nanotechnology and materials followed by application of the materials in various fields of life requires researchers to continuously innovate. One of most studied nanomaterials is the zinc oxide (ZnO) nanostructure. Nanostructured ZnO has attracted much attention from material researchers due to its various structures, unique properties or characteristics, and promising applications in many devices. ZnO has a high surface area and is = easier to be synthesized than other nanomaterials due to expensive and sophisticated equipment. At room temperature and normal atmospheric pressure, ZnO crystals are stable in hexagonal wurtzite structures [1]. ZnO is a metal oxide semiconductor with a wide band gap of 3.37 eV, high exciton binding energy (60 meV) [2], and work function of 5.3 eV [3]. In addition, ZnO can be synthesized into various structures or morphologies by changing the synthesis parameters, providing unique electrical and optical properties and good thermal and chemical stability [4]. ZnO nanostructures can also be applied in UV sensors [5], solar cells [6], heavy-metal absorbers [7], and other optic and electrical devices.

Kathalingam et al. [8] presented two different nucleation processes in ZnO solution during the synthesis process: homogeneous and heterogeneous. Homogeneous nucleation leads to the formation and deposition of larger ZnO particles in the precursor solution. Meanwhile, the formation of ZnO nanostructures on the substrate surface occurs due to heterogeneous nucleation. The equation of the reaction occurring at the formation of ZnO is formulated as follows [9]:

\[
\text{Zn(NO}_3\text{)}_2\text{(aq)} + \text{C}_6\text{H}_{12}\text{N}_4\text{(aq)} \rightarrow [\text{Zn(C}_6\text{H}_{12}\text{N}_4)]^{2+}\text{(aq)} + 2\text{NO}_3^-\text{(aq)} + \text{C}_6\text{H}_{12}\text{N}_4\text{(s)}
\]

(1)

\[
\text{Zn(NO}_3\text{)}_2\text{(aq)} + 4\text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_{12}\text{N}_4\text{H}_2\text{O} + 4\text{OH}^-
\]

(2)

\[
[\text{Zn(C}_6\text{H}_{12}\text{N}_4)]^{2+}\text{(aq)} + 4\text{OH}^-\text{(aq)} \rightleftharpoons \text{Zn(OH)}_4^{2-}\text{(aq)} + \text{C}_6\text{H}_{12}\text{N}_4
\]

(3)

\[
\text{Zn(OH)}_4^{2-}\text{(aq)} \rightarrow \text{Zn(OH)}_2\text{(s)} + 2\text{OH}^-\text{(aq)}
\]

(4)

\[
\text{Zn(OH)}_2\text{(s)} \rightarrow \text{ZnO(s)} + \text{H}_2\text{O}
\]

(5)

Properties and characteristics of ZnO crystal are affected by the size and preparation method [10]. Several existing methods to produce ZnO nanostructures are chemical vapor deposition [11], thermal evaporation [12], electrochemical deposition [13], and laser pulse deposition [14]. Unfortunately, these methods require complex preparation and equipment as well as complex control parameters such as high temperature, gas flow concentration, and vacuum state. A simpler synthesis method known as the hydrothermal or immersion method is a popular method for synthesizing ZnO nanostructures, because this method can be performed with low reaction temperature, simple and low-cost equipment, and can easily control the growth of sample structures. In addition, this method has been known to be a low cost and environmentally friendly method. Because the nature and characteristics of the ZnO nanostructure are influenced by its morphology, many studies have examined the effect of several synthesis parameters on the ZnO properties produced using the hydrothermal method. Among the parameters are pH, solution concentration, reaction time, ZnO temperature [15], and annealing environment [5].

In this study, two different concentrations of ZnO precursors were prepared to study the effect of molarity on the ZnO structure and its corresponding properties. A simple hydrothermal method using an oven as the heating process was used to synthesize ZnO structures. Moreover, this study avoids the use of harmful and hazardous chemicals such as KOH [16], NaOH [16, 17], and hydrazine hydrate [18], which are commonly used to produce ZnO in the hydrothermal method.

