Research Article

Influence of the Mixing Ways of Reactants on ZnO Morphology

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ZnO particles with various morphologies were synthesized by mixing ZnSO_4 and NaOH solutions at 25°C followed by aging of the suspensions at $40\text{--}80^\circ\text{C}$ for 2.0 h, keeping the initial molar ratio of Zn^{2+} to OH^- at 1:4. ZnO irregular plates were prepared by adding NaOH to ZnSO_4 while $\epsilon\text{-Zn(OH)}_2$ rhombic particles were produced using the opposite mixing way. After aging of the slurries at 80°C for 2.0 h, the ZnO plates were kept stable while the $\epsilon\text{-Zn(OH)}_2$ rhombic particles were converted to ZnO whiskers with a length of $1.0\text{--}4.0\ \mu\text{m}$ and a diameter of $0.03\text{--}0.3\ \mu\text{m}$. Thermodynamic analysis indicated that the formation of the Zn-bearing precipitates (ZnO or $\epsilon\text{-Zn(OH)}_2$) at room temperature was connected closely with the solution composition.

1. Introduction

The synthesis of ZnO with varying morphologies such as the multipods [1], the wires [2], the tubes [3], and the flowers [4] via the liquid-phase routes, including the chemical deposition [5], the microemulsion [6], the hydrothermal/solvothermal/sol-gel ways [7–9], the template-assisted method, and so forth [10], has attracted much attention in recent years owing to the moderate condition and the easy control of the properties of the ZnO products. Many former researchers have focused on the influence of surfactants on the morphology control of ZnO. For example, Sun et al. [11] synthesized ZnO nanorods from Zn via the cetyltrimethylammonium-bromide- (CTAB-) assisted route and found that the presence of CTAB promoted the erosion of Zn and the hydrothermal formation of the ZnO nanorods at 180°C . The needle- and flower-like ZnO nanocrystals were fabricated at 85°C by using ZnCl_2 and NaOH as the reactants in the presence of $0.2\ \text{mol}\cdot\text{L}^{-1}$ sodium dodecyl sulfate (SDS) [12]. Some researchers have also studied the influence of the reactants, the solvent, and the pH on the morphology of ZnO. For example, Gao et al. [13] fabricated the rotor-like ZnO at 100°C by treating the suspension containing the rod-like ZnO powders, which were produced from the $\text{NH}_3\cdot\text{H}_2\text{O}$

and ZnCl_2 and a saturated Zn(OH)_4^{2-} solution obtained by dissolving ZnO in $5\ \text{mol}\cdot\text{L}^{-1}$ NaOH. Zheng et al. [14] prepared the porous octahedron- and rod-shaped ZnO architectures from $\text{ZnC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$, which was produced by the solvothermal treatment of the mixture of ZnCl_2 , $\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$, N-dimethylformamide (DMF), and methyl orange (MO) at 180°C . Pal et al. [15] synthesized ZnO crystals with granular, flower-like and rod-like morphology by adjusting the pH of the suspension containing $\text{Zn(CH}_3\text{COO)}_2\cdot 2\text{H}_2\text{O}$ and ethylenediamine (EDA) at $80\text{--}100^\circ\text{C}$.

Herein, a facile precipitation-aging method was developed in this paper to synthesize ZnO nanoparticles and ZnO whiskers simply by changing the mixing of ZnSO_4 and NaOH solutions at room temperature followed by aging of the suspensions at $40\text{--}80^\circ\text{C}$. The influence of the solution composition on the formation of the Zn-bearing precursors and the morphology of the aging products were investigated.

2. Experimental

In a typical procedure, 20 mL of $8.0\ \text{mol}\cdot\text{L}^{-1}$ NaOH was added drop-wise ($0.67\ \text{mL}\cdot\text{min}^{-1}$) into 20 mL of $2.0\ \text{mol}\cdot\text{L}^{-1}$ ZnSO_4 at 25°C , or using the opposite mixing way. The initial molar

FIGURE 1: Morphology of the precipitates formed at 25°C. Mixing of reactants: (a) adding NaOH to ZnSO_4 ; (b) adding ZnSO_4 to NaOH.

ratio of Zn^{2+} to OH^- was 1 : 4. After being stirred (150 min^{-1}) for 1.0 h, the suspension was transferred to a Teflon-lined stainless autoclave with an inner volume of 60 mL and kept under isothermal condition at 80°C for 2.0 h. The suspension was then cooled down to room temperature naturally; the precipitate was filtered, washed with deionized water for three times, and dried at 80°C for 4.0 h.

The morphology and structure of the samples were characterized by the field-emission scanning electronic microscope (FE-SEM, JOEL 7401F, Japan) and the X-ray powder diffraction (XRD, D8 Advance, Bruker, Germany) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), respectively. The solution pH was detected by the pH meter (FE20, METTLER-TOLEDO, Germany). The concentrations of soluble Zn^{2+} and OH^- were analyzed by the ethylene diaminetetraacetic acid (EDTA) titration and the acid-base neutralization methods, respectively.

