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Hydrothermal synthesis of zinc oxide powders with controllable morphology

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Abstract

Crystalline zinc oxide powders with various morphologies have been prepared by hydrothermal treatment of zinc acetate in pure water, KOH or ammonia aqueous solution. It was found that the selected solvents play a different role in controlling the morphologies of the obtained powders. The variation of morphology of the obtained ZnO powder with solvents mainly depends on the different zinc species and their environment during the hydrothermal processing.

Keywords: D. Zinc oxide; Morphology; Hydrothermal method

1. Introduction

Recently, shape control has raised significant concern in the fabrication of semiconductor nanocrystals [1,2], metal nanocrystals [3,4], and other inorganic materials such as $BaCrO_4$ and $BaSO_4$ [5,6], which may add alternative variables in tailoring the properties of these materials. Although several examples have been demonstrated, shape control has been somewhat difficult to achieve and turns out to be a great challenging problem for the future. Zinc oxide, an n-type II–VI compound semiconductor with a wide direct-band gap of 3.3 eV, has attracted more and more attention over the past few years because it can find applications in various fields, such as photosensitization, field emission display, gas sensors, varistors and transducers, etc [7]. However, in order to obtain ZnO powders with appropriate chemical, electrical and optical properties specific for their intended applications, control of morphology as well as chemical composition, purity and particle size during their synthesizing process is important. Up to now, different shapes of ZnO powders including prismatic [8], ellipsoidal [9], bi-pyramidal and dumbbell-like [10], nanowire [11], and nanorod [12] and so forth, had been prepared via different synthesis methods or under different preparation conditions. However, there is no systematic investigation in the effect of solvents on the morphology of ZnO powders.

As a method for preparing high-quality ceramic powders, the hydrothermal synthetic route [13,14] has advantages to obtain high-crystallized powders with narrow grain size-distribution and high purity without heat treatment at high temperature. [15,16] The particle properties such as morphology and size can be controlled via the hydrothermal process by adjusting the source species, reaction temperature and time, etc. Previous literatures [8–10] have proposed the hydrothermal process for the synthesis of ZnO oxide using the newly-prepared hydroxide colloids $Zn(OH)_2$ as a precursor or employing $Zn(CH_3COO)_2$ by the pressure-relief method. In this paper, we shall report the synthesis of ZnO oxide directly by hydrothermal treatment of $Zn(CH_3COO)_2$ in pure water, potassium hydroxide or ammonia solutions. This study was aimed at preparation of ZnO particles with controllable morphologies by a simple hydrothermal method. The effects of the solvents including water, potassium hydroxide and ammonia solutions on the morphology of as-prepared ZnO powders have been examined in detail.

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2. Experimental

Analytical grade zinc acetate was adopted as the source material for zinc species. Zinc acetate was dissolved in deionized water for preparing zinc cation solution. Deionized water, potassium hydroxide (0.25–2.00 mol/l) and ammonia solution (0.025–0.20 mol/l) are employed as the solvents. In a typical procedure, the solvent (26 ml) was added to a Teflon-lined autoclave of 40 ml capacity filled with $Zn(CH_3COO)_2$ solution (1.0 mol/l, 6.5 ml) while stirring vigorously. The autoclave was maintained at 200 °C for 2 h and then air cooled to room temperature. The precipitate was flitted off, washed with deionized water. The white products were dried in air at 120 °C for 30 min.

The products were characterized by X-ray powder diffraction (XRD, Japan Rigaku D/Max-3C) in the 2θ ranges from 20 to 80°, using a diffractometer equipped with a graphite monochromatized Cu K_α radiation ($\lambda = 1.5405$ Å). The scanning electron microcopy (SEM) images were conducted on a Hitachi SEM S-3500N.

3. Results and discussion

The typical XRD patterns for the ZnO powders obtained in different solvents are shown in Fig. 1. The sharp diffraction peaks of the powders imply their good crystallinity. All diffraction peaks in the XRD patterns of as-prepared ZnO powders can be assigned to the hexagonal structure (JCPDS 36-1451). Although the relative intensities of diffraction peaks vary slightly, the XRD patterns of other samples obtained in KOH and NH_3H_2O solutions of different concentrations (KOH: 0.25 – 2.00 mol/l, NH_3H_2O: 0.025 – 0.20 mol/l) are similar to Fig. 1, which indicates that phase-pure hexagonal structure ZnO has been successfully synthesized in various solutions via this hydrothermal method at 200 °C.