**Materials and Methods**

ZnO micro-nanorod structures were synthesized using a hydrothermal method. ZnO solutions with concentrations of 0.05 and 0.1 M were prepared by dissolving commercially available zinc nitrate tetrahydrate (Zn(NO\(_3\))\(_2\)·4H\(_2\)O) and hexamethylenetetramine (HMT, C\(_6\)H\(_{12}\)N\(_4\)) as starting materials in 200 mL of aquades in a capped glass bottle. The details of the precursor weights for each concentration are presented in Table 1.

| Table 1. Precursor Weights for Different Concentrations of ZnO Precursors |
|-----------------------------|-----------------------------|-----------------------------|
| **Molarity in 200 mL aquades** | **0.05 M** | **0.1 M** |
| Zinc nitrate tetrahydrate (Zn(NO\(_3\))\(_2\)·4H\(_2\)O) | 2.610 g | 5.220 g |
| Hexamethylenetetramine (HMT, C\(_6\)H\(_{12}\)N\(_4\)) | 1.409 g | 2.804 g |

![Figure 1. Schematic of Synthesis Process of ZnO Micro-Nanorod Structures](image-url)
The solution was stirred for an hour at room temperature followed by heating for 4 hours in an oven (MEMMERT UNB Universal oven) at 95 °C. The solution was filtered and dried in the oven to produce a fine powder of ZnO, and the schematic diagram of synthesis process is shown in Figure 1. ZnO powder was collected and characterized using X-ray Diffraction (XRD) Rigaku Miniflex600 40 kW 15 mA Cu K-α and using scanning electron microscope (SEM-JEOL JSM-6510LA) operated at an accelerating voltage of 20kV.

Results and Discussion

Figure 2 presents the SEM images of the resulted ZnO powder synthesized at 0.05 and 0.1 M. In general, ZnO powder samples consisted of several structures such as rods, flower-like, agglomerated structures, and other non-crystal structures. Both samples show a high concentration of ZnO with the domination of agglomerated hexagonal rod structures, as seen in Figure 2a and 2d. The rod diameters ranged from hundred nanometers to several micrometers. Petal flower-like structures were also observed in the 0.05 M sample, as indicated by the yellow arrow in Figure 2a. This formation occurred due to the lack of needed stirring or heating time during the synthesis process. The ZnO sample synthesized at precursor concentration of 0.1 M had a larger diameter that ranged up to 6.6 μm. This large diameter occurred due to the higher precursor concentration. Unsmooth and larger rod diameter, the absence of petal flower-like structure, and the formation of agglomerated ZnO flake structure.

![Figure 2. SEM Results of ZnO Micro-Nanorod Structures Synthesized at Concentration of 0.05 and 0.1 M](image-url)
(red arrow in Figure 2d) showed that the structure of ZnO powder synthesized at 0.1 M exhibited lower quality than the structure of the ZnO powder synthesized at 0.05 M. However, more parameter optimization is required to produce a higher quality of ZnO nanorod structures via this method. XRD patterns of ZnO samples synthesized at different concentrations are presented in Figure 3. The patterns are consistent with ICDS collection data (PDF reference code: 01-075-0576). The results revealed that the samples have a hexagonal crystal structure belonging to the P63 mc space group with cell parameters $a = 3.2427$ Å and $c = 5.1948$ Å. Low peaks observed at 20 around 32° (between 100 and 002 planes) belong to the Zn(OH)$_2$ complex, and other studies have shown that these peaks relate to the treatment time [19]. From the reactions in Equations (4) and (5), the solid Zn(OH)$_2$ is not fully decomposed to solid ZnO and H$_2$O. Therefore, optimizations such as added reaction time or other treatments are required to produce a higher purity of ZnO.

In general, the XRD peaks of the 0.1 M sample were more intense than the XRD peaks of the 0.05 M sample due to its higher precursor concentrations. This was in agreement with previous studies in [20, 21] where the increased solution molarities resulted in increased XRD intensity peaks accompanied by a lower full-width half maximum (FWHM). Overall peaks showed hexagonal phases of ZnO with different intensities and orientations. The more intense peak indicated that the growth of ZnO is preferred to that orientation and has a better crystallinity. Both samples showed that the most prominent peak was centered around a 20 of 36°. This indicates that the growth of ZnO micro-nanorods structures in this study preferred the 101 plane orientation or nonpolar a-plane growth [22]. The prominent growth was then followed by nonpolar 100 m-plane and 002 polar c-plane orientation [22, 23]. Similar ZnO structure growth reported to have good optical characteristics and be suitable for use in high-efficiency light emitting diodes (LEDs) and humidity sensor applications [24, 25]. Strong, narrow, and sharp XRD peaks show that the

![Figure 3. XRD Patterns of ZnO Samples Synthesized at Different Concentrations. XRD Pattern of ZnO from ICDS Collection Data (PDF reference code: 01-075-0576) ](image-url)
synthesized ZnO structures have a fair crystallinity and purity [26, 27]. The crystallite sizes of ZnO particles were calculated using Debye-Scherrer’s formula [28, 29], as given by Equation 1:

\[
D = \frac{0.91}{\beta \cos \theta}
\]

Where \( \lambda \) represents the X-ray wavelength (0.154 nm), \( \beta \) represents the FWHM and \( \theta \) represents the half diffraction angle. The Debye-Scherrer formula based on FWHM has been commonly used to analyze the estimated crystallite size of ZnO particles [17, 28-31]. The crystallite size (\( D \)) is defined as an individual domain that coherently diffracts the X-ray [28]. Details of XRD peaks and estimated crystallite sizes of ZnO samples using the FWHM calculation are presented in Table 2.

