

## Effects of Deposition Parameters of Hydrothermal Method on Synthesis of ZnO-based Nanowires

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ZnO-based nanomaterials can be used as sensors for different applications, including gas and ultraviolet (UV) ray sensors. To grow ZnO nanowires by the hydrothermal method, a ZnO seed layer was prepared by a sputtering method to deposit ZnO films on  $\text{SiO}_2/\text{Si}$  substrates of about 200 nm thickness. Next,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{12}\text{N}_4$  were used as reagents, and DI water was used as a solvent, and they were mixed to the designed compositions. We found that when  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{12}\text{N}_4$  were used as reagents to grow ZnO nanostructured materials, growth temperature, the concentration of the diluted solution, growth time, and the position of the substrates were four important factors affecting the synthesis results. The surface morphologies of ZnO nanowires were observed by field-emission scanning electron microscopy (FESEM), and crystalline phases were analyzed using X-ray diffraction (XRD) patterns. The FESEM images and XRD patterns were used to determine the effects of synthesis parameters on the morphologies and crystalline properties of the grown nanostructured materials. First, we found that 100 °C was the optimum synthesis temperature for growing pure ZnO nanowires, because ZnO-based nanowires could be successfully synthesized at different concentrations of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{12}\text{N}_4$  and different synthesis times. The effects of growth time, the position of the substrates on the carry sheet glass, and concentrations of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{12}\text{N}_4$  on the growth of nanostructured materials were also investigated.

### 1. Introduction

Nowadays, it is necessary to investigate gas sensors for detecting volatile and toxic gases existing in the environment because of environmental and atmospheric pollutions and the requirements for the safety of factories and daily life. One-dimensional (1D) and two-dimensional (2D) ZnO nanostructures have attracted considerable interest because they have a large surface-to-volume ratio, which enables them to absorb more gases or test molecules or accept more measured gases or signals on their surfaces; thus, they can act as highly efficient

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sensors. ZnO-based nanostructured materials can be used as one of the promising materials for gas sensors to detect different volatile and toxic gases because of their electrochemical stability, nontoxicity, and low cost.<sup>(1–3)</sup> ZnO-based nanorods (or nanowires) are an excellent group of quasi-1D nanostructured materials.

There are many different physical and chemical methods of growing or synthesizing ZnO-based nanostructured materials. However, conventional methods need strictly controlled synthesis environments, complicated procedures, and expensive equipment, and some high-temperature synthesis processes.<sup>(4,5)</sup> For example, Scalisi *et al.* used metal organic chemical vapor deposition (MOCVD) to grow high-quality ZnO nanomaterials on various substrates.<sup>(6)</sup> However, the MOCVD system is expensive, has problems with toxic gases, and requires sensors for alarm to release toxic gases. The decomposition of zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2$ ) was investigated to fabricate high-purity ZnO nanowires in air ambient, but the precursors need to be decomposed at 300 °C.<sup>(7)</sup> In contrast to the above mentioned techniques, using an aqueous solution to synthesize and grow ZnO-based nanowires is a simpler and more cost-effective technique. This technique does not only have these disadvantages of expensive equipment, rigorous conditions, and complex processes, but also low-yield growth and high synthesis temperature.

The hydrothermal method is one of the most popular techniques using an aqueous solution to grow ZnO nanowires at low temperatures, and many different reagents have been used in this method. For example, Niarchos *et al.* used an alternative aqueous chemical growth (ACG) process to investigate a reliable and low-cost method, and they could grow large-scale ZnO nanorods on patterned Si substrates by a low-temperature process.<sup>(8)</sup> Li *et al.* used Zn foil and an aqueous  $\text{Na}_2\text{C}_2\text{O}_4$  solution to successfully synthesize ultralong ZnO nanowires by a simple hydrothermal reaction at 140 °C.<sup>(9)</sup> They also found that the grown ZnO nanowires could be used as sensors for  $\text{NH}_3$  and  $\text{N}(\text{C}_2\text{H}_5)_3$  vapors, and showed excellent response characteristics towards low concentrations of  $\text{NH}_3$  and  $\text{N}(\text{C}_2\text{H}_5)_3$  vapors. The detection limits for  $\text{NH}_3$  and  $\text{N}(\text{C}_2\text{H}_5)_3$  vapors at the working temperature of 180 °C are about 0.2 and 0.15 ppm, respectively.<sup>(9)</sup> Moreover, Hsu *et al.* used a vapor solid method to synthesize ZnO films at a temperature range of 400–700 °C on Si substrates and investigated them as humidity sensors.<sup>(10)</sup> ZnO nanostructures could also be grown on glass and  $\text{SiO}_2/\text{Si}$  substrates from an equimolar aqueous solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{12}\text{N}_4$  at temperatures below 100 °C.<sup>(11–14)</sup> Thus, the concentrations of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{12}\text{N}_4$  in deionized (DI) water were an important factor affecting the growth properties of the synthesized ZnO-based nanostructured materials.