3. Results and Discussion

3.1. Influence of the Mixing Way on the Formation of the Zn-Bearing Precipitates. Figures 1 and 2 show the morphology and the XRD patterns of the Zn-bearing precipitates formed at 25°C. Wurtzite ZnO (space group $P6_3mc$, $a = b = 3.250 \text{ \AA}$, $c = 5.207 \text{ \AA}$) irregular plates with a diameter of 0.3–0.6 μm were prepared if NaOH was added to ZnSO_4 , while ϵ - $\text{Zn}(\text{OH})_2$ (space group $P212121$, $a = 8.490 \text{ \AA}$, $b = 5.162 \text{ \AA}$, $c = 4.917 \text{ \AA}$) agglomerated octahedral particles with a diameter of 1.0–3.0 μm were produced if ZnSO_4 was added to NaOH.

Figure 3 shows the variation of the total Zn^{2+} concentration ($[\text{Zn}]_{\text{T}}$) and the solution pH with the reaction time at 25°C. In the case of adding NaOH to ZnSO_4 (Figure 3(a)), with the increase of the reaction time from 0 to 60 min, $[\text{Zn}]_{\text{T}}$ decreased from $2.0 \text{ mol}\cdot\text{L}^{-1}$ to $0.08 \text{ mol}\cdot\text{L}^{-1}$ and the solution pH increased from 3.8 to 12.6; in the case of adding ZnSO_4 to NaOH (Figure 3(b)), the increase of the reaction time from 0 to 60 min led to the decrease of $[\text{OH}^-]$ from $8.0 \text{ mol}\cdot\text{L}^{-1}$ to $1.4 \text{ mol}\cdot\text{L}^{-1}$, while the $[\text{Zn}]_{\text{T}}$ increased from

0 to $0.36 \text{ mol}\cdot\text{L}^{-1}$ at the initial 30 min and then decreased gradually to $0.19 \text{ mol}\cdot\text{L}^{-1}$ as the reaction time increased from 30 min to 60 min.

Table 1 shows the possible equilibrium reactions existed in the ZnSO_4 -NaOH- H_2O system. The equilibrium constants in Table 1 were calculated from the HSC 7.1 software.

Based on the simultaneous equilibrium principle, the equilibrium concentrations of the soluble ions in varying time can be calculated from the knowing concentrations of total soluble Zn^{2+} , OH^- , Na^+ , and SO_4^{2-} . To simplify the calculation process, the activity of each species was replaced by concentration due to the shortage of the basic data. Based on these equations above and the experimental data in Figure 3, the concentrations of the soluble Zn-bearing species at different reaction time were calculated and the results are shown in Figure 4.

In the case of adding NaOH to ZnSO_4 (Figure 4(a)), $\text{Zn}(\text{OH})_{2(\text{aq})}$ was the predominant species and the increase of the reaction time from 10 min to 60 min led to the decrease of $[\text{Zn}^{2+}]$ and $[\text{ZnOH}^+]$ and the increase of $[\text{Zn}(\text{OH})_3^-]$, $[\text{HZnO}_2^-]$, $[\text{Zn}(\text{OH})_4^{2-}]$, and $[\text{ZnO}_2^{2-}]$. In the case of adding ZnSO_4 to NaOH (Figure 4(b)), all of the Zn-bearing species were kept quite stable within 60 min, and the order of concentrations for these species was $[\text{Zn}(\text{OH})_4^{2-}] \approx [\text{ZnO}_2^{2-}] > [\text{Zn}(\text{OH})_3^-] \approx [\text{HZnO}_2^-] > [\text{Zn}(\text{OH})_{2(\text{aq})}] > [\text{ZnOH}^+] > [\text{Zn}^{2+}]$. The difference in the solution composition may be one of the major reasons for the formation of different precipitates (ZnO and ϵ - $\text{Zn}(\text{OH})_2$).

3.2. Aging of the ZnO and ϵ - $\text{Zn}(\text{OH})_2$ Precipitates. The morphology and the XRD patterns of the aging products formed from ZnO and ϵ - $\text{Zn}(\text{OH})_2$ precursors were shown in Figures 5 and 6, respectively. Irregular ZnO plates with a similar morphology using the ZnO precursor were formed after aging treatment at 40–80°C, indicating that ZnO precursor was quite stable under the experimental conditions. In the case of the ϵ - $\text{Zn}(\text{OH})_2$ precursor, the precursor was stable up to 40°C, but changed

FIGURE 2: XRD patterns of the precipitates formed at 25°C. Mixing of reactants: (a) adding NaOH to ZnSO₄; (b) adding ZnSO₄ to NaOH. ★: ZnO, •: ε-Zn(OH)₂.

