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# Preparation of ZnO nanorod by solvothermal reaction of zinc acetate in various alcohols

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**Abstract**

Solvothermal reaction of zinc acetate in various alcohols resulted in the formation of zinc oxide (ZnO) nanorods. The effects of reaction conditions on the product morphology as well as crystallization mechanism were investigated by using X-ray diffraction (XRD), infrared spectroscopy (IR), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM) techniques. It was found that average diameter and length of the nanorods increased with an increase in reaction temperature or the initial concentration of zinc acetate. On the contrary, the aspect ratio of the product depended upon type of alcohol used as the reaction medium. The aspect ratio of ZnO nanorods increased from 1.7 to 5.6 when the alcohol was changed from 1-butanol to 1-decanol. An investigation of the reaction mechanism suggested that the formation of ZnO nanorods was initiated from the esterification reaction between zinc acetate precursor and alcohol to form ZnO seeds.
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*Keywords:* D. ZnO; Nanorod; Alcohol; Solvothermal

## 1. Introduction

Nanostructured materials have received increasing attention due to their potential uses as active components or interconnects in nanoscaled electronic, optical, optoelectronic, electrochemical, and electromechanical devices [1]. One material that has been in great interest from wide range of technological field associated with nanotechnology is zinc oxide (ZnO) [2]. ZnO is a material with large direct band gap (3.3 eV) and excellent chemical and thermal stability. It has unique optical and acoustic properties, as well as electronic properties of the II–VI semiconductor with large exciton binding energy (60 meV) [3]. Therefore, zinc oxide has been used in various applications, e.g. as varistor, gas-sensor, catalyst and pigment. According to great function of zinc oxide, several techniques have been proposed for zinc oxide synthesis, e.g. hydrothermal synthesis [4,5], thermal decomposition method [6,7], sol–gel synthesis [8], flame spray pyrolysis [9], and precipitation method [10].

Control of the particle shape is another concern for nanostructured material synthesis because electrical and optical properties of nanomaterials depend sensitively on both size and shape of the particles. Therefore, it is desired to synthesize nanomaterial in a controllable shape and size by simple approach. For zinc oxide particles, various shapes including nanorods [11–13], whiskers [14,15] and nanowires [16] have been successfully prepared. However, it was the result from different synthesis methods under different preparation conditions [17].

In this study, the solvothermal method was employed to synthesize ZnO nanorods. This technique is based on thermal decomposition of organometallic compound in organic solvent and has been successfully applied for the synthesis of various types of nanosized metal oxide with large surface area, high crystallinity and high thermal stability [18–20]. The influences of reaction conditions, i.e. type of solvent, concentration and

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reaction temperature, on physical properties of the synthesized nanorods as well as the mechanism were investigated. An interesting correlation between aspect ratio of the ZnO products and physical properties of the solvent was observed and presented in this work.

## 2. Experiment

### 2.1. Preparation of ZnO

Zinc acetate ($Zn(CH_3CO_2)_2$) in a predetermined amount in the range of 10–25 g was suspended in 100 ml of alcohol in a glass vessel, which was then placed in a 300 ml autoclave. Alcohols used in this work were 1-butanol, 1-hexanol, 1-octanol and 1-decanol, respectively. The gap between autoclave wall and the glass vessel was filled with 30 ml of the same alcohol. The autoclave was completely sealed and purged with nitrogen. The mixture was heated to desired temperature, in the range of 250–300 °C, at a constant heating rate of 2.5 °C/min, and held at that temperature for 2 h. Subsequently, after the autoclave was cooled, the product obtained in the vessel was collected by centrifugation, washed with methanol and dried in air at room temperature.

### 2.2. Characterization

The prepared samples were examined by X-ray diffraction (XRD) analysis using a SIEMENS XRD D500 diffractometer with Cu Kα radiation. The morphology and crystallite size of the nanoparticles were observed on a JEOL JSM6400 Scanning Electron Microscope (SEM) and a JEOL JEM1220 Transmission Electron Microscope (TEM). Infrared spectra of the products were also obtained using Nicolet FT-IR spectrophometer model Impact 400. Each sample was mixed with KBr in the ratio of 1:100 and then pressed into a thin pellet. Infrared spectra were recorded at wave number in the range of 400 and 4000 $cm^{-1}$.