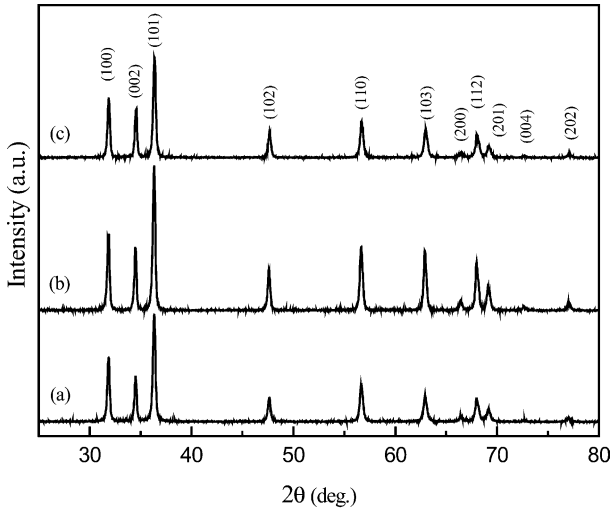


Fig. 1. XRD pattern of ZnO powder hydrothermally prepared at 200 °C for 2 h with (a) H_2O, (b) 0.50 mol/l KOH, (c) 0.025 mol/l $NH_3{\cdot}H_2O$.

The SEM image of the ZnO powders prepared by hydrothermal treatment of $Zn(CH_3COO)_2$ aqueous solution at 200 °C for 2 h is shown in Fig. 2. As can be seen, the shape of the obtained ZnO powders is pencil-like.

The SEM images of ZnO powders prepared in KOH solutions of different concentrations are shown in Fig. 3. It is observed that the morphology of the obtained ZnO particles changes in turn from twinned pyramidal, shortened prismatic, sheet-like to prismatic-like, as the concentration of KOH solutions varies from 0.25 to 2.00 mol/l.

According to the above results, it is concluded that the morphology of as-prepared ZnO powders markedly depends on the concentration of KOH solution. In different solvents, before the hydrothermal treatment, the zinc species and their environment in the reactor are different. In pure water, CH_3COO^- ions hydrolyze and release OH^- ions, then Zn^{2+} ions connect with OH^- and form $Zn(OH)_2$. However, due to the weak hydrolyzing ability of CH_3COO^- ions, Zn^{2+} ions are the main zinc species in solution.

$$CH_3COO^- + H_2O \leftrightarrow CH_3COOH + OH^-$$

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2\downarrow$$

In 0.25 mol/l KOH solution, the ratio of Zn^{2+} to OH^- is 1:1. The reaction in the solution can be expressed as following:

$$2Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)^2 \downarrow + Zn^{2+}$$

The newly formed $Zn(OH)_2$ and excessive Zn^{2+} co-exist in the solution.

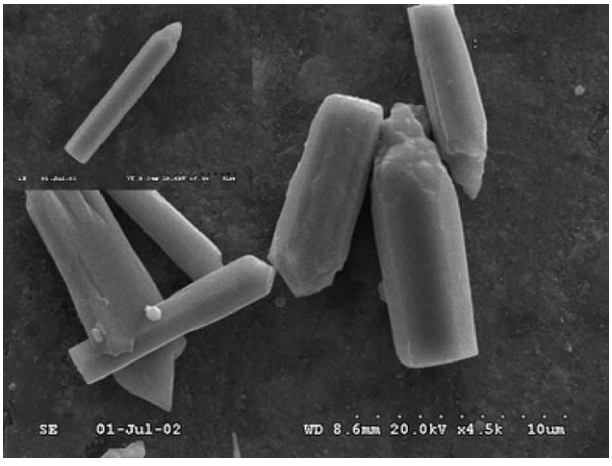


Fig. 2. SEM ZnO powder hydrothermally prepared at 200 °C for 2 h.

In 0.50 mol/l KOH solution, the ratio of Zn^{2+} to OH^- is just 1:2, then the OH^- ions completely precipitate the Zn^{2+} ions and form $Zn(OH)_2$.

