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Research Article

Fabrication and Superhydrophobic Property of ZnO Micro/Nanocrystals via a Hydrothermal Route

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Superhydrophobic ZnO micro/nanocrystals were fabricated on a large scale using a facile one-pot hydrothermal process successfully. The morphologies and chemical composition of as-synthesized ZnO were investigated by the scanning electron microscope (SEM) and X-ray powder diffraction (XRD). The morphology of ZnO products changed from uniform size microrods to flower-like micronanostructures, when the temperature changed from 120°C to 180°C. The morphology of ZnO was strongly affected by the pH. The wettability of the as-synthesized ZnO micro/nanocrystals was studied by measuring water contact angle (CA). The largest static CA for water is 167°, which is closely related to both the ZnO micro/nanostructure and chemical modification. Furthermore, the as-prepared ZnO surface showed superhydrophobicity for some corrosive liquids such as basic and acidic aqueous solutions. The CAs of the surface modified with ZnO prepared at 160°C were over 155° in the range of pH = 1–13.

1. Introduction

In the past decade, the synthesis of functional nanostructures and their important applications have attracted great concern [1–7]. Semiconductor oxide nanomaterials such as ZnO, Ga_2O_3, In_2O_3, and SnO_2 have become a hot research topic for their widely used applications in transparent conductive film, optoelectronic devices, and gas sensing [8–11]. Among them, ZnO attracted more interest for the applications in low voltage, light-emitting diodes and diode lasers [12], a solar cell [13], the photocatalyst [14], and so forth. Most of all, Fortunato et al. reported the Ga-doped ZnO films prepared by RF magnetron sputtering, which is the first report of exploiting the GZO [15].

Currently, many interesting ZnO nanostructures such as nanobelt, nanosheet, and nanobridge structures have been synthesized by oxide thermal evaporation manner [16–18]. ZnO nanowires and nanorods prepared by solvothermal method have also been reported [19–21]. Various techniques that synthesize ZnO nanostructures have been developed, where hydrothermal method is very attractive owing to their low cost, catalyst-free state, and scalable synthesis [22, 23]. However, toxic, hazardous, and expensive reagents such as amines were inevitably used during the solvothermal process. In this paper, we adopt a more energy saving hydrothermal method (the assisted hydrothermal route) to synthesize ZnO micro/nanomaterials at low temperature without any toxic, hazardous, and expensive reagents and demonstrate their potential superhydrophobic property of the rough surface that is constructed by ZnO micro/nanomaterials. The products were characterized by XRD and SEM. We suppose that this method of preparation of superhydrophobic surface of ZnO may provide guidance for the preparation of other functional inorganic materials.

2. Experimental

2.1. Synthesis. All the chemicals used for synthesis of the ZnO were of analytical grade and used as received without any further purification. Growth of ZnO micro/nanocrystals was performed by a PEG1000 assisted hydrothermal method.

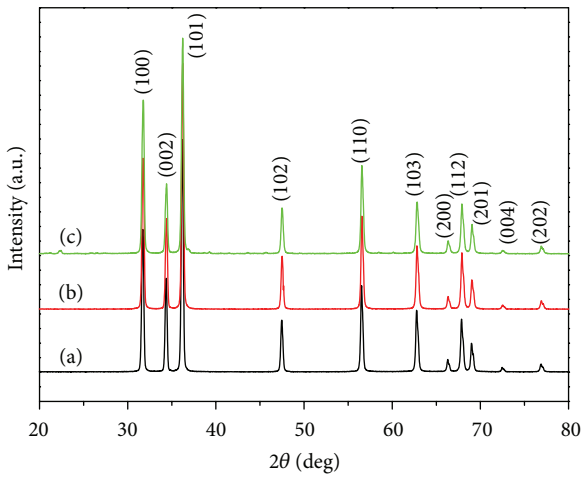

Figure 1: XRD patterns of ZnO samples prepared at different temperatures: (a) 120°C, (b) 160°C, and (c) 180°C.