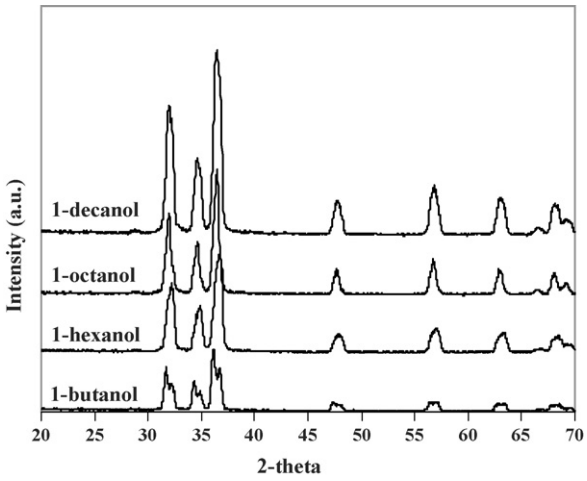


Fig. 1. The X-ray diffraction patterns of ZnO powder prepared by solvothermal reaction at 250 °C for 2 h in various alcohols.

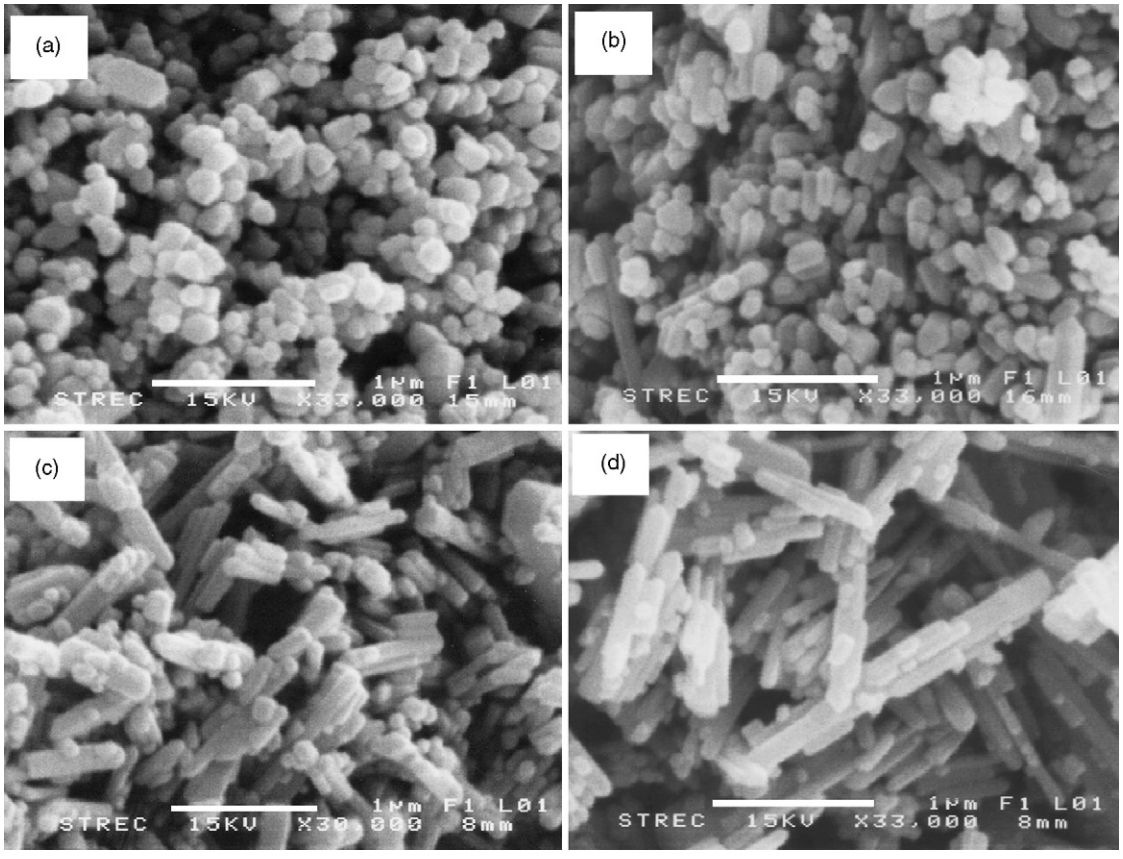


Fig. 2. SEM images of as-synthesized ZnO synthesized at 250 °C for 2 h in: (a) 1-butanol, (b) 1-hexanol, (c) 1-octanol and (d) 1-decanol.

