Facile synthesis of ZnO hollow fibres

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Abstract. In this paper, cotton fibres were used as bio-template to successfully synthesize new ceramic materials, ZnO hollow fibres and in an effort to explore the synthesis condition, and simplify the synthesis procedure. In this synthesis, a direct thermal decomposition of zinc acetate dihydrate coated on the surface of cotton fibres was explored. The wall porosity of the ZnO hollow fibres was controlled by changing the concentration of zinc acetate aqueous solution.

Keywords. Biomorphic; cotton fibres; ZnO hollow fibres; synthesis.

1. Introduction

Zinc oxide, as a II–VI semiconductor with a wide band gap (3.2 eV) and a large exciton binding energy of 60 meV at room temperature, has been extensively studied due to its wide applications in photonics devices, gas sensors and dye-sensitized solar cells (for its optoelectronic, electrical and photoelectrochemical properties) (Huang *et al* 2001; Gao *et al* 2005). Recently, a variety of ZnO micromaterials such as microrods, microboxes, microspheres, etc (Turge-man *et al* 2005; Zhao *et al* 2006; Zhang *et al* 2007) have been synthesized. However, the synthesis procedure is very complex and not suitable for use in industries.

As we all know the natural materials exhibit a hierar-chically built anatomy, optimized from nature in respect to their mechanical and functional properties by evolution over a long period of time, and they are also cheap, abundantly available and reproducible. Hence, using natural materials with special structures like wood, filter paper, silk and eggshell membrane as bio-templates to produce new ceramic materials has drawn a lot of scientific atten-tion in recent years (Vogli *et al* 2001; Huang and Kuni-take 2003; Xu *et al* 2006; Dong *et al* 2006).

In this paper, biomorphic ZnO hollow fibres, as long as the cotton templates, are prepared first by a direct thermal decomposition of zinc acetate dihydrate coated on the surface of cotton fibres. The wall porosity of the ZnO hollow fibres can be controlled by changing the concen-tration of zinc acetate aqueous solution. The reagent used in this paper is handy and environment-friendly and the synthesis procedure is also very simple.

2. Experimental

2.1 Preparation

Some dried and loose cotton fibres (see figure 1) used as biological templates were dipped in 3.5, 7 and 10.5 wt.% zinc acetate aqueous solution at room temperature for 2 min and then dried at 50°C for 2 h. Thus zinc acetate dihydrate was successfully coated on the surface of cotton fibres to form the precursors. These precursors were then placed into an alundum crucible and calcinated at 600°C in an oven under air atmosphere for 2 h and then naturally cooled to room temperature. The cotton templates were removed and the ZnO hollow fibres with porous walls were thus obtained. The slow cooling was maintained to

Figure 1. Representative source cotton fibres used as biological template.

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avoid the distortion in the walls of the hollow fibres due to some type of stress and strain.

2.2 Characterization

The morphologies and structures of ZnO fibres were characterized and analysed by JSM-5600LV scanning electron microscope (SEM, Japan) equipped with an energy-dispersive X-ray spectrometer (EDS), JEM-100SX transmission electron microscope (TEM, Japan) and BD-86 X-ray diffraction (XRD, Japan). TEM samples were prepared by dispersing the ZnO fibres in ethanol by ultrasonic treatment, dropping them onto a carbon coated copper grid, and then drying them in air. The precursor was analysed with a PE-PYRIS Diamond TG-DTA instrument at a heating rate of $10^{\circ}\text{C min}^{-1}$ in air atmosphere.

3. Results and discussion

3.1 XRD analysis

Figure 2 shows the XRD pattern of ZnO hollow fibres obtained by sintering the precursor at 600°C for 2 h in air atmosphere. The obtained sample is highly crystalline and all peaks match well with the ZnO wurtzite structure recorded in the standard data (JCPDS, 36-1451). So sintering these precursors at 600°C for 2 h in air atmosphere can bring about the conversion of $\text{Zn}(\text{CH}_3\text{COO})_2$ to ZnO to obtain ZnO structural materials and the peaks of other impurity elements are not observed and this indicates that the purity of biomorphic ZnO fibres is high.

3.2 SEM observation

Figure 3 shows the SEM micrograph of ZnO fibres obtained at 7 wt.% of zinc acetate solution. From figure 3, it can be seen that the ZnO fibres retain the original fibrous cotton morphology, their length are several centimeters

Figure 2. XRD pattern of ZnO hollow fibres.

and the diameter is basically in the range of 5–20 μm . This may be attributed to the abundant surface hydroxyl groups and the wetting characteristics of cotton fibres (Fan *et al* 2005).