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2\downarrow$$

In 1.00 mol/l KOH solution, the ratio of Zn^{2+} to OH^- is 1:4. The following reactions may happen in the solution:

$$Zn^{2+} + 2OH^- \leftrightarrow Zn(OH)_2\downarrow$$

$$Zn(OH)^2 + 2OH^- \leftrightarrow Zn(OH)_4^{2-}$$

The medial product $Zn(OH)_2$ dissolves in the alkali solution and forms $Zn(OH)_4^{2-}$ complexes in the solution. When the concentration of KOH solution increases to 2.00 mol/l, the ratio of Zn^{2+} to OH^- is 1:8, the $Zn(OH)_4^{2-}$ complexes are surrounded by a large amount of OH^-.

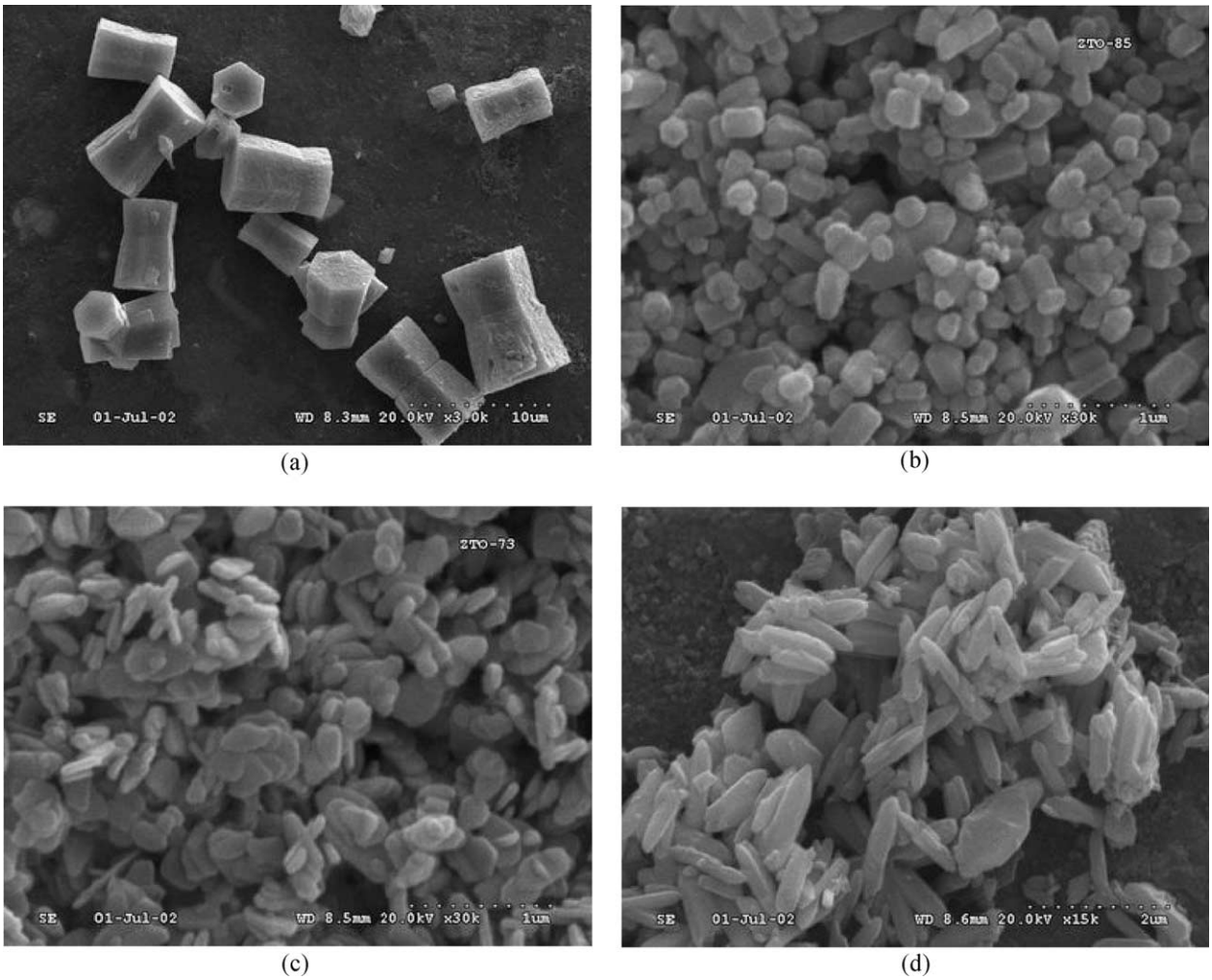
From the above analysis, it is obvious that before the hydrothermal treatment the initial zinc species and their environment such as the concentration of K^+ and/or OH^- in the reactor are varied with the variation in the concentration of KOH solution (see Table 1). The nucleation and growth of ZnO crystal is related to the initial zinc species and their environment in the reactor and affects the morphology of as-formed ZnO powder [14].