Previously, we successfully investigated a two-step method of synthesizing pure ZnO nanostructured materials, where the sputtering method was used to deposit the seed ZnO films and the hydrothermal method was used to grow nanowires (nanorods) and nanoflowers.<sup>(12)</sup> Because we used  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{12}\text{N}_4$  as reagents and  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  or  $\text{In}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  as the dopant, we could synthesize Eu- and In-doped ZnO nanowires by the hydrothermal method. We also had found important novelties that the concentrations of  $\text{Eu}^{3+}$  and  $\text{In}^{3+}$  ions could reduce the required synthesis temperatures of ZnO-based nanowires and enhance their photoluminescence excitation (PLE) and photoluminescence (PL) emission properties.<sup>(13,14)</sup> We also found that if  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{12}\text{N}_4$  were used as reagents

to grow the ZnO nanostructured materials, the concentration of the diluted solution, growth temperature, growth time, and the position of the substrates were the important factors affecting the synthesis results. We would investigate the effects of these parameters on the morphologies and crystalline structures of the synthesized ZnO-based nanomaterials.

## 2. Experimental Procedure

Many studies have shown that to synthesize and uniformly grow highly c-oriented ZnO nanorods (nanowires), a low-temperature hydrothermal method of forming a ZnO seed layer is necessary. ZnO powder (purity 99.999%) was used as a raw material and polyvinyl alcohol (PVA) was used as the binder. After mixing ZnO and PVA, the mixture was pressed into pellets of 6 mm thickness and 56 mm diameter, and the pellets were heated to 600 °C to debinder PVA. Each pellet was sintered at 1100 °C for 2 h to form the ZnO ceramic target. The SiO<sub>2</sub>/Si substrates were cleaned with DI water, acetone, and isopropyl alcohol. The RF magnetron sputtering method was used to deposit the ZnO seed layers on SiO<sub>2</sub>/Si substrates. Then, the ZnO/SiO<sub>2</sub>/Si layers and the hydrothermal technique were used as the substrates and method, respectively, to grow pure (undoped) ZnO nanowires. Previously, we used a well-designed structure to grow ZnO-based nanostructured materials by a hydrothermal method.<sup>(12–14)</sup> In this study, we also used the designed structure to grow ZnO-based nanostructured materials and investigated growth temperature, the concentration of the diluted solution, growth time, and the position of the substrates. We used Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and C<sub>6</sub>H<sub>12</sub>N<sub>4</sub> as reagents and the hydrothermal method to synthesize ZnO-based nanostructured materials. We also investigated the effects of growth time, the position of the substrates, and concentrations of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and C<sub>6</sub>H<sub>12</sub>N<sub>4</sub> to determine their relationships with the growth of nanostructured materials. First, Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and C<sub>6</sub>H<sub>12</sub>N<sub>4</sub> were mixed with DI water with the desired compositions of 0.01, 0.05, and 0.1 M. The ZnO nanomaterials were also synthesized at temperatures of 80, 100, and 120 °C with different durations by a hydrothermal method. Also, the positions of the SiO<sub>2</sub>/Si substrates on the carry sheet glass are shown in Fig. 1. The crystalline structures of the synthesized Ca<sub>2</sub>ZnMoO<sub>6</sub> powders were measured using X-ray diffraction (XRD)

