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Deposition of ZnO on the surface of Al metal particles by esterification reaction under solvothermal conditions

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Abstract ZnO nanoparticles were synthesized by esterification reaction between zinc acetate and absolute ethanol under solvothermal conditions. The influences of reaction parameters and different surfactants on the size and morphology of synthesized ZnO nanoparticles were studied. As the application of this reaction, ZnO particles were deposited on the surface of Al particles using the same solvothermal process. The deposition reaction time and amount of reactants to the distribution density of deposited ZnO nanoparticles were studied. X-ray diffraction and transmission electron microscopy were used to characterize the synthesized ZnO nanoparticles and ZnO/Al composite particles.

Introduction

The ceramic/metal structural composite materials, especially the nanocomposite materials, have been extensively explored recently. These composite structures can provide a new way to give them different properties with their corresponding single materials, such as mechanical, optical, structural, catalytic, electrical and magnetic properties [1–6]. Therefore, intensive efforts have been devoted to fabrication of these composite structures.

There have been various routes to fabricate structural composite materials, including electroless plating [7], surface reaction [8], surface seeding [9] and self-assembly [10]. Most of them make great efforts to achieve uniform and complete shell on core materials [11], however, it is more interesting to assembly of nanocrystals on substrate materials with tunable size and packing density [12].

In this paper, ZnO nanoparticles were selected to deposit on the surface of Al particles to tune their composite structures. ZnO is used widely in pigments [13], cosmetics [14], varistors [15], chemical sensors [16], and optoelectronics [17]. Recently, ZnO has attracted increasing attentions, as it is a II–VI compound semiconductor with a wide and direct band gap of 3.37 eV and a large excitation binding energy of 60 meV [18]. We reported a novel method to synthesize ZnO nanoparticles with high crystallinity and good monodispersibility via esterification between zinc acetate and absolute ethanol under solvothermal conditions, and similar results were obtained for CoO and Ni etc via esterification between metal acetates and absolute ethanol [19, 20]. Herein, deposition of ZnO on the surface of Al particles was prepared using the esterification under solvothermal conditions.

Experimental

Synthesis of ZnO nanoparticles under solvothermal conditions

Zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$) and absolute ethanol were used as starting materials. A typical experiment was done as follows: 0.01 mol zinc acetate and 50 mL absolute

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ethanol were sealed in a Teflon lined stainless steel autoclave of 100 mL capacity allowing 50–60% filling. When the temperature is over 200 °C, the stainless autoclave was used. The autoclave was heated at 80–250 °C for 4–24 h under continuous stirring. After it was cooled down to room temperature, a high yield (>90%) of ZnO particles was obtained by centrifugation and washing with absolute ethanol for several times and drying in air at room temperature. In some cases, the surfactants including cetyltrimethylammonium bromide (CTAB), polyethylene glycol (PEG) and polyvinylpyrrolidone (PVP) were used to tune the size and morphology of synthesized ZnO particles.

Deposition of ZnO on the surface of Al metal particles under solvothermal conditions

When preparing ZnO deposited on Al particle surface, Al powder was added to the mixture solution of zinc acetate and absolute ethanol. The autoclave was maintained from 80 to 120 °C for different time and cooled down to room temperature naturally. Finally, Al particles deposited with ZnO were obtained by centrifugation and washing with absolute ethanol for several times and drying in air at room temperature.

Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Philips X́Pert PRO MPD X-ray diffractometer operated at 40 kV and 30 mA with Cu Kα radiation (λ = 1.5418Å). Transmission electron microscopy (TEM) images were obtained on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV.

Results and discussion

ZnO nanoparticles synthesized under solvothmeral conditions

As we reported before, ZnO can be synthesized by esterification reaction between zinc acetate and ethanol under solvothermal conditions [21]. It was found, from the XRD spectrum, that the all peaks of the products were well indexed to hexagonal crystalline ZnO (JCPDS card No. 36–1451) without impurities detected.

The reaction between zinc acetate and ethanol was possibly contained some coupling reactions. First, OH^- anions were produced by esterification reaction between CH_3COO^- and ethanol as given in Eq. 1:

$$CH_3COO^- + HO - CH_2CH_3 \rightarrow OH^- + CH_3COOCH_2CH_3 \quad (1)$$

Second, Zn^{2+} cations reacted with OH^- anions to form ZnO under solvothermal conditions as given in Eq. 2:

$$Zn^{2+} + 2OH^- \rightarrow ZnO\downarrow + H_2O \quad (2)$$

And the whole reaction mechanism can be expressed as given in Eq. 3:

$$Zn(Ac)_2 + 2HO - CH_2CH_3 \rightarrow ZnO\downarrow + 2CH_3COOCH_2CH_3 + H_2O \quad (3)$$

The esterification (Eq. 1) acted as OH^- reservoir and released OH^- gradually, which might be an important factor to synthesize ZnO nanoparticles with uniform shape and size. The presence of ethanol and ester could help to improve the dispersibility of the synthesized ZnO nanoparticles.