However, then, in the hydrothermal process, $Zn(OH)_2$ precipitates dissolve in the supersaturated solution. Zn^{2+} complex with OH^- ions and form $Zn(OH)_4^{2-}$:

$$Zn(OH)_2 + 2H_2O \leftrightarrow Zn^{2+} + 2OH^- + 2H_2O$$

$$\leftrightarrow Zn(OH)_4^{2-} + 2H^+$$

Then, due to heat convection, diffusion of ions and deregulation movement among molecules and ions in the solution, the clusters $Zn_xO_y(OH)_z^{(z+2y-2x)-}$ are formed by the dehydration reaction of $Zn(OH)_4^{2-}$. When the particle size of the cluster $Zn_xO_y(OH)_z^{(z+2y-2x)-}$ reaches a certain value, the ZnO nucleus is formed and then the ZnO is precipitated [14]. In these processes, the



(a) (b) (c) (d)

Fig. 3. SEM of the samples hydrothermally prepared at 200 °C for 2 h with (a) 0.25, (b) 0.50, (c) 1.00, (d) 2.00 mol/l KOH.

Zn^{2+} species and their environment are key parameters in formation and growth of ZnO nucleus. Therefore, for better governing the morphology of ZnO powder, the nucleation and growth during hydrothermal processing should be precisely controlled by adjusting the concentration of the solvent.

The SEM images of ZnO powders obtained in ammonia solution of different concentrations are illustrated in Fig. 4. As can be seen from Fig. 4, the shapes of as-prepared ZnO particles change from ellipsoidal to long prism-like with increasing concentration of ammonia solution. The aspect ratio of ZnO particles is found to increase by raising the concentration of ammonia solution. This high aspect ratio of ZnO powder prepared in the range of high concentration of ammonia solution is related to its preferential growth in *c*-axis. Moreover, the shapes of as-prepared ZnO particles in ammonia solution are different from those obtained in

Table 1
Dominating zinc species and their environment in KOH solutions of different concentrations and corresponding morphology of the resultant ZnO powders

KOH concentration (mol/l)	Zn^{2+}:OH^-	Dominating zinc species and their environment	Morphologies
0 (pure water)	–	Zn^{2+}	Pencil-like
0.25	1 : 1	$Zn(OH)_2$, Zn^{2+}, K^+	Twinned pyramidal-like
0.50	1 : 2	$Zn(OH)_2$, K^+	Shortened prismatic-like
1.00	1 : 4	$Zn(OH)_4^{2-}$, K^+	Sheet-like
2.00	1 : 8	$Zn(OH)_4^{2-}$, K^+, OH^-	Prismatic-like

