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Preparation of zinc oxide nanoparticles coated with homogeneous Al_2O_3 layer

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Abstract

Zinc oxide nanoparticles coated with Al_2O_3 were prepared by calcining basic carbonate of zinc (BCZ) powders coated with $Al(OH)_3$ precipitation at 400–600 °C. $Al(OH)_3$ was coated on the surface of BCZ powders which are precursor for ZnO, in stead of calcined ZnO particles. The size and shape of BCZ powders are different after coating with Al_2O_3, as a result, ZnO particles with about 50–80 nm were prepared by calcining coated BCZ at 600 °C. There is a homogeneous coating with about 5 nm on the surface of as-calcined ZnO nanoparticles. TEM, XPS and zeta potentials were used to characterize the coated ZnO nanoparticles.

Keywords: Zinc oxide; Surface structure; Coatings; Precipitation; Nanomaterials; Zeta potentials

1. Introduction

Zinc oxide nanoparticles have received considerable attention due to their unique properties, such as high reactivity, low sintering temperature, and good electrical–optical properties [1–4]. They are well known as UV blocking materials, especially in UV-A region, which make them widely used in cosmetic, paint and fiber application. As the main ingredient of varistors, it has been found that varistors prepared with ZnO nanoparticles have excellent properties [5]. However, the dispersibility and stability of ZnO nanoparticles must be considered in some applications, such for photo and oxidation catalysis. It is reported that particle surface coating is one of the effective way to improve their stability and agglomeration condition [6–10].

Particle surface coating has been studied widely. Kratohvil and Matijevic [11] produced alumina surface coatings on hematite, chromia and TiO_2 by hydrolyzing aluminum sulfate solutions at elevated temperatures in the presence of urea. Hu and Rahaman [12] synthesized composite powders by coating the individual inclusion particles (ZrO_2) with a cladding of matrix powder (ZnO) using chemical precipitation from a solution of a zinc salt. Their study showed that use of coated powders in the formation of polycrystalline ZnO matrix composites containing ZrO_2 particulate inclusions resulted in a remarkable improvement in the sinterability of the composites. Masui et al. [6] synthesized the BN-modified CeO_2 fine powder by means of reaction between boric acid and urea on the surface of ceria. The results showed the BN-coating was very effective in reducing the catalytic activity of the ceria. Tago et al. [9] prepared silica-coated ceria nanoparticles using water-in-oil micromemulsion. Guo et al. [10] prepared highly monodispersed ZnO nanoparticles using poly(vivyl pyrrolidone) (PVP) as capping molecules. These nanoparticles exhibit distinct excitonic absorption features, markedly enhanced near-bandedge UV photoluminescence, and significantly reduced defect-induced green emission.

In this study, zinc oxide nanoparticles coated with alumina were prepared by calcining basic carbonate of zinc (BCZ) particles coated with $Al(OH)_3$, rather than on

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calcined ZnO. The morphology of precursor and as-calcined ZnO were observed. The change of zeta potentials for ZnO after coating was examined.

2. Experimental

Reagent grade $ZnSO_4 \cdot 7H_2O$, NH_4HCO_3 and $Al_2(SO_4)_3 \cdot 18H_2O$ were the starting materials. They were dissolved in distilled water, and the concentrations were 1.5 mol/l zinc sulfate, 2.5 mol/l NH_4HCO_3 and 0.1 mol/l $Al_2(SO_4)_3$. $Al_2(SO_4)_3$ solution equivalents to 1–5 wt.% Al_2O_3/ZnO by weight.

22.3 ml of $ZnSO_4$ solution was added to 25.5 ml of NH_4HCO_3 solution with continuous stirring. The reaction temperature was kept at 45 °C using thermostatic water bath. The final pH value of slurry was 6.8–7.0. After precipitation of white basic carbonate of zinc (BCZ), it was stirred for another 30 min to make them react completely. The slurry was washed and filtered so as to remove SO_4^{2-} ions in the filtered solution (detected with 10% $BaCl_2$ solution). Next, the washed BCZ was dispersed again in 100 ml of distilled water using ultrasonic oscillator, and another 10 ml of NH_4HCO_3 solution was added. Then, $Al_2(SO_4)_3$ solution was dropped slowly onto the suspension surface with stirring at constant speed. After $Al_2(SO_4)_3$ solution finishing, it was stirred for another 30 min. The precursor powders were prepared after the complex precipitate was washed, filtered and dried at 80 °C over night. Finally, zinc oxide nanoparticles with surface coating were produced by calcining the resulting precursor powders at 400–600 °C for 1 h.

