Synthesis of ZnO whiskers via hydrothermal decomposition route

SHI Wen-tao(史文涛), GAO Guo(高 国), XIANG Lan(向 兰)
Department of Chemical Engineering, Tsinghua University, Beijing 100084, China
Received 6 July 2009; accepted 23 March 2010

Abstract: ZnO whiskers with a length of 30–40 μm and a diameter of about 1 μm were synthesized by co-precipitation of ZnSO_4 and Na_2CO_3 solution at room temperature followed by hydrothermal treatment of the as-prepared Zn_5(CO_3)_2(OH)_6 precursor at 160 °C for 6 h. The increase of the initial solution pH promotes the hydrothermal conversion of the particulate Zn_5(CO_3)_2(OH)_6 to ZnO whiskers. The presence of minor amount of EDTA in the hydrothermal solution promotes the one dimensional growth of ZnO whiskers, leading to the formation of ZnO whiskers with a length of 50–60 μm and a diameter of 1–2 μm.

Key words: basic zinc carbonate; zinc oxide; whiskers; hydrothermal decomposition

1 Introduction

In recent years, one-dimensional (1D) oxides have attracted considerable interest due to their distinctive geometry characteristics and novel chemical and physical properties. As one of the 1D oxide materials, 1D ZnO materials can be used in many fields such as ceramics, electrics, solar cells, reinforcing rubbers and zinc alloys owing to their unique optical, electric and piezoelectric properties[1–3]. Many techniques have been employed to synthesize 1D ZnO materials. Among them, the vapor phase transport process with the assistance of noble metal catalysts and thermal evaporation are the two major methods to fabricate 1D ZnO nanostructures[4–5]. The solution-based hydrothermal methods have also been used for the synthesis of 1D ZnO. Compared with the vapor phase methods, the hydrothermal method has some distinctive advantages such as moderate reaction condition and easy control of the solution composition[7–11]. It was reported that ZnO whiskers with a diameter of around 4 μm and a length of up to 20 μm were synthesized at 110 °C for 12 h using zinc acetate dehydrate and ammonia as the raw materials[12]. The multi-pod-like ZnO whiskers with a length of 2–4 μm and a diameter of ~150 nm were formed using Zn(NO_3)_2 and ammonia as the raw materials[13]. Some surfactants have been adopted to obtain the 1D ZnO with high aspect ratio involving polyvinyl alcohol, polyethylene glycol, cetyltrimethyl ammonium bromide (CTAB)[14–15] and so on. In addition, the presence of some organic solvents, such as the n-hexane, n-decane and benzene [16], is favorable for the 1D growth of ZnO. Up to now, little work has been reported on the formation of 1D ZnO in ZnSO_4-Na_2CO_3 system.

In the present work, a facile hydrothermal decomposition method was developed to synthesize ZnO whiskers in alkaline media, using ZnSO_4 and Na_2CO_3 as the reactants. The influence of the reaction time and the solution pH on the morphology and composition of the hydrothermal products was investigated. The hydrothermal decomposition process was discussed primarily based on the experimental detections and the thermodynamic analysis.

2 Experimental

2.1 Synthesis of ZnO whiskers

In a typical experiment, certain amounts of 0.2 mol/L ZnSO_4 and 0.25 mol/L Na_2CO_3 were mixed, keeping the molar ratio of ZnSO_4 to Na_2CO_3 as 1:(1–4). The slurry formed at room temperature was then transferred to a Teflon-lined stainless steel autoclave with an inner volume of 80 mL, heated to 160 °C and kept under isothermal condition for 6–12 h. After the
hydrothermal treatment, the product was filtrated, washed and dried at 60 °C in vacuum for 12 h.

2.2 Analysis
The morphology of the sample was examined with the field emission scanning electron microscopy (JSM7401F, JEDL, Japan). The structure and composition of the sample were identified by the X-ray powder diffractometer (D/max2500, Rigaku, Japan). The content of ZnO was analyzed by EDTA titration method, and the solution pH was detected by pH meter (DELTA 320, METTLER-TOLEDO, China).

3 Results and discussion

3.1 Formation and conversion of basic zinc carbonate
Fig.1 shows the morphology and XRD patterns of the precipitates before and after hydrothermal treatment (160 °C, 6 h). The precipitate formed at room temperature was composed of basic zinc carbonate (PDF No.19−1458) with poor crystallinity. The precipitate after hydrothermal treatment was a mixture of the particles and the whiskers (a length of 30−40 μm and a diameter of about 1 μm). The XRD pattern shows that Zn₅(CO₃)₂(OH)₆ and ZnO coexisted in the hydrothermal product, implying that the whiskers may be composed of ZnO phase.