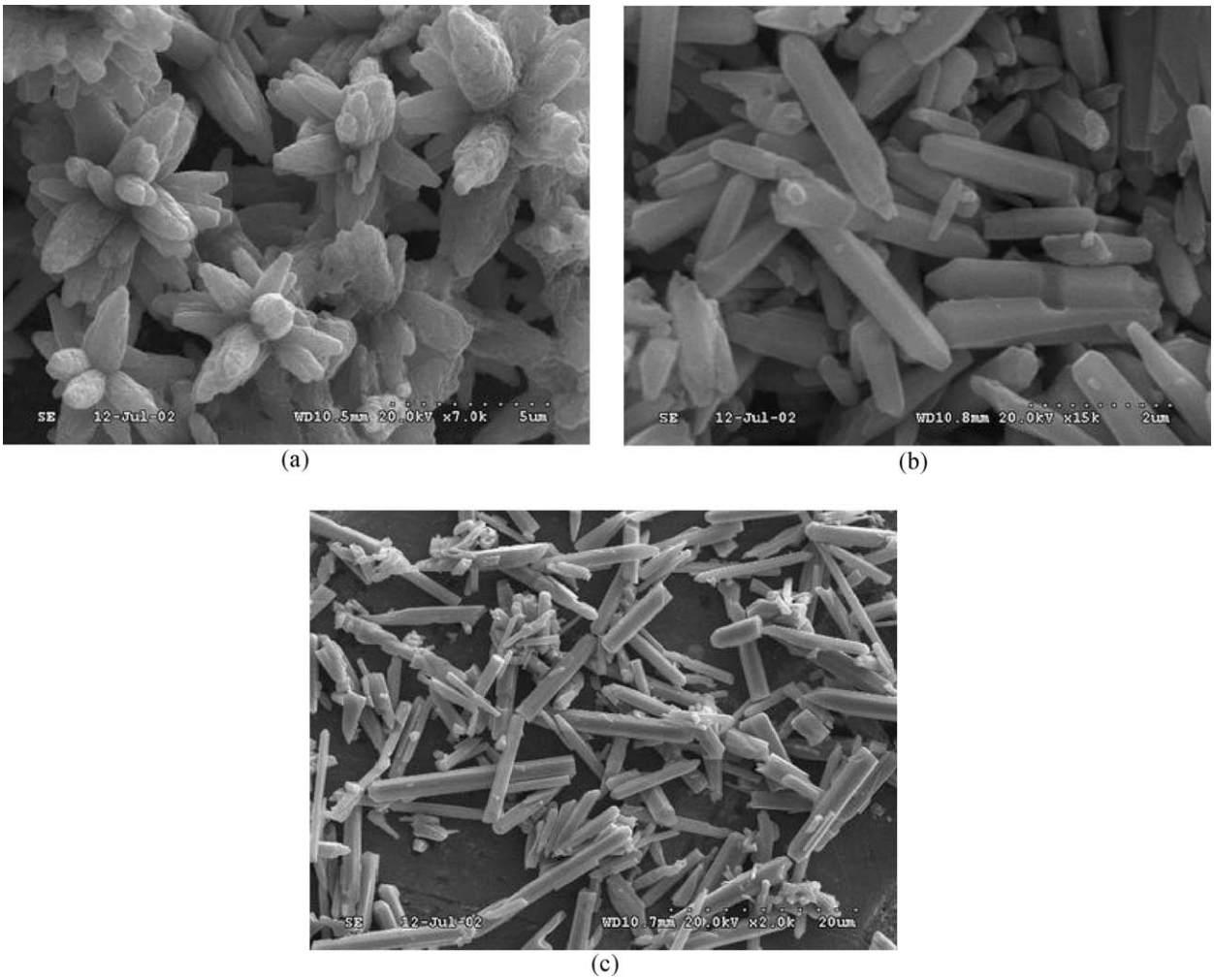


Fig. 4. SEM of the samples hydrothermally prepared at 200 °C for 2 h with (a) 0.025, (b) 0.05, (c) 0.20 mol/l $NH_3{\cdot}H_2O$.

KOH solutions. It is suggested that the effect of NH_3 or NH_4^+ ion is different from that of K^+ ion during the crystal growth process of ZnO particles under hydrothermal condition. In ammonia solutions, $Zn(NH_3)_4^{2+}$, $Zn(OH)_2$ or $Zn(OH)_4^{2-}$ may be formed, so it is more complicated than in KOH solutions.

4. Conclusions

In summary, well-crystallized ZnO powders with different morphology have been successfully prepared by a convenient hydrothermal method under mild conditions. In pure water, the pencil-like ZnO particles are obtained. Upon using KOH solutions of different concentrations as the solvents, the morphologies such as twinned pyramidal, shortened prismatic, sheet and prismatic-like of the ZnO powders are obtained. If ammonia solutions of different concentrations are employed as the solvents, the shapes of the ZnO particles are ellipsoidal and long prismatic-like. It is suggested that the zinc species and environment including OH^-, K^+ or NH_4^+ and NH_3 are the crucial factors on the morphologies of obtained ZnO powders. Such knowledge would allow one to synthesize ZnO with anticipated morphology simply by selecting the appropriate solvents and their concentrations.

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