Figure 4 exhibits that those fibres obtained at different concentrations are all hollow and the wall thickness is estimated to be around 100 nm. The walls of the obtained ZnO fibres are porous when the concentration is relatively low such as 3.5 wt.% and become dense when the concentration increases. It is because much quantity of zinc acetate dihydrate is coated on the cotton fibres when the concentration increases. Hence, the concentration of the zinc acetate solution must be controlled in order to obtain ZnO fibres with different morphologic walls.

3.3 TEM observation

It can be seen from figure 5 that the walls of ZnO hollow fibres obtained at various concentrations are made of large amounts of coalescent ZnO grains, and the grain size is estimated to be 40–60 nm. These large grains may be ascribed to the improvement of crystallization at a high temperature of 600°C (Samarasekara *et al* 2007). Figure 5a also indicates that there are a number of holes between the grains, which may further confirm the porosity in the walls of the ZnO hollow fibres in figure 4a. Obviously the holes between the grains become fewer and fewer with increasing concentration of zinc acetate aqueous solution. So the walls of ZnO hollow fibres become denser and denser with increasing concentration of zinc acetate aqueous solution.

3.4 TG-DTA measurement

To clarify the chemical reactions of zinc acetate dihydrate occurring in the pyrolysis process of the cotton fibre, TG–

Figure 3. SEM image of ZnO fibres obtained at 7 wt.% zinc acetate aqueous solution.

Figure 4. Magnified SEM images of ZnO hollow fibres obtained at different concentrations of zinc acetate aqueous solution: a. 3.5 wt.%, b. 7 wt.% and c. 10.5 wt.%.

Figure 5. TEM images of ZnO hollow fibres obtained at different concentrations of zinc acetate aqueous solution: a. 3.5 wt.%, b. 7 wt.% and c. 10.5 wt.%.

DTA curves of the precursor were measured. The fabrication process of long biomorphic ZnO hollow fibres in our paper can be separated into two steps: one is the reproduction of the microstructural morphology of the goal material by coating zinc acetate dihydrate onto the surfaces of the biomorphic cotton templates and the other is burning out the cotton templates at a proper and high enough temperature under air atmosphere to result in the formation of ZnO hollow material. The biomorphic ZnO hollow fibres are produced by the following chemical reactions (see (1)–(3)) (Paraguay *et al* 1999). Since cotton is mainly composed of cellulose, its decomposition process starts below 300°C, and completes at 450°C. Basic products of such thermal decomposition reactions include CO, CO₂, H₂O and other volatile hydrocarbons.

Figure 6. TG-DTA curves of the precursor at 7 wt.% of zinc acetate aqueous solution.

The TG-DTA curves of the precursor at 7 wt.% of zinc acetate aqueous solution are shown in figure 6. The total

Figure 7. EDS spectra of the sample obtained at 600°C.

weight loss is 96.5% and it occurred in three steps up to 450°C. The first step shows a weight loss of 24.6% between 25 and 248°C, this may be attributed to the evaporation of the surface humidity and the dehydration of zinc acetate dihydrate. The second step has a weight loss of 40.8% between 248 and 368.1°C, this may be related to the decomposition of zinc acetate dihydrate. In the third step of the weight loss (368.1–450°C), a 31.1% weight loss associated with two exothermic peaks at 365.1 and 414.2°C occurred, the exothermic peak at 365.1°C may be due to the preliminary crystallization of ZnO, the exothermic peak at 414.2°C can be ascribed to the decomposition of the cotton fibre.

3.5 EDS analysis

As shown in figure 7, the main inorganic elements found in the EDS spectrum of the sample obtained by calcinating the precursor at 600°C for 2 h under air atmosphere are Zn and O, and other elements produced in cotton ash are hardly detected. Hence, the purity of biomorphic ZnO hollow fibres is high, which is also consistent with the XRD results.

4. Conclusions

ZnO hollow fibres were prepared by a direct thermal decomposition of zinc acetate dihydrate after being coated on the surface of cotton fibres. The ZnO fibres retain the

original fibrous cotton morphology and the wall thickness is around 100 nm. The hollow fibres are as long as several centimeters and the inner diameter of the fibres is basically in the range of 5–20 µm. During the fabrication process, the wall porosity can be controlled by changing the concentration of zinc acetate aqueous solution. The reagent used here is handy and environment-friendly, the synthesis procedure is also very simple. This approach provides a simple and efficient route to prepare ZnO hollow fibres with different morphologic walls and shows a prospect to prepare a large variety of ZnO materials using the abundant biological materials as templates.

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