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Synthesis of well-dispersed ZnO nanomaterials by directly calcining zinc stearate

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1. Introduction

Due to the fundamental size-dependent properties and the important technological applications, nanoscale oxide materials have gained considerable attention in recent years [1,2]. ZnO, a direct-band gap semiconductor material, has a large band gap of 3.37 eV and a large excitation binding energy of 60 meV, which make it widely used in many fields [3-7]. Up to now, various methods, such as microemulsion method and hydrothermal method, have been proposed to prepare nano-sized ZnO materials [8-10]. In addition, the direct thermal decomposition of metal-oleate complex in octadecene solution provides a simple method to prepare metal oxide nanostructures with uniform morphology [11,12]. However, this route often suffers from both the decomposition of the combustible reagent at high temperature, especially in largescale synthesis, and the difficulties in the removal of undesirable impurities from the surface of the products. Comparatively, the direct pyrolysis of the metal complex in air provides a dry environment for the controllable preparation of ZnO nanorods [13], ZnO zeptoliter bowls and troughs [14], NiO nanoparticles [15] and ZrO₂ nano-laminate [16], with relatively high purity. Following the thermal-decomposing route, herein, we report the fabrication of different ZnO nanostructures via the formation of zinc stearate and the subsequent calcination of the precursor of zinc stearate. Compared with the PVP, the ligand of zinc stearate is not only much easier to decompose, but also more effective to assist the removal of

ABSTRACT

Well-dispersed ZnO nanomaterials were synthesized by direct calcination of zinc stearate. Results from Fourier transform infrared (FT-IR) spectra and X-ray diffraction (XRD) indicated both the decomposition degree of organic ligand and the purity of calcined products were increased with the calcination temperature. The influence of decomposition temperature on the morphology of ZnO nanomaterials was investigated by field-emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The experimental results revealed the morphology of ZnO transformed from nanosheets to hexagonal nanopyramids and then to nanoparticles at 573, 673 and 773 K respectively. Finally, a morphology evolution model of ZnO nanomaterials under different temperatures was proposed. © 2008 Elsevier B.V. All rights reserved.

impurities adsorbed on the surface of ZnO products. Thus, wurtzitetype ZnO materials with far higher purity are obtained. Moreover, due to the protection of organic compounds in thermal decomposition process, the ZnO nanopyramids and nanoparticles are well-dispersed and size-homogeneous.

2. Experimental procedure

All reagents are analytical purity and used without further purification. To prepare the metal complex, $0.01 \text{ mol} (2.97 \text{ g}) 2n(NO_3)_2$ · $6H_2O$ and 0.02 mol (5.69 g) stearic acid were dissolved in 100 ml ethanol at 343 K. Then, 0.02 mol (2.8 ml) triethy-lamine was dropped into the solution with vigorously stirring. White precipitate was instantly appeared in the solution. After being filtered and washed with hot ethanol, the precipitate was dried at 353 K for 12 h. Finally, the produced zinc stearate was calcined in a muffle furnace at 573, 673 and 773 K for 3 h in air, respectively.

The FT-IR spectra of zinc stearate and calcined products were recorded by Fourier transform infrared spectroscopy (FT-IR, Nicolet, AVATAR-370MCT) in the range from 400 to 4000 cm⁻¹. The morphology of ZnO was characterized by the field-emission scanning electron microscope (FE-SEM, JEM-6700F) and the transmission electron microscope (TEM, JEOL-2010). The selected area electron diffraction (SAED) was also obtained form the transmission electron microscope. The products were also characterized by X-ray powder diffraction (XRD) on a Rigaku D/Max 2500V B2+/PC diffractometer.

3. Result and discussion

Fig. 1 is the FT-IR spectra of zinc stearate and calcination products. The main absorption bands at ~3438, ~2916, ~1539 and ~1464 cm⁻¹ are consistent with the O–H, C–H, symmetric and asymmetric C=O stretching vibrations of zinc stearate, respectively (Fig. 1A). Compared with the bands in Fig. 1A, the band at ~3438 cm⁻¹ disappears in Fig. 1B for products calcined at 573 K for 3 h. The intensity of the peaks at ~2916, ~1539 and ~1464 cm⁻¹ is



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Fig. 1. FT-IR spectra of zinc stearate (A) and the products calcined at different temperatures (B) 573 K, (C) 673 K and (D) 773 K.

significantly decreased in Fig. 1B. These results indicate that zinc stearate is partly decomposed at 573 K. The process include the dehydration and the subsequent destroying of the C–H and C=O bonds. Further increasing the temperature to 673 and 773 K, the bands at ~2916, ~1539 and ~1464 cm⁻¹ nearly totally disappear and the new bands appear at 460 and 473 cm⁻¹ (Fig. 1C and D). The new bands at 460 and 473 cm⁻¹ are the typically stretching vibrations of ZnO. These indicate the nearly complete transformation of complex precursors to the final inorganic ZnO product if the calcination temperature is higher than 673 K.



Fig. 2. XRD patterns of ZnO products at different temperatures.