## 3. Results and discussion

### 3.1. Effect of various reaction conditions

XRD patterns of powders synthesized by the solvothermal reaction in various alcohols at 250 °C are shown in Fig. 1. All peaks of the obtained product were corresponding to the hexagonal wurtzite structure of ZnO with lattice parameters *a* and *c* of 3.24 and 5.19 Å, respectively. No peak from either ZnO in other phases or impurities was observed. This result confirmed that ZnO was successfully synthesized by the solvothermal reaction in all alcohols investigated. Nevertheless, it should be noted that the XRD pattern of the product synthesized in 1-butanol showed slight split for all XRD peaks, which suggested non-homogeneity in the crystal structure of the ZnO product.

Fig. 2a–d show SEM images of the products synthesized in 1-butanol, 1-hexanol, 1-octanol and 1-decanol, respectively. It was clearly illustrated that morphology of particles synthesized in these alcohols were significantly different. Nearly spherical particles were obtained when 1-butanol was used as the reaction medium, while smooth solid hexagonal rods were observed in the product prepared in 1-decanol. Therefore, it could be taken that the product from the solvothermal synthesis in alcohol was ZnO nanorods and the length of the rods increased when alcohol with longer molecule was employed.

Morphology of the primary ZnO particle was examined from TEM images, as shown in Fig. 3. The results confirmed with SEM observation that nanorods synthesized were straight and non-porous. The selected area electron diffraction (SAED) patterns shown as the inset in Fig. 3 suggested that each primary particle was a rod-shaped single crystal of ZnO. The observed morphology was consistent with the hexagonal nanorods grown in 0 0 1 direction. It was also found that all synthesized ZnO nanorods were quite uniform in size. The distributions of diameter of the rods measured from TEM micrographs are shown in Fig. 4. According to Fig. 4, it was shown that the synthesized ZnO nanorods had narrow size distribution, regardless of the type of alcohol employed. The average diameter and length as well as the calculated aspect ratio of the particles are summarized in Table 1.

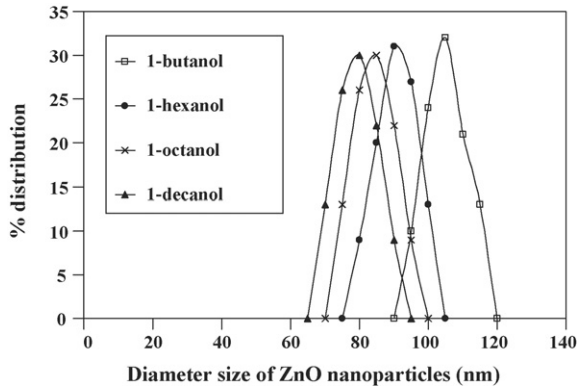


Fig. 4. The size distributions for diameter of ZnO nanorods synthesized in: (a) 1-butanol, (b) 1-hexanol, (c) 1-octanol and (d) 1-decanol.

According to Table 1, ZnO synthesized in alcohol having long carbon chain tended to be nanorods that were longer and had