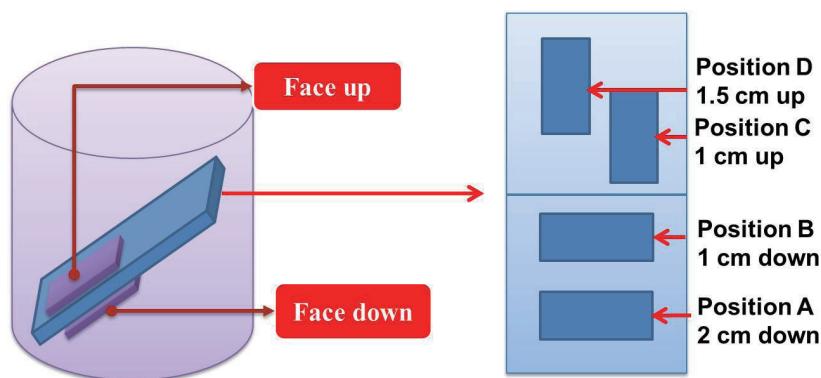


Fig. 1. Positions of SiO<sub>2</sub>/Si substrates on carry sheet glass.

patterns with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at a scanning speed of  $2^\circ$  per min. Scanning electron microscopy was carried out to observe the morphologies of all the synthesized ZnO nanomaterials with an acceleration voltage of 10 kV.

### 3. Results and Discussion

The general surface morphologies of the hydrothermally synthesized ZnO nanomaterials were examined by field-emission scanning electron microscopy (FESEM). Figure 2 shows the surface morphologies of the ZnO nanomaterials with different magnifications and synthesized at different durations, and the solution was 0.01 M with face up at position D. As shown in Fig. 1, regardless of whether the ZnO/SiO<sub>2</sub>/Si substrates were face down (not shown here) or face up, no ZnO nanowires were formed and nanoscale particles were formed and dispersed on the surfaces of the substrates. When the growth time was 3 h, as shown in Figs. 2(a) and 2(b), microscale rhombus or lozenge particles were formed, and as more rhombus or lozenge particles aggregated together, they would form a microscale flower. When the synthesis time was increased to 5 h, as shown in Figs. 2(c) and 2(d), the lengths of the microscale rhombus or lozenge particles increased and the particles changed into microscale cicada-pupa-structured particles. As shown in Figs. 2(b) and 2(d), the rhombus or cicada-pupa-structured particles were bound with the nondiscerned nanowires, which did not have hexagonal prismatic structures.