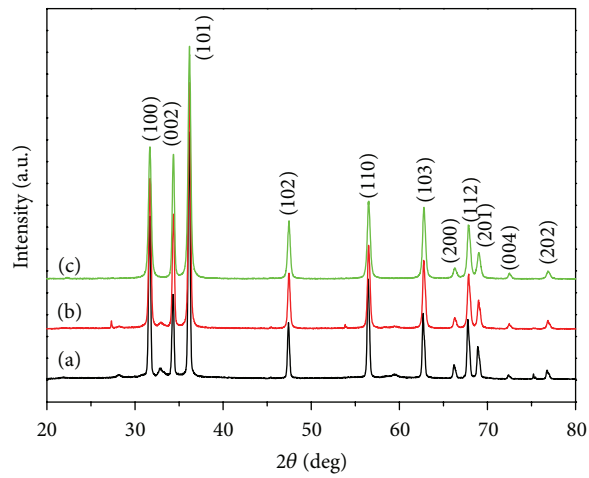

Figure 2: XRD patterns of ZnO samples prepared at 120°C with different pH values: (a) pH = 8, (b) pH = 10, and (c) pH = 12.

In a typical synthesis, 0.6 g $Zn(CH_3COO)_2{\cdot}2H_2O$ was added to 6 mL deionized water to form precursor solution, and 10 mL NaOH solution was added into above solution with stirring to form white suspension. Then, 0.1 g PEG1000 was added to the white suspension. After stirring for 30 min at room temperature, adjust the pH value of the solution to 8 with 1 mol/L of HCl solution. The mixture was transferred to and sealed in a teflon-lined autoclave; the autoclave was sealed and maintained at 140°C for 24 h. The products were spontaneously cooled to room temperature in the furnace to get the ZnO micro/nanomaterials samples. The products were collected by centrifugation and washed with deionized water and absolute alcohol. The final samples were obtained after drying at 60°C for 12 h in vacuum. With a similar procedure, the other samples were prepared by adjusting the pH values of the solution to 10 and 12 with HCl solution, respectively. Then, we study the characterization of the ZnO.

2.2. Characterization. The morphologies of ZnO samples were characterized by scanning electron microscopy (SEM, JSM-6700F). The phase analysis was performed by X-ray diffractometer (XRD). The XRD patterns were measured on a MiniFlex2 goniometer, employing a scanning rate of $0.02^\circ\ s^{-1}$ in the 2θ range from 5° to 70°, and the operating voltage and current were maintained at 30 kV and 15 mA, respectively. Water contact angle (CA) and sliding angle measurements were carried out by using a Model 250 (p/n 250-F1) goniometer (ramé-hart instrument Co, USA) at ambient temperature. Water droplets (5 uL) were carefully dropped onto the surfaces, and the average value of five measurements obtained at different positions in the samples was used as the final contact angle.

3. Results and Discussion

XRD was used to characterize the crystalline phase and purity of the sample. Figure 1 shows the XRD patterns of the as-synthesized ZnO products prepared at different temperature. All diffraction peaks are in good agreement with those in the JCPDS Card no. 36-1451. The indexed diffraction peaks can be ascribed to ZnO with a pure wurtzite structure [23] and lattice constants of $a = 3.250$ Å, $b = 3.250$ Å, and $c = 5.207$ Å. No diffraction peaks of impurities are observed, indicating that the pure ZnO micro/nanocrystals can be obtained by this method. As showed in Figure 1, the diffraction peak intensity and the half-peak width of ZnO prepared at different temperatures are comparable, which indicates that the reaction temperature has little effect on the crystallinity of ZnO.

The XRD patterns of the as-synthesized ZnO products at different pH values are shown in Figure 2. All diffraction peaks are in good agreement with those in the JCPDS Card no. 36-1451. The indexed diffraction peaks can be ascribed to ZnO with a pure wurtzite structure [24] and lattice constants of $a = 3.250$ Å, $b = 3.250$ Å, and $c = 5.207$ Å. No diffraction peaks of impurities are observed. The strong peak intensity of (002) revealed that the ZnO nanorods grew along the (001) direction [25]. As shown in Figure 2, the diffraction peak intensity and the half-peak width of ZnO prepared at different pH values are similar, which indicates that the pH has little effect on the crystallinity of ZnO. Thus, ZnO can be synthesized in a wide pH range.