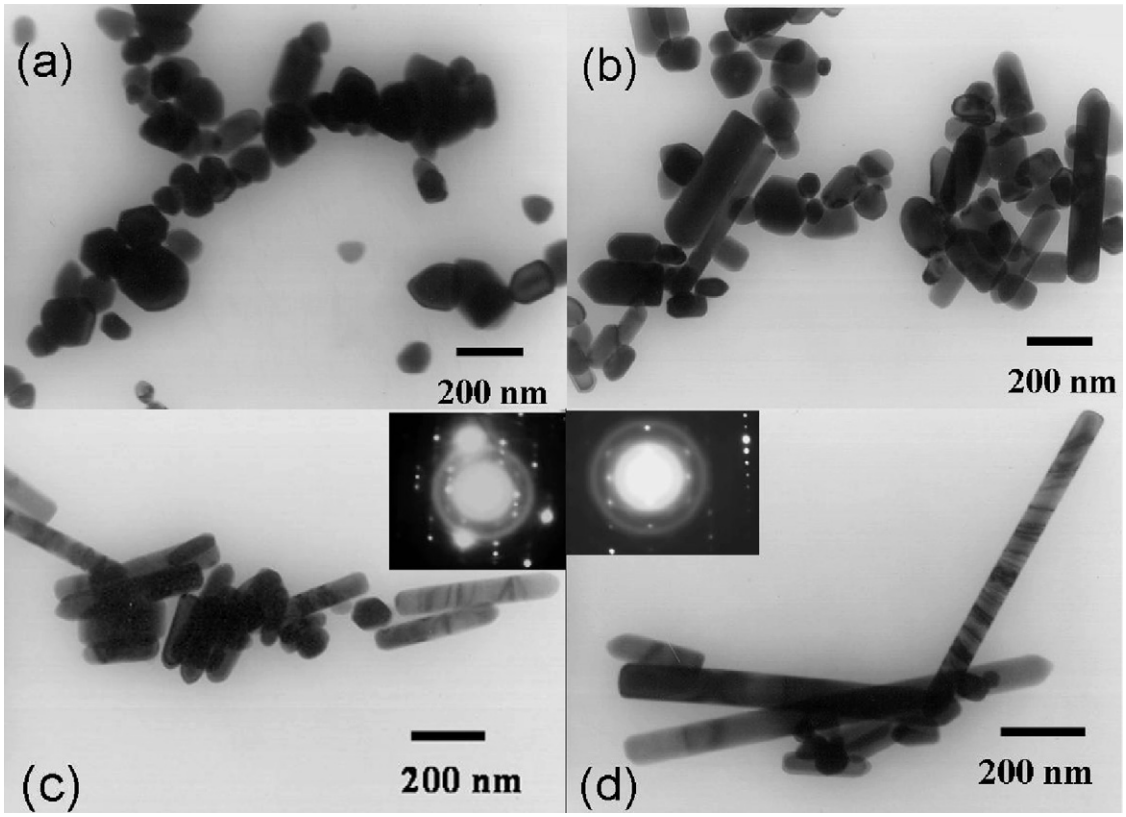


Fig. 3. TEM images of as-synthesized ZnO synthesized in: (a) 1-butanol, (b) 1-hexanol, (c) 1-octanol and (d) 1-decanol.

Table 1
The crystallite size and aspect ratio of ZnO nanorods

| Solvent | Synthesis emperature (°C) | Amount of zinc acetate used (g) | Average diameter of product (nm) | Average length (nm) | Aspect ratio |
|---|---|---|---|---|---|
| 1-Butanol | 250 | 15 | 107 | 184 | 1.7 |
| 1-Hexanol | 250 | 15 | 91 | 264 | 2.9 |
| 1-Octanol | 200 | 15 | 67 | 284 | 4.2 |
| 1-Octanol | 230 | 15 | 75 | 308 | 4.1 |
| 1-Octanol | 250 | 10 | 79 | 316 | 4.0 |
| 1-Octanol | 250 | 15 | 84 | 343 | 4.1 |
| 1-Octanol | 250 | 20 | 97 | 385 | 4.0 |
| 1-Octanol | 300 | 15 | 110 | 472 | 4.3 |
| 1-Decanol | 200 | 15 | 69 | 392 | 5.7 |
| 1-Decanol | 230 | 15 | 74 | 419 | 5.7 |
| 1-Decanol | 250 | 10 | 76 | 423 | 5.6 |
| 1-Decanol | 250 | 15 | 81 | 455 | 5.6 |
| 1-Decanol | 250 | 20 | 91 | 506 | 5.6 |

diameter smaller than those synthesized in short-chain alcohol. The aspect ratio of the obtained nanorods increased corresponding to an increase in length of the carbon chain of the reaction medium. When 1-decanol was used instead of 1-butanol, the length of nanorods increased from 184 to 455 nm, while the average diameter decreased from 107 to 81 nm. Consequently, the aspect ratio increased approximately three-fold.

Table 1 also summarizes dimension of ZnO particles synthesized under various reaction conditions. It was found that both average diameter and length of the ZnO nanorods increased with an increase in either initial concentration of the precursor (i.e. zinc acetate) or reaction temperature. This observation suggested the increase in crystal growth with number of nuclei sites as well as the energy of the system. However, it should be noted that the aspect ratio of ZnO particles was not affected by either the temperature or amount of precursor. In the other words, the change in the reaction conditions did not alter the growth of ZnO nanoparticles into preferential orientation. Type of alcohol employed as the reaction medium was the only major factor affecting the aspect ratio of the synthesized particles.

The aspect ratio of ZnO nanorod was determined from relative growth rates from various faces of the crystal. The rate of crystal

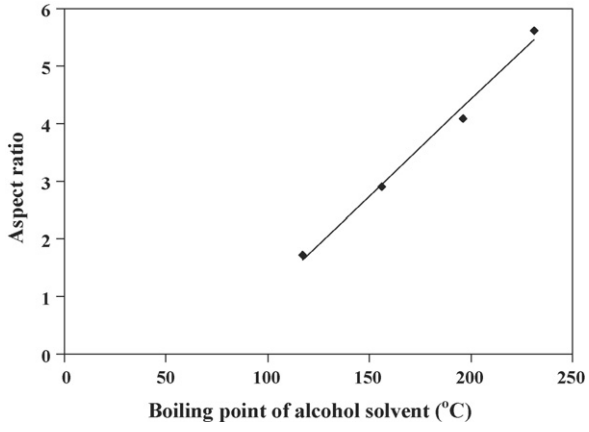


Fig. 5. The correlation between boiling points of the employed solvent and aspect ratio of ZnO products.