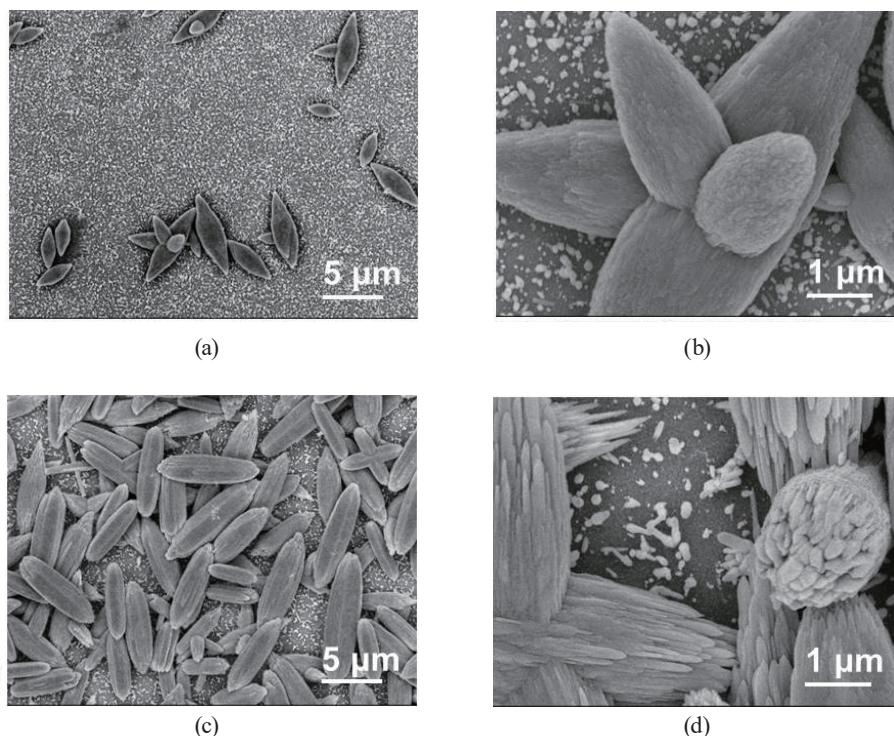


Fig. 2. Surface morphologies of ZnO films with different magnifications and synthesized at different durations. The solution was 0.01 M with face up. (a) and (b) 3 h with lower and higher magnifications and (c) and (d) 5 h with lower and higher magnifications, respectively.

To grow ZnO nanomaterials,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  [or  $\text{Zn}(\text{NO}_3)_2$ ] was used as the source material. When hexamethylenetetramine [ $(\text{CH}_2)_6\text{N}_4$ , HMT] was added into the solution at room temperature, no precipitates were formed and sank to deposit on the substrates as they were initially mixed. When the temperature was increased to around  $100^\circ\text{C}$ , the HMT began to decompose into  $\text{NH}_3$  and  $\text{HCHO}$ , and  $\text{OH}^-$  ions were formed because  $\text{NH}_3$  would react with  $\text{H}_2\text{O}$  to form  $\text{NH}_3 \cdot \text{H}_2\text{O}$  and then decomposed into  $\text{NH}^{+4}$  and  $\text{OH}^-$  ions. The  $\text{Zn}^{2+}$  ions would react with  $\text{OH}^-$  and  $\text{Zn}(\text{OH})_2$  precipitated. Because the mixed solution was heated,  $\text{Zn}(\text{OH})_2$  would decompose into  $\text{ZnO}$  and  $\text{H}_2\text{O}$ , and  $\text{ZnO}$  nuclei precipitated and were synthesized to form the  $\text{ZnO}$  nanomaterials on the substrates. These can be represented by the following reactions:



The theorem of the hydrothermal method uses low temperatures and high pressures to obtain nondissolved or hardly dissolved solutes depending on their dissolutions in water. If the solutes used can be easily dissolved in water, for example, nitrates [ $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is used in this study], their concentrations can be easily controlled and the hydrothermal temperatures will be lower. When the hydrothermal method is used to synthesize the  $\text{ZnO}$ -based nanomaterials, the difference in temperature in the hydrothermal bottle will cause the water convection to form the saturated solution and then precipitates will grow into the designed crystals. During the precipitate concentration, temperature, hydrogen ion exponent (PH), and the amount of added dopant are the parameters for controlling the growth of (hetero-) nucleation on the substrates. Liu *et al.* found that when the hydrothermal method was used to synthesize the  $\text{ZnO}$  nanostructured materials, the hydrophilic terminal hydroxyl groups of polyethylene glycol would be adsorbed on HMT-chelated Zn oligomers.<sup>(15)</sup> For that, the rather hydrophobic oxyethylene chain would be exposed to the 2-methoxyethanol and the micelles formed would act as microreactors, in which the Zn oligomers were enveloped.<sup>(15)</sup> Because of that, the  $\text{ZnO}$  nanowires were not easily formed. As the composition was 0.01 M, the concentration was very low, and the  $\text{ZnO}$ -based nanomaterials could not grow or be synthesized in the vertical direction and could only precipitate and aggregate in the horizontal direction.