The average crystallite size from Debye-Scherrer equation using FWHM calculation is usually chosen from the more intense peak [28, 29], which in this study corresponded to the ZnO 101 orientation and approximately had a \( \theta \) of 36°. Thus, the average estimated crystallite sizes of

| Sample | 2\( \theta \) (°) | d (Å)  | Intensity (cps) | FWHM (°) | h k l | Crystallite size (nm) |
|--------|----------------|-------|----------------|----------|------|----------------------|
| 0.05 M | 31.565         | 2.8321| 4246           | 0.306    | 1 0 0 | 26.968               |
|        | 34.228         | 2.6176| 3483           | 0.268    | 0 0 2 | 31.004               |
|        | 36.036         | 2.4903| 6814           | 0.332    | 1 0 1 | 25.153               |
|        | 47.316         | 1.9196| 1249           | 0.38     | 1 0 2 | 22.815               |
|        | 56.37          | 1.6307| 2093           | 0.428    | 1 1 0 | 21.050               |
|        | 62.64          | 1.4818| 1314           | 0.511    | 1 0 3 | 18.191               |
|        | 66.24          | 1.4098| 240            | 0.41     | 2 0 0 | 23.126               |
|        | 67.71          | 1.3827| 1202           | 0.516    | 1 1 2 | 18.532               |
|        | 68.85          | 1.3626| 612            | 0.56     | 2 0 1 | 17.192               |
| 0.1 M  | 31.691         | 2.8212| 7027           | 0.251    | 1 0 0 | 32.888               |
|        | 34.323         | 2.6106| 4603           | 0.280    | 0 0 2 | 29.683               |
|        | 36.161         | 2.4820| 10309          | 0.291    | 1 0 1 | 28.707               |
|        | 47.435         | 1.9151| 2085           | 0.347    | 1 0 2 | 24.996               |
|        | 56.443         | 1.6290| 3298           | 0.365    | 1 1 0 | 24.692               |
|        | 62.724         | 1.4801| 2108           | 0.463    | 1 0 3 | 20.086               |
|        | 66.220         | 1.4106| 372            | 0.40     | 2 0 0 | 23.699               |
|        | 67.780         | 1.3815| 2004           | 0.428    | 1 1 2 | 22.351               |
|        | 68.92          | 1.3614| 1010           | 0.41     | 2 0 1 | 23.491               |

![Figure 4. Estimated Crystallite Sizes of ZnO Samples Synthesized at Different Concentrations](image-url)
the ZnO samples synthesized at 0.05 M and 0.1 M were calculated as 25.153 nm and 28.707 nm, respectively. The calculated crystallite size distribution of the ZnO samples synthesized at different precursor concentrations is presented in Figure 4. SEM and XRD results showed that a better quality with more uniform structure with smaller particles or nanorod sizes was produced using the 0.05 M precursor concentration. However, more optimization parameters or treatments are needed to produce a higher purity of ZnO nanorod structure from this method. Hence, their further applications are optimized. As reported elsewhere, ZnO has many applications in various fields such as electronic and optical devices, heavy-metal removers [32], cosmetics [33], biomedical devices [34], and many more fields. Similar results to this work revealed that ZnO nanorod structures produced from the hydrothermal method are suitable for gas sensors [35], solar cells [36, 37], and LEDs [38].

Conclusions

ZnO micro-nanorod structures were successfully synthesized using a low-cost hydrothermal method at two different concentrations. SEM analysis revealed that the ZnO powder sample synthesized using 0.05 M precursor concentration has a better surface morphological structure than the 0.1 M sample. SEM results showed that the ZnO has a hexagonal rod structure with a diameter ranging from hundreds of nanometers to several micrometers. XRD results also confirmed that the sample has a hexagonal crystal structure that belongs to the P63 mc space group with the most prominent growth at nonpolar a-plane 101 lkl orientation. However, further optimization and characterization are needed to produce ZnO micro-nanorod structure with a better morphology and crystallinity. Moreover, the FWHM XRD peaks showed that the crystallite sizes of ZnO were calculated as 25.153 nm for the 0.05 M sample and 28.707 nm for 0.1 M sample. ZnO micro-nanorod structures synthesized from this method can be applied in various electronic and optical devices such as solar cell, sensors, and LEDs.

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