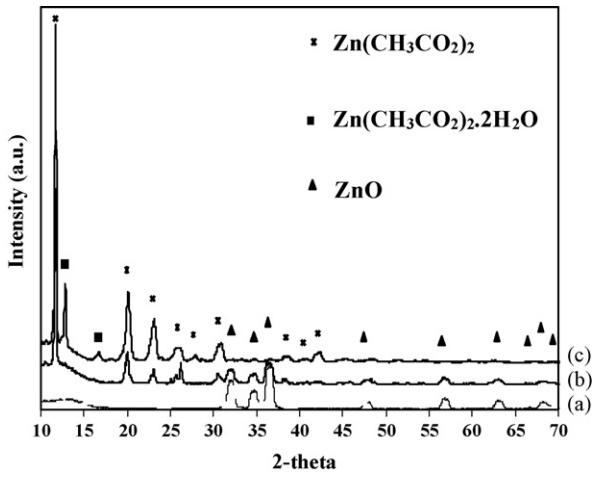


Fig. 6. The X-ray diffraction patterns of: (a) the reaction precursor, i.e. zinc acetate, (b) ZnO synthesized in 1-octanol at 150 °C and (c) ZnO synthesized in 1-octanol at 200 °C.

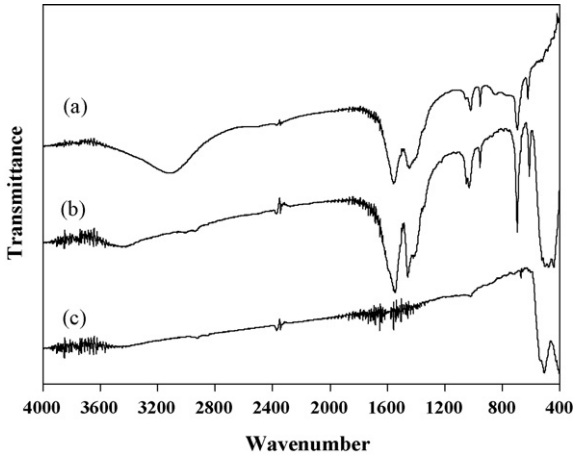


Fig. 7. IR spectra of: (a) the reaction precursor, i.e. zinc acetate, (b) ZnO synthesized in 1-octanol at 150 °C and (c) ZnO synthesized in 1-octanol at 200 °C.

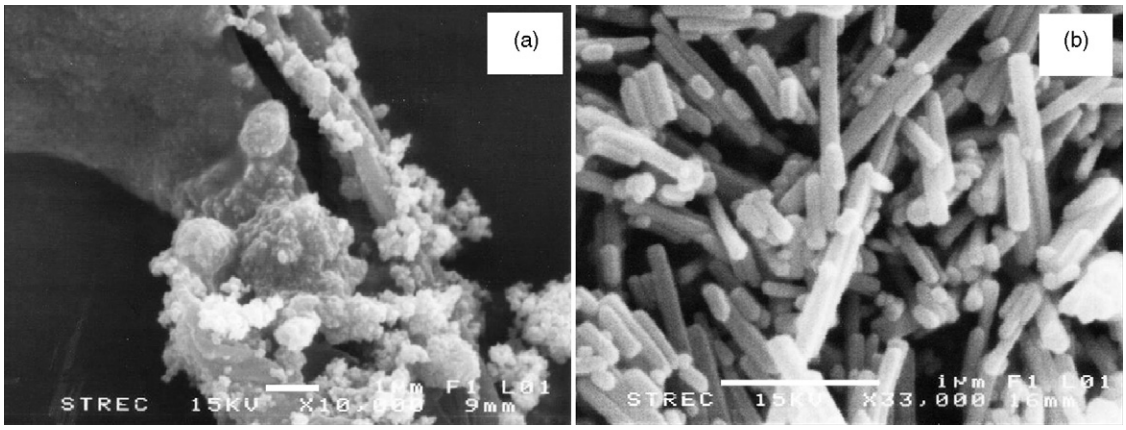


Fig. 8. SEM images of ZnO synthesized in 1-octanol for 2 h at (a) 150 °C and (b) 250 °C.