To investigate the effect of synthesis temperature on the growth properties of hydrothermally grown  $\text{ZnO}$  nanomaterials, the synthesis temperature was set at  $120^\circ\text{C}$ . Previously, we found that when undoped  $\text{ZnO}$  nanomaterials were grown at  $80^\circ\text{C}$ , no  $\text{ZnO}$  nanowires were formed on the  $\text{ZnO}/\text{SiO}_2/\text{Si}$  substrates and only irregular  $\text{ZnO}$  nanoparticles were observed (not shown here).<sup>(14)</sup> When the synthesis temperature was  $100^\circ\text{C}$ ,  $\text{ZnO}$  nanowires were successfully grown

on the ZnO/SiO<sub>2</sub>/Si substrates, and the diameters of the synthesized ZnO nanowires were in the range of 80–120 nm (not shown here).<sup>(14)</sup> The surface morphologies of the 120 °C-synthesized ZnO nanomaterials are shown in Fig. 3(a) with face up and in Fig. 3(b) with face down, and the solution used was 0.1 M, the synthesis time was 3 h, and the substrate was located at point D (Fig. 1). As shown in Fig. 3(a), only disk-type particles were observed, and as shown in Fig. 3(b), large aggregated particles were formed on the nanoscale particles. However, the ZnO nanowires were not synthesized and formed as the synthesis temperature was 120 °C. The reasons for this are that the ZnO nuclei precipitate rapidly, they have insufficient time to carry out the self-assembly process, and no ZnO nanowires were formed.

The surface morphologies of the ZnO nanomaterials with a synthesis time of 3 h, a temperature of 100 °C, a solution of 0.1 M, and SiO<sub>2</sub>/Si substrates at different positions on the carry sheet glass are shown in Fig. 4. When the SiO<sub>2</sub>/Si substrate was placed at points A and B, the hexagonal prismlike microscale wires (or rods) in the horizontal direction were obtained. For the substrates located at points A and B, the lengths of the microscale wires ranged from 5 to 17 μm and 8 to 25 μm, as shown in Figs. 4(a) and 4(c), and the diameters were about 3 and 4 μm, as shown in Figs. 4(b) and 4(d), respectively. The results shown in Figs. 4(b) and 4(d) prove that the hexagonal prismlike rods are assembled or accumulated by the small nanoscale particles. A comparison of the results shown in Figs. 4(b) and 4(d) suggests that hexagonal prismlike rods with the substrate located at point A had poorer growth properties than those with the substrate located at point B, and the reason will be discussed later.

Figure 5 shows the surface morphologies of the ZnO nanostructured materials with different magnifications. The synthesis time was 3 h, the solution was 0.1 M, and the substrate was face up and located at point D. The SEM images of the sample shown in Fig. 5 reveal that not only the ZnO nanowires of 40–120 nm diameter were really observed, but also large particles or aggregated clusters were formed above the layer of uniform nanowires. The high-magnification image in Fig. 5(b) shows that the clusters were composed of rectangular or cubic crystals with a side length of 200–800 nm and Fig. 5(c) shows that the large particles also had rectangular or cubic structures with the a side length of 1200–2000 nm.

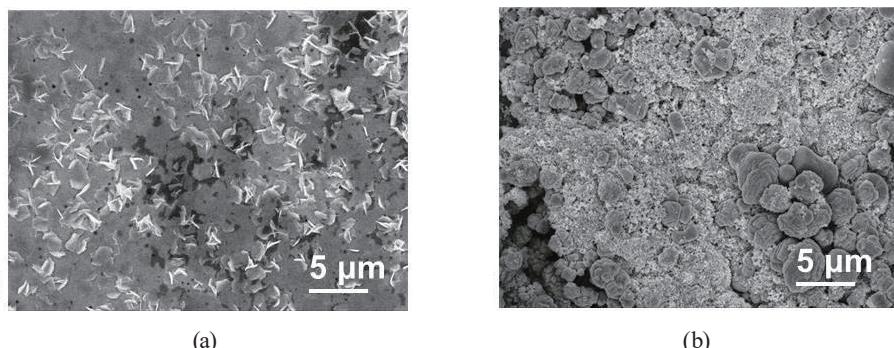


Fig. 3. Surface morphologies of 120 °C-synthesized ZnO nanomaterials. The solution was 0.1 M with (a) face up and (b) face down.