SEM images of the as-synthesized ZnO products prepared at different temperatures are shown in Figure 3. As showed in Figure 3, when the reaction temperature was 120°C, ZnO products mainly consisted of uniform size microrods with the mean particle size of 6 μm (Figure 3(a)). With the increasing of the reaction temperature, ZnO nanorods appeared in the products (Figure 3(b)) and the microrods became shorter with the lengths of about 4 μm. When the reaction temperature was increased to 180°C, more ZnO nanorods were observed and formed flower-like micro/nanostructures (Figure 3(c)). The results suggested that the reaction temperature has an important influence on the morphology of the ZnO. Therefore, the changing of

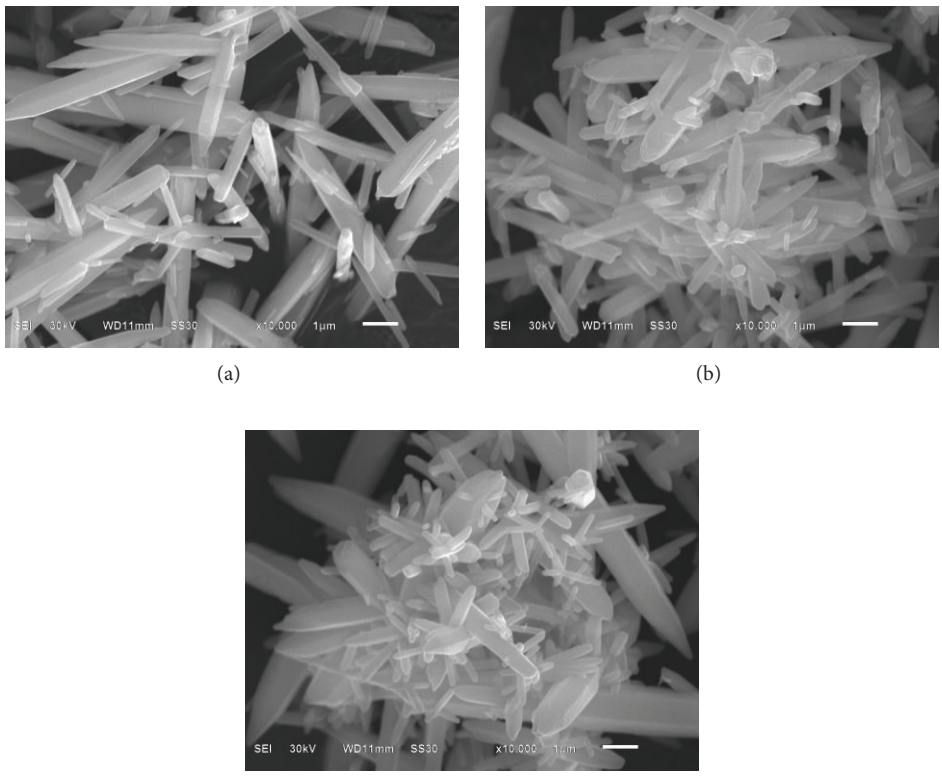

Figure 3: SEM images of ZnO samples prepared at different temperatures: (a) 120°C, (b) 160°C, and (c) 180°C.

the reaction temperature can change the morphology of ZnO products.

The SEM images of the as-synthesized ZnO products prepared at different temperatures are shown in Figure 4. When the pH value of the reaction solution was 12, morphology of the ZnO mainly consisted of uniform size composition leaves shaped nanosheets (Figure 4(c)). When the pH value of the reaction solution was 10, ZnO products mainly consisted of uniform size nanorods with length of 5 μm and the middle width of 200 nm in average (Figure 4(b)). When the reaction solution pH was decreased to 8, most of the obtained products were uniform nanorods with the lengths of about 1–10 μm and width of 120 nm in average as shown in Figure 4(a). Obviously, the pH value plays an important role in the morphological evolution of ZnO nanocrystals, especially in an alkaline environment. The decreasing of the pH value of reaction solution led to the formation of nanorods.