Fig. 2 is the XRD patterns of ZnO products calcined at different temperatures. The product calcined at 573 K has a broad diffraction peak at around 22°, which is resulted from the amorphous carbon produced in the decomposition process of zinc stearate. Except this broad peak, other peaks are all attributed to the characteristic ones of wurtzite-type ZnO (JCPDS, 36-1451). Comparatively, all diffraction peaks of product at 673 and 773 K can be indexed to the hexagonal ZnO with wurtzite structure, and no any peaks of impurities can be detected in the XRD pattern. The XRD result is



Fig. 3. SEM images of zinc stearate (A) and the products calcined at different temperatures (B) 573 K, (C) 673 K and (D) 773 K.



Fig. 4. TEM and SAED images of ZnO products at different temperatures (A) 573 K, (B) 673 K and (C) 773 K.

in agreement with that of FT-IR spectra that zinc stearate is nearly completely decomposed if the temperature is higher than 673 K.

Fig. 3 shows the SEM images of zinc stearate and the products calcined at different temperatures. Zinc stearate presents a sheet-like structure with average area of $1.4 \,\mu\text{m} \times 1.4 \,\mu\text{m}$ (Fig. 3A). The products calcined at 573 K formed the nanosheets with a thickness of around 25 nm (Fig. 3B). It is clear that there are some powders filling the vacancy of the sheet-like products. Accord-

ing to the XRD results, the nanosheets are the mixture of zinc stearate and ZnO. Due to the similarity of product morphology in Fig. 3A and B, it can be concluded that the decomposition at 573 K is uniform in each position of the nanosheets. However, the direct thermal decomposition at 673 K would result in the formation of ZnO nanopyramids with average size of 230 nm (Fig. 3C). The relatively uniform size of ZnO nanopyramids indicates the quick collapse of the former nanosheet-like products and the for-



Scheme 1. Morphology evolution model of ZnO nanomaterials at different temperatures.

mation of small nanopyramids in large quantity. Similarly, the decomposition at 773 K leads to the formation of uniform ZnO nanoparticles with diameter of about 150 nm (Fig. 3D). The morphology and size of ZnO powders were further investigated by TEM. Fig. 4A clearly shows that the nanosheets consist of nanorods with diameters of 25-65 nm and lengths of 300-900 nm. There are many holes around the nanorods, indicating the in situ thermal decomposition and the release of gases (i.e. steam, CO₂ or CO, etc.) from the nanosheets in the decomposition process. After ultrasonic treatment in ethanol, the nanorods were separated from the nanosheets. This phenomenon indicates the weak interaction between nanorods and further proves our deduction that the formation of ZnO is resulted from the in situ decomposition of zinc stearate. Probably, the low temperature provides the opportunity for the new ZnO species self-assembly to nanorods. Comparatively, the calcination at 673 or 773 K is intense and the release of gases would be quickly. Therefore, the sheet-like texture is unable to maintain but collapse guickly to form nanopyramids or nanoparticles in large quantity. SAED pattern (inset in Fig. 4B and C) indicates that as-prepared ZnO nanopyramids and nanoparticles are single crystal.

ZnO nanopyramids and nanoparticles are well-dispersed, due to the above quick formation of many small seeds simultaneously. It is the in situ protection of organic compounds around the ZnO species which prevents the agglomeration of ZnO particles. Although our experiment is carried out at different temperatures separately, the product after higher temperature decomposition is due to the further transform of mediate product formed at low temperature. Therefore, the nanoparticles at 773 K are formed due to the further transformation of nanopyramids, as shown in Scheme 1. Obviously, the temperature of 773 K makes the melting of the rigid surface of nanopyramids (at 673 K) become much smooth and round surface of ZnO particles. The fast elevating to 773 K for 3 h is different from that of elevating to 673 K for 3 h and the subsequent elevating to 773 K. Much smaller seeds in high concentration may be simultaneously produced in the former mode as compared with that in the latter one. Thus, the size of product at 773 K for 3 h (Fig. 4C) is smaller than that at 673 K for 3 h (Fig. 4B). Moreover, temperature of 773 K seems somewhat higher for the thermal decomposition of such materials and leads to the further agglomeration of ZnO nanoparticles after the total evaporation or decomposition of organic compounds (Fig. 4C). From this viewpoint, it is necessary to provide a much large space (i.e. suspending ZnO nanoparticles by gases in fluidized bed) to avoid the contact and aggregation of ZnO nanoparticles. The related investigation is currently being undertaken in our lab.

4. Conclusion

In summary, well-dispersed ZnO nanomaterials were prepared via the formation of zinc stearate precursor and its subsequent thermal decomposition in air. Controlling the calcination temperature is effective to tailor the morphology of as-prepared ZnO nanomaterials. The uniform decomposition of nanosheet-like precursor results in the formation of well-dispersed ZnO nanomaterials. FT-IR and XRD results show the gradual decomposition of precursor to produce ZnO with relatively high purity. A morphology evolution model is proposed to explain the formations of products at different temperatures.

Apparently, the synthesis route of ZnO nanoparticles in the present work is relatively simple. The results can be easily repeated and are useful for the large-scale controllable production at low cost. It is also expected other metal oxide nanomaterials could be synthesized by the same method.

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