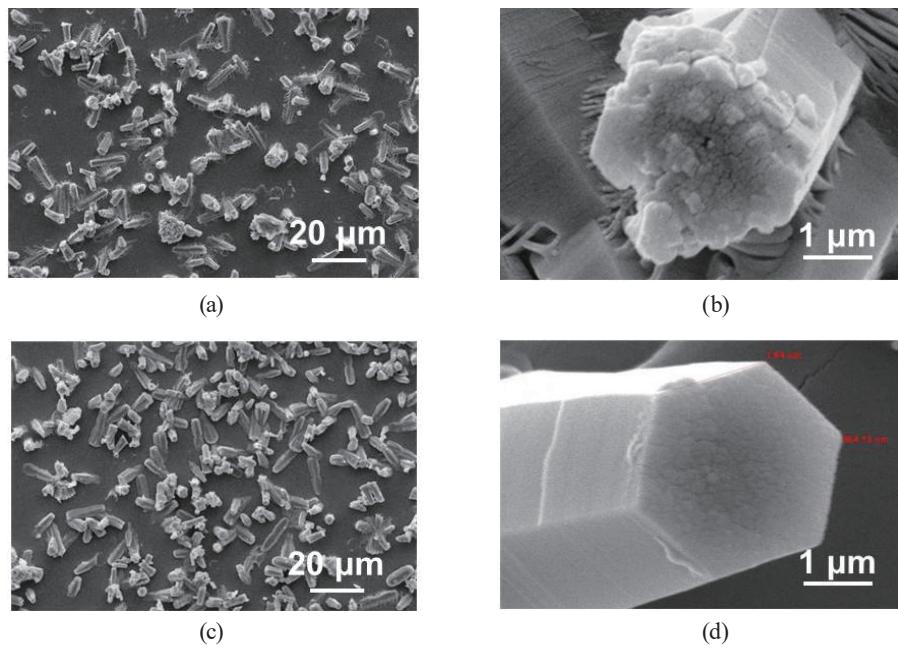


Fig. 4. Surface morphologies of ZnO nanomaterials with different magnifications. The synthesis time was 3 h, the solution was 0.1 M, and the SiO<sub>2</sub>/Si substrates were located at different positions (Fig. 1) on the carry sheet glass. (a) and (b) Substrates located at position A. (c) and (d) Substrates located at position B.

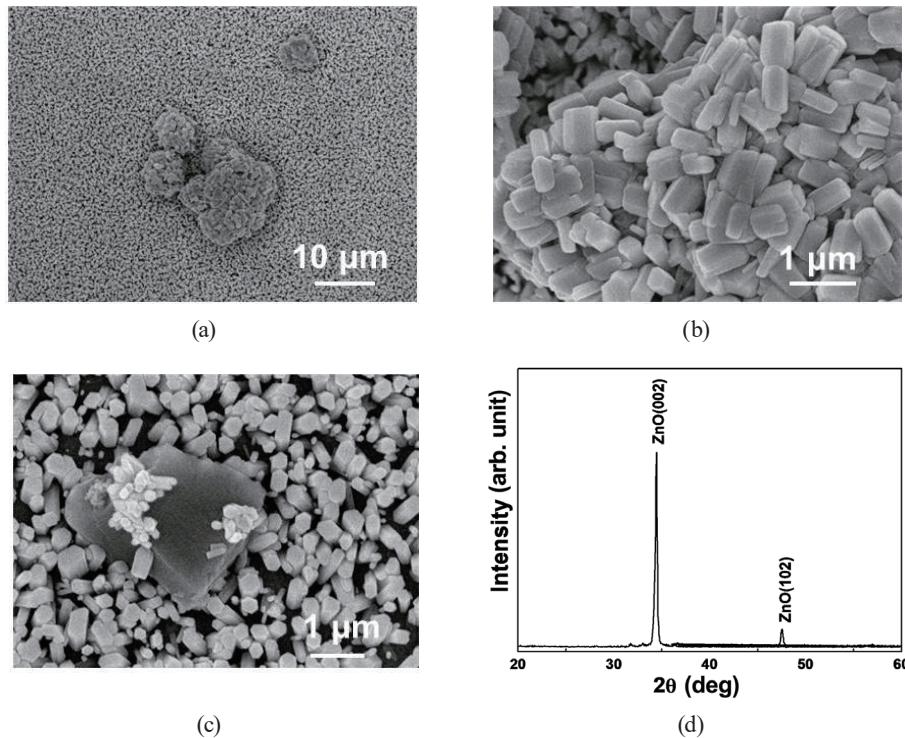


Fig. 5. Surface morphologies of the ZnO films with different magnifications. The synthesis time was 3 h and the solution was 0.1 M and face up. (a) Low magnification, (b) and (c) high magnification at different positions, and (d) XRD pattern.