Figure 1 shows TEM images of synthesized ZnO nanoparticles under solvothermal conditions. It can be seen that all the ZnO nanoparticles exhibit nearly uniform diameter about 30–50 nm and no agglomeration was found in the products. By changing the reaction temperature and time, the particles size of synthesized ZnO can be easily tuned under solvothermal conditions. The ZnO nanoparticles about 50 nm in diameter were synthesized at 150°C for 4 h, as shown in Fig. 1a. When the reaction time extended to 8 h, the diameters slightly increased to about 70 nm, as shown in Fig. 1b. On the other hand, the size of ZnO nanoparticles can also be influenced substantially by adjusting the reaction temperature. The ZnO nanoparticles were near 60 nm in diameter as the temperature increased to 200 °C with the reaction time about 4 h, as shown in Fig. 1c, while the diameters shown in Fig. 1d became about 100 nm when the temperature increased to 250 °C with the reaction time 4 h unchanged.

Figure 2 shows TEM images of ZnO nanoparticles synthesized with various surfactants. It is found that the surfactants can not only affect the dispersibility of the synthesized ZnO nanoparticles, but also change their growth habit. After added surfactants in the reactor, the dispersancy of synthesized ZnO was improved, and the PVP is apparently the best one. When PEG and CTAB were added, the growth direction of ZnO is preferential to one dimension, which results in the rod-like ZnO synthesized, as shown in Fig. 2c, d, and this growth habit is more preferential when CTAB surfactant was used. Although surfactants can improve their dispersible conditions, compared with ZnO particles synthesized without surfactants, shown in Fig. 2a, it is clear that there is no distinct difference after surfactants were used. As we mentioned above, the ethanol reactant and produced ester can help to improve their dispersible conditions.

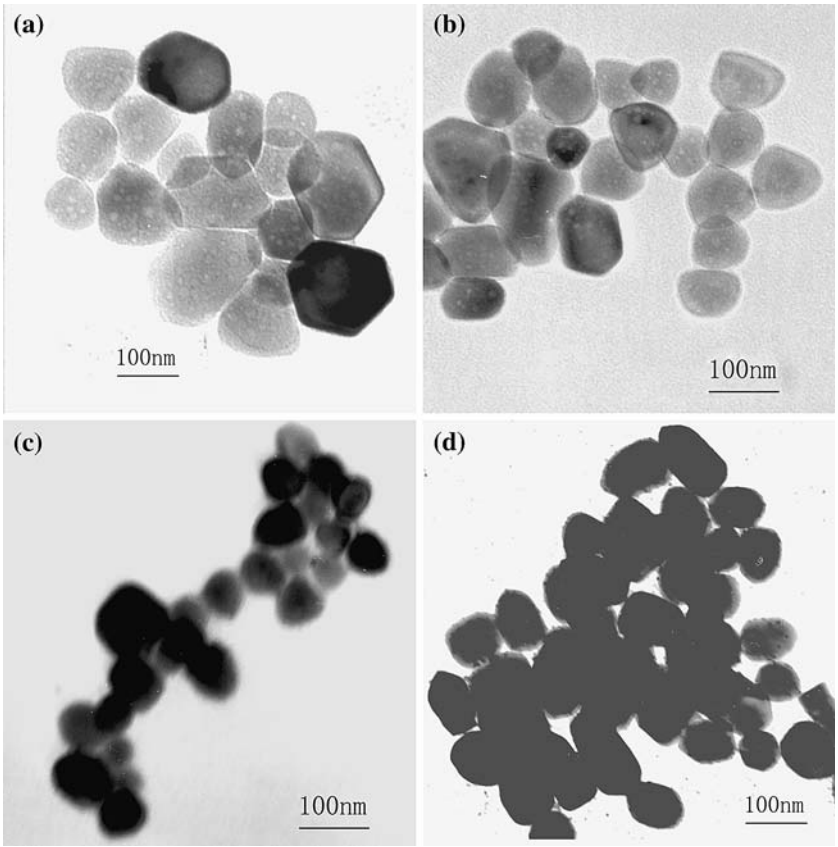

Fig. 1 TEM images of ZnO nanoparticles synthesized under different reaction time and temperature. (**a**) 0.1 mol $Zn(Ac)_2{\cdot}2H_2O$, 150 °C for 4 h, (**b**) 0.1 mol $Zn(Ac)_2{\cdot}2H_2O$, 150 °C for 8 h, (**c**) 0.05 mol $Zn(Ac)_2{\cdot}2H_2O$, 200 °C for 4 h, (**d**) 0.05 mol $Zn(Ac)_2{\cdot}2H_2O$, 250 °C for 4 h