At the beginning of our experiment, OH^- is first introduced into the solution of Zn^{2+}, and $Zn(OH)_2$ colloid is produced. $Zn(OH)_2$ colloids can be decomposed into Zn^{2+} and OH^-. When the concentrations of Zn^{2+} and OH^- reach saturation, ZnO will be generated. There is a dissolution equilibrium between $[Zn(OH)_4]^{2-}$ and $Zn(OH)_2$. With increasing the concentration of OH^-, $[Zn(OH)_4]^{2-}$ will be obtained from the reaction of $Zn(OH)_2$ and OH^-. With increasing the concentration of Zn^{2+} in the solution, the reverse reaction of $[Zn(OH)_4]^{2-}$ will produce $Zn(OH)_2$, and ZnO will be obtained finally

$$Zn^{2+} + 2OH^- \longleftrightarrow Zn(OH)_2 \quad (1)$$

$$Zn(OH)_2 \longrightarrow Zn^{2+} + 2OH^- \quad (2)$$

$$Zn^{2+} + 2OH^- \longleftrightarrow ZnO \downarrow + H_2O \quad (3)$$

$$Zn(OH)_2 + 2OH^- \longleftrightarrow [Zn(OH)_4]^{2-} \quad (4)$$

The mechanism of this synthesis is not very clear yet, but, on the basis of the experimental results and observations, we propose a possible mechanism for the formation of the structure of ZnO obtained in our approach that is mainly caused by the effect of PEG1000. It is generally believed that PEG1000 can be adsorbed on the surface of ZnO material. When PEG1000 was adsorbed by ZnO surface, the activity of ZnO nanostructures in certain areas of the surface will be inhibited, so the growth rate of ZnO nanostructures in some directions will slow down (Figure 5). Thus, PEG1000 adding ZnO nuclei will change the growth kinetics, leading to the formation of the crystal growth anisotropy 1D ZnO nanostructures [26–28].

The corresponding surface wettability of the as-synthesized samples was studied by measuring the water CA using a water droplet (pH = 7) of 10 μL (Figure 6). The CA

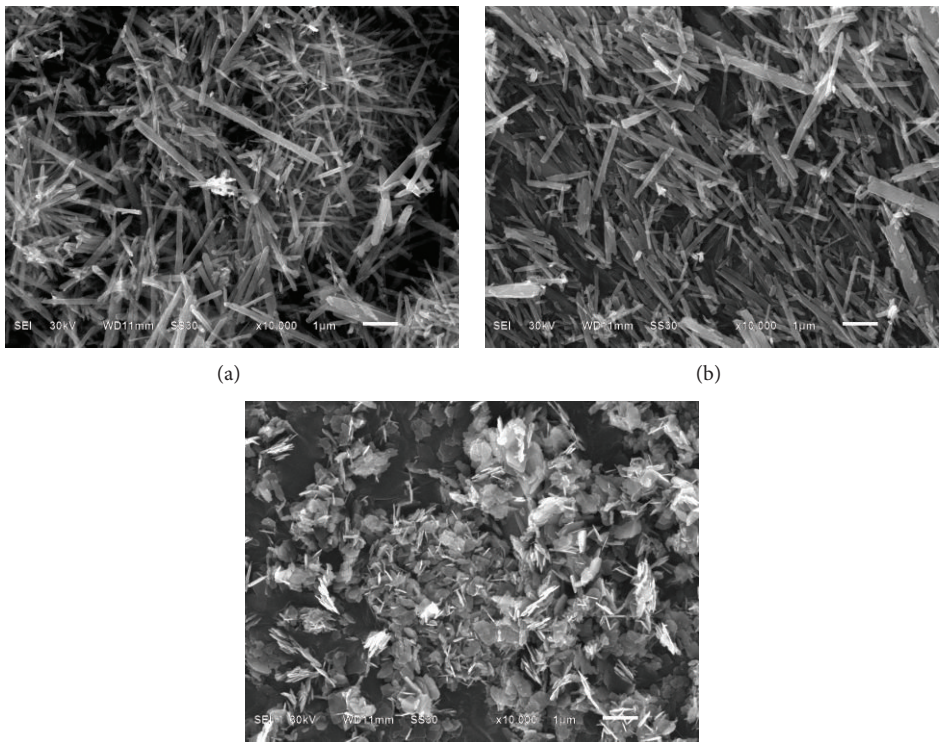

Figure 4: SEM images of ZnO samples prepared with different pH values: (a) pH = 8, (b) pH = 10, and (c) pH = 12.