The co-existence of Zn₅(CO₃)₂(OH)₆ particles and ZnO whiskers in the hydrothermal product indicated the incomplete conversion of Zn₅(CO₃)₂(OH)₆ in the experimental condition. The gradual decrease of solution pH may be one of the major reasons for the inhibition of the conversion of Zn₅(CO₃)₂(OH)₆ to ZnO.

3.2 Influence of pH on hydrothermal conversion of basic zinc carbonate
Fig.3 shows the influence of initial solution pH on the morphology of hydrothermal products formed at 160 °C for 12 h. No Zn₅(CO₃)₂(OH)₆ was converted to ZnO at pH=6.5; Zn₅(CO₃)₂(OH)₆ and ZnO whiskers coexisted at pH=9.5; ZnO whiskers (with a length of 40−50 μm and a diameter of about 1−2 μm) coexisted with minor amount of Zn₅(CO₃)₂(OH)₆ particles at pH=10.0. Only ZnO whiskers were detected in the case of pH 10.5. The solution with a comparatively high initial pH was favorable for the conversion of Zn₅(CO₃)₂(OH)₆ to ZnO, producing ZnO whiskers with low aspect ratio due to the quick dissolution of Zn₅(CO₃)₂(OH)₆ and the quick formation of ZnO.

Fig.4 shows the influence of the initial solution pH on the hydrothermal conversion of Zn₅(CO₃)₂(OH)₆ to ZnO. After 12 h of reaction, 8.6% and 87.3% (mass fraction) of ZnO were detected in the cases of initial pH 9.5 and 10.0, respectively, while Zn₅(CO₃)₂(OH)₆ was completely converted to ZnO within 2 h of reaction in the case of the initial pH 11.0, reconfirming that a high initial pH promoted the hydrothermal decomposition of Zn₅(CO₃)₂(OH)₆.
The mechanical mixture model, in which the complex compound is considered as a combination of several simple compounds[7], was employed to estimate the $\Delta_f G^\circ_T$ for Zn$_5$(CO$_3$)$_2$(OH)$_6$:

$$\Delta_f G^\circ_T [\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6] = 2 \Delta_f G^\circ_T [\text{ZnCO}_3] + 3 \Delta_f G^\circ_T [\text{Zn(OH)}_2] \quad (3)$$

The basic thermodynamic data of the substances involved in the hydrothermal conversion of Zn$_5$(CO$_3$)$_2$(OH)$_6$ to ZnO were originated from the HSC software[8].

The variations of the $\Delta_f G^\circ_T$ for reactions (1) and (2) are shown in Fig.5. The positive $\Delta_f G^\circ_T$ values for reaction (1) in the temperature range of 0–200 °C indicated the thermodynamic impossibility for the conversion of Zn$_5$(CO$_3$)$_2$(OH)$_6$ to ZnO in acidic media. The negative $\Delta_f G^\circ_T$ values for reaction (2) and the gradual decrease tendency of the $\Delta_f G^\circ_T$ with the increase of temperature revealed possible conversion of Zn$_5$(CO$_3$)$_2$(OH)$_6$ to ZnO in the alkaline media and the enhanced decomposition tendency of Zn$_5$(CO$_3$)$_2$(OH)$_6$ at elevated temperatures.

### 3.4 Influence of EDTA on hydrothermal product

Fig.6 shows the morphologies of the products formed in the absence and presence of EDTA, keeping the hydrothermal condition as follows: 160 °C, 12 h and initial pH 10.5. Compared with the result without EDTA, the presence of minor amount of EDTA promoted the 1D growth of ZnO whiskers, leading to the formation of ZnO whiskers with a length of 50–60 μm and a diameter of about 1–2 μm. It was suggested that the chelating of
EDTA with Zn$^{2+}$ and the possible selective adsorption of EDTA on the specific planes of ZnO may be the main reasons for the enhanced preferential growth of ZnO along one direction and the details are still on research.

![Fig.5 Variation of $\Delta G^\circ_T$ with temperature](image)

**Fig.5** Variation of $\Delta G^\circ_T$ with temperature

![Fig.6 Influence of EDTA on morphology of products: (a) Without EDTA; (b) 5 mmol/L EDTA](image)

**Fig.6** Influence of EDTA on morphology of products: (a) Without EDTA; (b) 5 mmol/L EDTA

### 4 Conclusions

1) A facile hydrothermal method is developed to synthesize ZnO whiskers in alkaline media, using ZnSO$_4$ and Na$_2$CO$_3$ as the reactants.

2) The increase of the solution pH accelerates the hydrothermal decomposition of the particulate Zn$_5$(CO$_3$)$_2$(OH)$_6$ precursor but leads to the formation of ZnO whiskers with low aspect ratios.

3) The presence of $5 \times 10^{-3}$ mol/L of EDTA promotes the hydrothermal growth of ZnO whiskers along one direction, producing ZnO whiskers with a length of 50–60 μm and a diameter of 1–2 μm.

### References


(Edited by LI Xiang-qun)