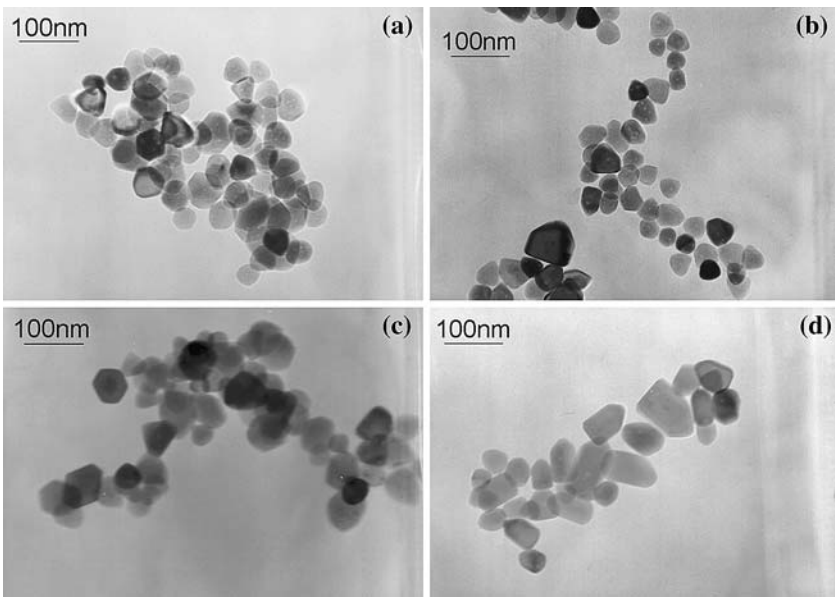

Fig. 2 TEM images of ZnO nanoparticles synthesized with different surfactants (**a**) without surfactants, (**b**) PVP, (**c**) PEG and (**d**) CTAB

Deposition of ZnO on the surface of Al particles

As seen from the TEM images mentioned above, the morphology of synthesized ZnO nanoparticles is hexagonal lamella, which is facile to form close bind with the substrate. Considering this regular hexagonal lamellar morphology, it is feasible to deposit these ZnO nanoparticles on the surface of substrate, and further construct their array by tuning their distribution density. In addition, the feature of the esterification reaction can give OH^- gradually, which makes it easy to control the reaction rate under solvothermal conditions by tuning the reaction temperature

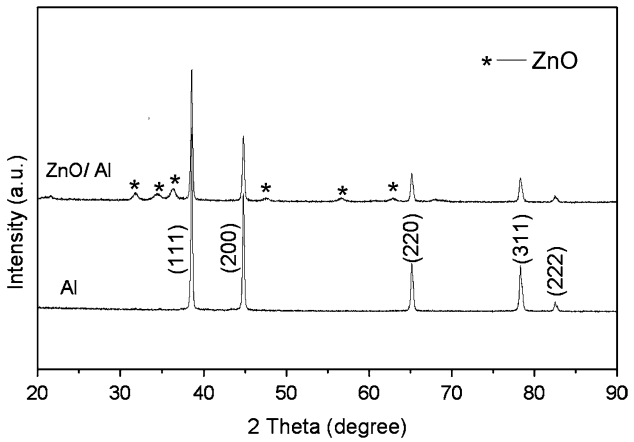

Fig. 3 XRD patterns of Al and ZnO/Al composite particles synthesized under solvothermal conditions at 80 °C for 24 h

and time. And this feature is very important for deposition of ZnO on metal/ceramic particle surface, because it can help to prevent the homogenous nucleation of ZnO in the solution and make it deposited on the surface of Al particles. Therefore, as the application of this esterification reaction, ZnO particles were deposited on the surface of Al particles using the same solvothermal process. Here, lamellar Al particles were selected as typical core particles to deposit ZnO nanoparticles, and absolute ethanol was selected as the solvent.

Figure 3 shows XRD patterns of the synthesized ZnO/Al composition particles. Typical diffraction peaks of ZnO were clearly observed as marked in the figure, which indicated the formation of ZnO crystal with hexagonal structure. Further investigation showed that the structure of Al remained unchanged during this process.