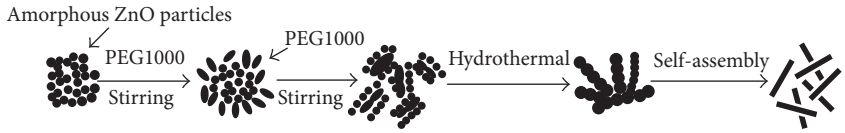

Figure 5: Illustration of the growth and self-assembly of the macro/nanorods.

values of the glass treated with as-synthesized samples doping with different amounts of methanol solution of 2% (v/v) PFOTS were measured. It is well known that the solid surfaces with contact angles over 150° are attributed to superhydrophobicity [29]. As showed in Figures 6(a)–6(c), the CA values of ZnO prepared at 120°C, 160°C, and 180°C are 167°, 163°, and 140°, respectively. In Figures 6(d)–6(f), the CA values of ZnO prepared with pH values of 8, 10, and 12 are 160°, 160°, and 161°, respectively. Experimental results show that the reaction temperature has an effect on the wetting property of ZnO. With the increasing of the reaction temperature, the contact angle becomes smaller. When the reaction temperature is increased to 180°C, ZnO structure rough surface does not have superhydrophobic properties. The pH value has little effect on the wetting property of ZnO. In the range of pH = 8–14, rough surface constructed by ZnO has a superhydrophobic property.

Figure 7 shows the relationship between pH values of the water droplet and the CA on the ZnO superhydrophobic surfaces prepared at different temperature. The figure shows that static CAs of ZnO superhydrophobic surface prepared at 120°C were over 150° in the range of pH = 3–13. The CAs of ZnO superhydrophobic surface prepared at 160°C were over 155° in the range of pH = 1–13.

Figure 8 shows the relationship between pH values of the water droplet and CA on the ZnO superhydrophobic surfaces prepared at different pH values. The curves of contact angles of the modified surfaces at different pH values show similar law. The CA increases with the pH value firstly and then decreases slowly. Static contact angles of ZnO superhydrophobic surface prepared at different pH values are all over 150°.

4. Conclusions

In this work, ZnO micro/nanocrystals were synthesized by a simple hydrothermal method assisted by PEG1000. The samples show excellent superhydrophobic property at different reaction temperatures and pH values. The results show that the ZnO materials present long-term stability in the air as well as excellent resistance to corrosive liquids, including weak acidic and alkaline solutions. Therefore, this kind of