growth from any particular face was controlled by a combination of internal factors (e.g. intermolecular bonding preference or dislocation in crystal) and external factors (e.g. supersaturation condition, reaction temperature and type of solvent) [21]. ZnO in wurtzite structure is a polar crystal with (0 0 1) facet having higher-symmetry (C6v) than the other faces. Therefore, crystal growth along *c*-axis, or (0 0 1) direction, is a typical behavior observed from wurtzite ZnO. Nevertheless, Cheng and Samulski [4] have reported that the growth rate from each face of ZnO under the condition of hydrothermal synthesis is also controlled by properties of solvent that affected the interface–solvent interactions. The results in this work supported this report. It was found that the aspect ratio of the ZnO product was correlated with physical properties of the solvent. Fig. 5 shows a plot between boiling points of solvent and aspect ratio of the ZnO product. Interestingly, a linear relationship was observed. Although direct relationship between the boiling point of solvent and the preferential crystal growth may not have scientifically significance, the boiling point of alcohol could be used as an index for ''non-polar'' nature of alcohol molecule. For all alcohols investigated, the hydrogen bonding and the dipole–dipole interactions among molecules are roughly the same, but the van der Waals dispersion forces are stronger in alcohol with longer hydrocarbon chain and it results in an increase in boiling point of alcohol. As the long-chain alcohol was employed as the reaction medium, the interaction between the alcohol molecules and the (0 0 1) facet of the ZnO crystal, which was the slight positively charged Zn surface, was weak, allowing ZnO crystal to grow along the preferential *c*-axis.

Although the crystallization phenomenon of ZnO nanorod is unambiguously demonstrated by the presented correlation shown in Fig. 5, the detailed mechanism of the crystal growth is still under investigation. However, the behavior shown in Fig. 5 should prove useful in practical application, since the correlation allows and estimation of the aspect ratio of ZnO nanorod from type of alcohol used.

### 3.2. Investigation of reaction mechanism

To understand the reaction mechanism, the reaction temperature in octanol was decreased to 200 and 150 °C, respectively. Fig. 6 shows the XRD patterns of thus-obtained products. It was found that the powder prepared at 150 °C was a mixture of zinc acetate and zinc oxide. No shift in XRD pattern was observed. IR spectra of the product as shown in Fig. 7 also confirmed the existence of zinc acetate in the product synthesized at 150 °C without the presence of functional groups corresponding to alcohol. These results indicated that no intermediate was formed from the reaction between zinc acetate and alcohol.

Fig. 8 shows SEM images of the as-synthesized products prepared at various temperatures. The product prepared at 150 °C was composed of two types of particles, i.e. the particles with irregular shape, which was assigned to be zinc acetate and rod-shaped particles of ZnO. The elemental mapping showed that carbon atoms were distributed only on the irregular-shaped particles. The content of carbon decreased dramatically at the boundary between the irregular-shaped particles and rod-like particles. This SEM observation, together with XRD and FTIR results, indicated that ZnO rods grew from the ZnO seeds formed via the direct decomposition of zinc acetate.

To further investigate the reaction mechanism, the solvent recovered after the reaction was collected and analyzed by gas chromatography. Ester and water were detected in the remaining solvent. Therefore, it was proposed that the interaction between zinc acetate and alcohol under the solvothermal conditions resulted in esterifaction reaction, which proceeded to form ZnO, ester and water, according to the following reaction:

$$Zn(CH_3COO)_2 + 2R\text{-}OH \rightarrow ZnO + 2CH_3\text{-}CO\text{-}R + H_2O$$

Once the ZnO seeds were formed, further reaction resulted in crystal growth of ZnO nanoparticles. The size and shape of the particles were controlled by the reaction condition, as discussed previously.

## 4. Conclusion

Zinc oxide nanorods were successfully prepared by one-step solvothermal reaction of zinc acetate in alcohols. The as-synthesized ZnO was found to be an aggregation of nanorods having aspect ratios of 1.7, 3, 4 and 5.6 when 1-butanol, 1-

hexanol, 1-octanol and 1-decanol, respectively, was used as the reaction medium. The interesting linear relationship between boiling point of the solvent used and aspect ratio of the product obtained was observed. This plot can be used to select the appropriate solvent for the preparation of zinc oxide nanorod with desired aspect ratio.

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