Figure 5(d) shows the XRD patterns of the ZnO nanostructured materials shown in Figs. 5(a)–5(c). They show that the nanomaterials have a hexagonal wurtzite structure. The pattern is in agreement with the diffraction data from the standard card (JCPDS) with No. 36-1451. Even when the (102) diffraction peak coexisted with the (002) diffraction peak, the (002) diffraction peak has a higher diffraction intensity, suggesting that the nanomaterials are c-oriented. Thus, these results in Figs. 2–5 prove that synthesis temperature, face up or face down, and the position of the SiO<sub>2</sub>/Si substrate are the important parameters that affect the morphology as well as crystal orientation of the ZnO-based microscale or nanostructured materials. These results also suggest that if the substrate is located at a higher position (position C or D in Fig. 1), the hydrothermal method can be used to synthesize ZnO-based nanomaterials with better assembly and crystallization properties.

Figures 6 and 7 show the surface morphologies and XRD patterns of the ZnO nanomaterials with a synthesis time of 3 h. The solution was 0.1 M and face up, and the substrates were located at positions C and D, respectively. The results in Figs. 6(a) and 7(a) show that the ZnO nanowires were also formed and had a hexagonal wurtzite structure, with an easily discerned

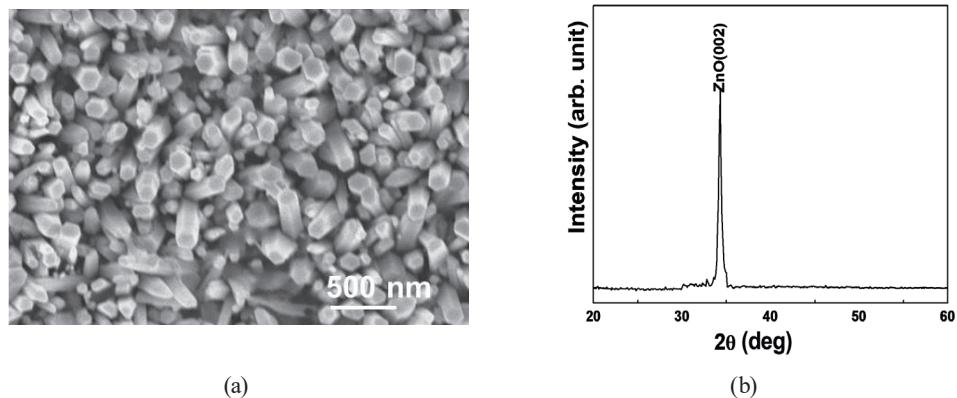


Fig. 6. (a) Surface morphology and (b) XRD pattern of ZnO nanomaterials with synthesis time of 3 h. The solution was 0.1 M and face up, and the substrates were located at position C.

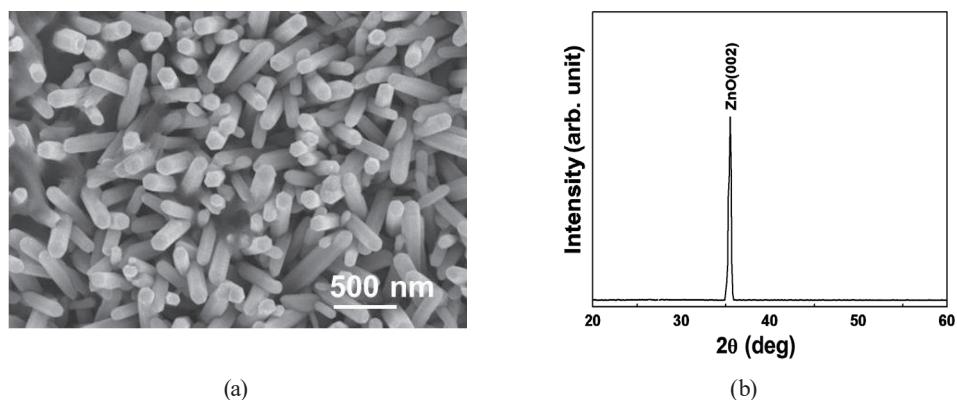


Fig. 7. (a) Surface morphology and (b) XRD pattern of ZnO nanomaterials with synthesis time of 3 h. The solution was 0.1 M and face up, and the substrates were located at position D.