FIGURE 3: Influence of the mixing ways of the reactants on [Zn]_T and pH. Mixing of reactants: (a) adding NaOH to ZnSO₄; (b) adding ZnSO₄ to NaOH; ■: [Zn]_T, □: pH.

to ZnO rods with a length of 0.1–0.4 μm and a diameter of 40–100 nm and ZnO whiskers with a length of 1.0–14.0 μm and a diameter of 0.03–0.3 μm after aging treatment at 60°C and 80°C, respectively. The different aging behaviors of ZnO and ε-Zn(OH)₂ precursors may be connected with their different dissolution abilities in NaOH solution.

Figure 7 shows the dissolution of ZnO and ε-Zn(OH)₂ after mixing excessive amount (3.500 g) of ZnO or ε-Zn(OH)₂ with 25 mL of 8.0 mol·L⁻¹ NaOH at 25–80°C for 2.0 h. The increase of temperature from 25°C to 80°C favored the dissolution of ZnO and ε-Zn(OH)₂ in NaOH solution. Compared with ZnO, ε-Zn(OH)₂ was more soluble, which favored the formation of ZnO whiskers via the dissolution-precipitation route [16]:

TABLE 1: Thermodynamic equilibrium reactions in ZnSO₄-NaOH-H₂O system (298 K).

Reactions	Constant	
H ₂ O = H ⁺ + OH ⁻	1.02 × 10 ⁻¹⁴	(1)
ZnSO ₄ = Zn ²⁺ + SO ₄ ²⁻	2.23 × 10 ³	(2)
HSO ₄ ⁻ = SO ₄ ²⁻ + H ⁺	1.04 × 10 ⁻²	(3)
H ₂ SO ₄ = HSO ₄ ⁻ + H ⁺	3.46 × 10 ⁹	(4)
NaOH = Na ⁺ + OH ⁻	8.45 × 10 ⁶	(5)
Na ₂ SO ₄ = 2Na ⁺ + SO ₄ ²⁻	4.73 × 10 ⁻¹	(6)
Zn ²⁺ + 2OH ⁻ = HZnO ₂ ⁻ + H ⁺	1.73	(7)
Zn ²⁺ + 2OH ⁻ = ZnO ₂ ²⁻ + 2H ⁺	2.90 × 10 ⁻¹³	(8)
Zn ²⁺ + OH ⁻ = ZnOH ⁺	1.44 × 10 ⁶	(9)
Zn ²⁺ + 2OH ⁻ = Zn(OH) _{2(aq)}	1.16 × 10 ¹³	(10)
Zn ²⁺ + 3OH ⁻ = Zn(OH) ₃ ⁻	2.50 × 10 ¹⁴	(11)
Zn ²⁺ + 4OH ⁻ = Zn(OH) ₄ ²⁻	4.61 × 10 ¹⁵	(12)

FIGURE 4: Variation of the soluble Zn-bearing species with time. Mixing of reactants: (a) adding NaOH to ZnSO_4 ; (b) adding ZnSO_4 to NaOH. ■: Zn^{2+} , ○: HZnO_2^- , ►: ZnO_2^{2-} , ☆: ZnOH^+ , ◄: $\text{Zn(OH)}_{2(aq)}$, ▲: Zn(OH)_3^- , ◇: Zn(OH)_4^{2-} .

FIGURE 5: Morphology of the aging products formed from ZnO ((a)–(c)) and ϵ - Zn(OH)_2 ((d)–(f)). Aging temperature ($^{\circ}\text{C}$): (a), (d): 40; (b), (e): 60; (c), (f): 80.

4. Conclusions

ZnO particles and whiskers were synthesized by changing the mixing ways of ZnSO_4 and NaOH at room temperature followed by aging of the suspensions at 40–80 $^{\circ}\text{C}$ for 2.0 h. Irregular ZnO plates were formed by adding NaOH to ZnSO_4 while ϵ - Zn(OH)_2 rhombic particles were produced using the

opposite mixing way. Thermodynamic analysis indicated that the formation of ZnO and ϵ - Zn(OH)_2 in different mixing ways of ZnSO_4 and NaOH should be attributed to the different solution compositions. The aging of the slurries containing ϵ - Zn(OH)_2 and NaOH at 80 $^{\circ}\text{C}$ for 2.0 h led to the formation of ZnO whiskers with a length of 1.0–4.0 μm and a diameter of 0.03–0.3 μm owing to the easy dissolving of

FIGURE 6: XRD patterns of the aging products formed from ZnO ((a)–(c)) and ϵ -Zn(OH) $_2$ ((d)–(f)). Aging temperature ($^{\circ}$ C): (a), (d): 40; (b), (e): 60; (c), (f): 80; $\star$: ZnO, $\bullet$: ϵ -Zn(OH) $_2$.

FIGURE 7: Dissolution curves of ϵ -Zn(OH) $_2$ and ZnO in NaOH solution; $\star$: ZnO, $\bullet$: ϵ -Zn(OH) $_2$.

ϵ -Zn(OH) $_2$ in NaOH solution, while the ZnO plates were quite stable throughout the aging treatment.

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