The morphology and particle size of precursor and as-calcined ZnO were observed using transmission electron microscope (TEM, H-8100). Phase development in the as-calcined powders was checked by X-ray diffraction (XRD) with Cu Kα radiation (Philips XGR3100). Zeta potentials of calcined ZnO were characterized using zetaplus (Brookhaven Instruments Co.). Surface composition was detected using X-ray photoelectron spectroscopy (XPS) [ESCA Lab-220i].

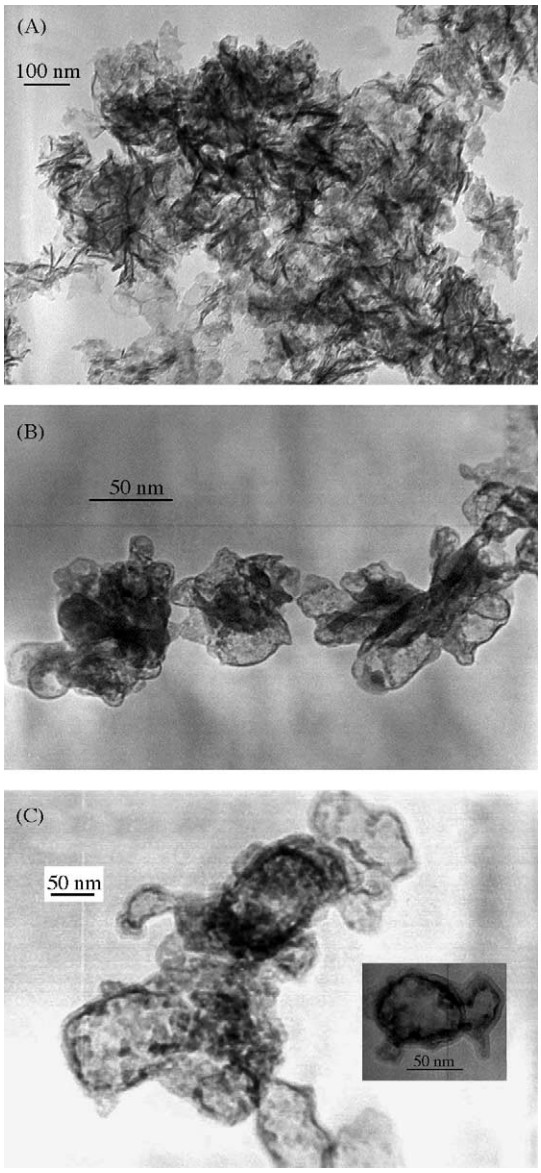

Fig. 1. TEM images of as-synthesized basic carbonate of zinc. (A) BCZ without coating, (B) BCZ coated with 3% Al_2O_3, (C) BCZ coated with 5% Al_2O_3.

3. Results and discussion

Fig. 1 shows TEM images of as-synthesized BCZ powders. It is apparent that the shape and size of as-synthesized BCZ powders are different after coating with Al_2O_3. As shown in Fig. 1A, the shape of BCZ particles without coating is need-like, and they are agglomerated. However, after coating, the shape of as-synthesized BCZ powders changes to nearly spherical. As shown in Fig. 1B, the shape of BCZ powders with 3% Al_2O_3 coating becomes spherical-like, although the powders are agglomerated with some BCZ particles. When the coated Al_2O_3 increases to 5%, the shape of BCZ powders is also spherical-like, as Fig. 1C indicates. The inset in Fig. 1C is a single powder, which shows that the coated powder is composed of many small particles. It is also found, from the TEM images, that there is a thin layer on the coated BCZ powders. As shown in Fig. 1B, almost every BCZ powder has a thin layer on the surface, although some of them agglomerate. As shown for BCZ powders coated with 5% Al_2O_3 in Fig. 1C, the thickness of coated layer increases with increase in coated Al_2O_3 content, and it is the coating that make the as-synthesized BCZ powders spherical.

In the precipitation process mentioned above, the BCZ particles are formed as the following Eq. (1). Concentration of $ZnSO_4$ and NH_4HCO_3 solution, pH value, reaction temperature and stirring rate can affect the properties of resulted BCZ particles. BCZ particles like to form plate-like and need-