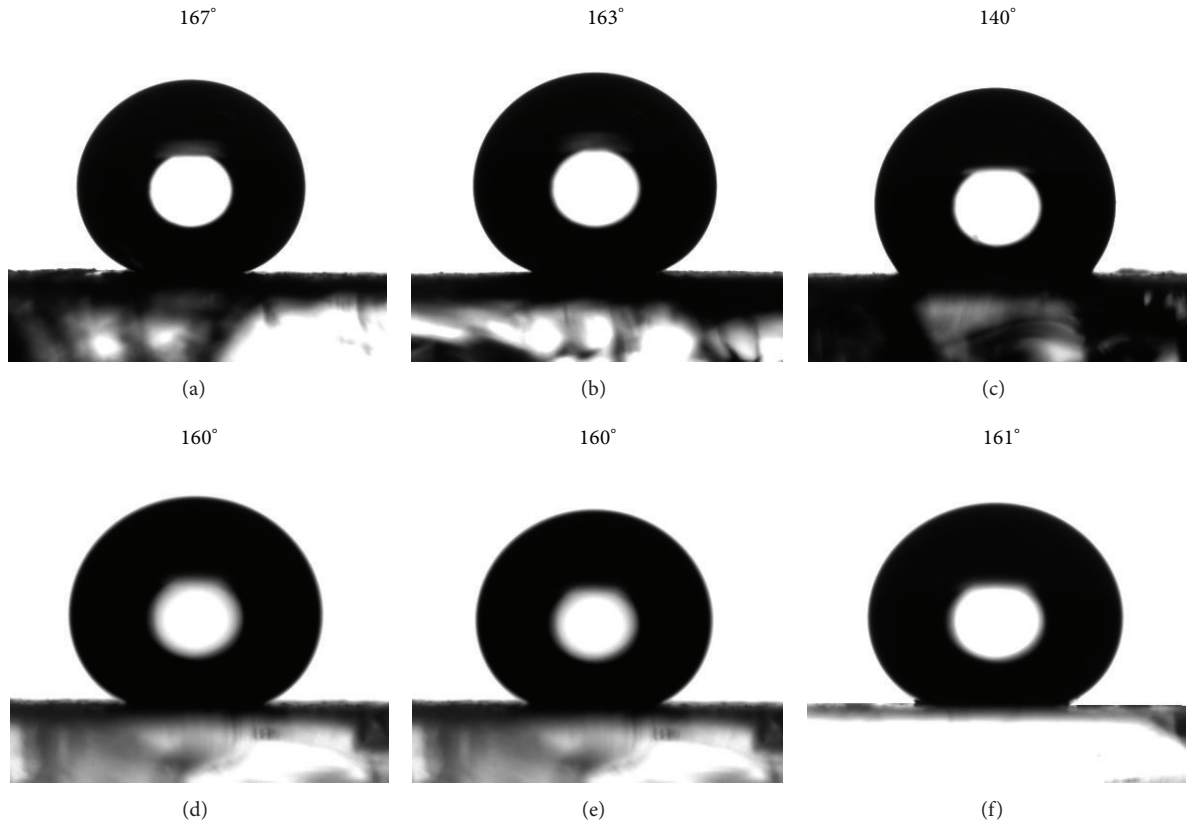

FIGURE 6: Wetting behavior of ZnO prepared at different temperatures: (a) 120°C, (b) 160°C, and (c) 180°C, and at 120°C with different pH values: (d) pH = 8, (e) pH = 10, and (f) pH = 12.

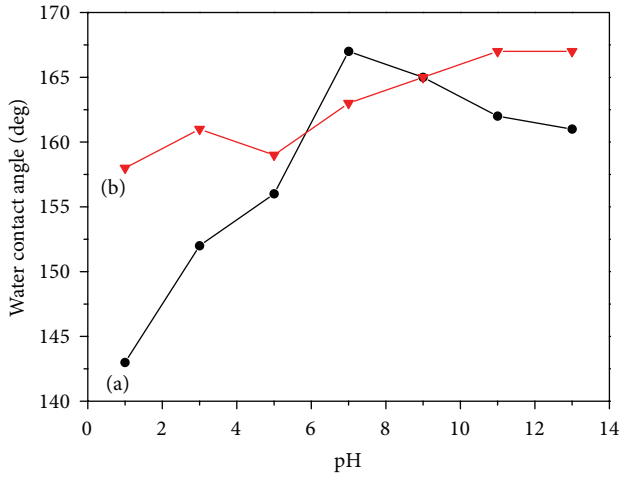

FIGURE 7: Water contact angles of the modified surface according to the pH of water droplet: ZnO prepared at (a) 120°C and (b) 160°C.

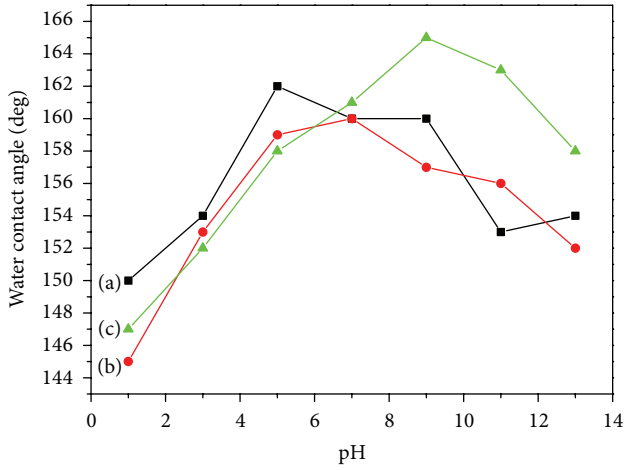

FIGURE 8: Water contact angles of the modified surface according to the pH of water droplet: ZnO prepared at 120°C with different pH values: (a) pH = 8, (b) pH = 10, and (c) pH = 12.

material may be a promising substitute for the conventional engineering materials.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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