Figure 4 shows the typical TEM images of Al and ZnO/Al samples prepared under solvothermal conditions. The lamellar shape of Al with smooth surface can be observed from Fig. 4a. After ZnO deposited on the surface of Al particles, it is clear that a different surface was found. Figure 4b shows the synthesized ZnO/Al particles using 0.26 g zinc acetate and 1 g Al under solvothermal conditions at 100 °C for 9.3 h. It can be seen that the ZnO nanoparticles were homogeneously distributed on the surface of lamellar Al particles. It is reasonable that ZnO nanoparticles deposited on the surface of Al particles were nearly spherical with uniform size as the ZnO nanoparticles synthesized under the same solvothermal conditions

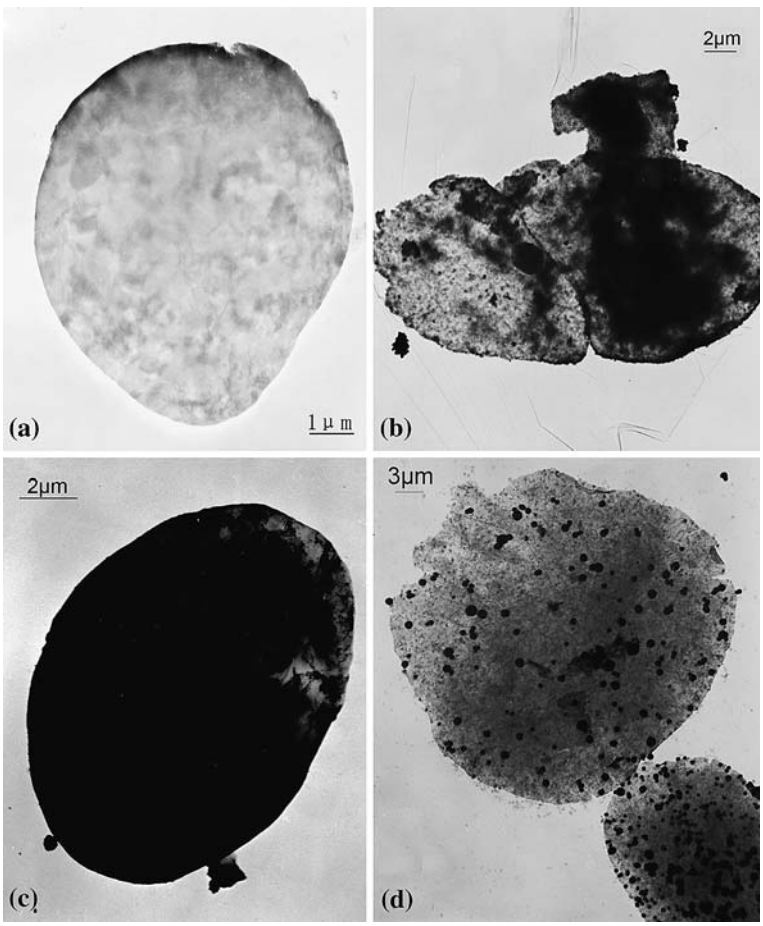

Fig. 4 TEM images of Al and ZnO/Al composite particles prepared under solvothermal conditions. (**a**) Al; (**b**) 0.26 g $Zn(Ac)_2{\cdot}2H_2O$, 1 g Al, 100 °C, 9.3 h; (**c**) 0.65 g $Zn(Ac)_2{\cdot}2H_2O$, 1.0 g Al, 100 °C, 9.3 h; (**d**) 0.26 g $Zn(Ac)_2{\cdot}2H_2O$, 1 g Al, 100 °C, 24 h

without Al particles mentioned above. The density of distributed ZnO nanoparticles on the surface of Al particles can be tuned by changing the amount of reactants, reaction time and temperature, as shown in Fig. 4c, d. When $Zn(Ac)_2{\cdot}2H_2O$ was increased from 0.26 to 0.65 g, the distribution density of ZnO particles deposited on the surface of Al particles increased, and the ZnO particles nearly covered the surface, as shown in Fig. 4c. When prolonging the reaction time, the ZnO particles size increased, as shown in Fig. 4d.

The deposited ZnO nanoparticles can be discretely distributed on the surface of Al particles as well as covered as a film. When increasing the zinc acetate amount, more ZnO nucleus can be formed resulting in the increase of distribution density. However, when increasing the reaction temperature, formed nucleus can grow to bigger particles, therefore, the particles size of deposited ZnO can be governed by tuning the reaction temperature.

The chemical compositions of the nanoparticles were analyzed by energy dispersive X-ray spectroscopy (EDX) affiliated to the TEM system by focusing the electron beam on the particles deposited on the Al surface [22]. The results show that only the characteristic peaks of Al, Zn, and Cu (come from the TEM sample grid) were detected and the weight ratio of Zn to Al element is about 1.5, which further certified the deposition of ZnO nanoparticles on the surface of Al particles.

Conclusion

ZnO nanoparticles with nearly uniform hexangular lamellar morphology and high dispersibility have been synthesized by esterification reaction between zinc acetate and absolute ethanol under solvothermal conditions. By changing the reaction temperature and time, the particles size was easily tailored from 30 to 100 nm. And this reaction is suitable to deposited ZnO nanoparticles on the surface of metal/oxide particles. Deposition of ZnO nanoparticles on the surface of Al particles was prepared under solvothermal conditions, and the distribution density of deposited ZnO particles can be well controlled by tuning the amount of reactants and reaction time.

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