hexagonal prism arrangement. The reason for the different morphologies of the synthesized ZnO-based nanomaterials obtained on the two faces is related to the nucleation mechanism in the solution.

When the hydrothermal method is used to synthesize the nanomaterials, nucleation is the first step in the formation of either a new thermodynamic phase or a new structure via self-assembly or self-organization. Thus, as the  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{12}\text{N}_4$  solutions are used to synthesize ZnO-based nanomaterials, two nucleation mechanisms, heterogeneous nucleation and homogeneous nucleation, will form during the synthesis process.<sup>(16)</sup> In heterogeneous nucleation, the nucleus is at the surface, which is much more common than homogeneous nucleation. In this research, we have proven in Fig. 2 that as the concentration of  $\text{Zn}^{3+}$  ions is 0.01 M, the synthesis temperature is 100 °C, and the  $\text{SiO}_2/\text{Si}$  substrate is face up or face down. At the lower position of the solution (carry sheet glass), the heterogeneous nucleation in the horizontal direction dominates the synthesis results of the ZnO nanomaterials.

As the concentration of  $\text{Zn}^{3+}$  ions is 0.1 M, the synthesis temperature is 120 °C, and the  $\text{SiO}_2/\text{Si}$  substrate is face up or face down. At the upper positions (points C and D) of the solution, the ZnO precipitate will deposit rapidly and no nucleation is formed. Because the nucleation mechanism cannot control the synthesis results of ZnO nanomaterials, no nucleation is formed during the self-assembly process and no ZnO nanomaterials are formed, as shown in Fig. 3. Thus, the results shown in Figs. 2–4 suggest that as the  $\text{SiO}_2/\text{Si}$  substrate is face down and the other parameters are unchanged, the synthesis results of ZnO nanomaterials can be controlled by heterogeneous nucleation. When the concentration of  $[\text{Zn}(\text{OH})_4]^{2-}$  ions is higher than the critical solubility,  $\text{Zn}^{2+}$  ions will directly transform into ZnO nuclei.<sup>(17,18)</sup> After that, more  $[\text{Zn}(\text{OH})_4]^{2-}$  complexes are preferably adsorbed and grow on the surfaces of ZnO nuclei, which are beneficial for enhancing the growth properties of ZnO-based nanomaterials (or nanowires) along the c-axis direction; the XRD patterns shown in Figs. 6(a) and 7(a) prove these results. When the concentration of  $[\text{Zn}(\text{OH})_4]^{2-}$  ions is relatively insufficient, the  $\text{C}_6\text{H}_{12}\text{N}_4$  molecules will occupy the dominant position and serve as structure-directing and assembling agents to some extent, and result in the formation of nutlike, hexagonal spherelike, oblatelike, and flowerlike structures.<sup>(18,19)</sup>

#### 4. Conclusions

We found that the synthesis temperature and time of 100 °C and for 3 h, respectively, were the optimum parameters for growing pure ZnO nanowires. As the solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{C}_6\text{H}_{12}\text{N}_4$  was 0.01 M, microscale rhombus or lozenge particles were formed. When more rhombus or lozenge particles were aggregated, they would form a microscale flower. As ZnO nanomaterials were synthesized at 120 °C, with face up and face down, the solution of 0.1 M, and the synthesis time of 3 h, only disk-type particles were observed and large aggregated particles were formed on the nanoscale particles. As the substrate was shifted from the lower position to the higher one, and the synthesis parameters were 100 °C, with face up and face down, 0.1 M, and 3 h, ZnO nanowires were also formed and had a hexagonal wurtzite structure, with an easily discerned hexagonal prism arrangement.

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