Tunable Deposition of ZnO on Al Particle Surface: From Nanoparticles to Films

Peng Hu,[1,2] Fangli Yuan,*[1] Xi Wang,[1,2] Shaohua Li,[1] Jinlin Li,[1] and Yunfa Chen[1]
[1]*Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100080, P. R. China*
[2]*Graduate School of the Chinese Academy of Sciences, Beijing 100049, P. R. China*

(Received January 11, 2006; CL-060043; E-mail: flyuan@home.ipe.ac.cn)

ZnO nanoparticles and ZnO films deposited on surface of Al particles were successfully synthesized via esterification between zinc acetate and ethanol under different solvothermal condition. As-synthesized ZnO particles were nearly spherical with uniform size close to 100 nm and homogeneously distributed on the surface of Al particles. By changing the reaction temperature, ZnO thin films were obtained instead of individual particles.

Ceramic/metal structural composite materials, especially nanocomposite materials, have been extensively explored recently. Fabrication of composite structures provides a new way to functional materials with fundamentally different properties from those of the single materials and those properties including mechanical, optical, structural, catalytic, electrical, magnetic, etc.[1–6] For example, Ag and Ru nanoparticles supported on alumina have been found to exhibit attractive catalysis for the direct aerobic epoxidation of alkenes because of its effective and selective catalysis for liquid phase.[7]

Up to now, various routes have been explored to fabricate structural composite materials, including electroless plating,[8] surface reaction,[9] surface seeding,[10] and self-assembling.[11] In most case, those methods give great assistance to achieve uniform and complete shell on core materials,[12] and now assembly of nanocrystals on substrate materials with tunable size and packing density is just made great interests to researchers.[13] Actually, this structure can be used to produce materials with tunable properties by controlling the size, distribution, crystal phase, and packing density of nanocrystals. Recently, we reported a novel method to synthesize nanosized ZnO with high crystallinity and good monodispersity via esterification between zinc acetate and ethanol under solvothermal condition,[14] and similar results were obtained for CoO, Ni, etc. via esterification between metal acetates and ethanol. Considering the advantages of controlled precipitation with slow rate and nonexistence of H_2O, solvothermal reaction can effectively prevent oxidation of metal nanoparticles synthesized in esterification between metal acetates and ethanol, so it is preferable to synthesize metal-coated particles using the esterification under solvothermal condition.

In this paper, we reported the preparation of ZnO/Al composite structure by using the mechanism of this method to deposit ZnO on Al particles. The preparation was started from a mixture of zinc acetate dihydrate (0.65 g) in absolute ethanol solution (70 mL) and Al powder (1 g). The mixture was first transferred into a 100-mL Teflon-lined autoclave under constant stirring, then the autoclave was maintained from 80 to 100 °C for different time and cooled down to room temperature on standing.

The structural characteristics of as-synthesized samples were investigated by an X-ray diffractometer (XRD, Philips X'Pert PRO MPD) operated at 40 kV and 30 mA with Cu Kα radiation ($\lambda = 1.5418$ Å) through the 2θ-range from 10 to 90 degree. As shown in Figure 1, typical diffraction peaks of ZnO were clearly observed as marked in the figure, which indicated the formation of ZnO crystal. Besides, hexagonal structure with high crystallinity of as-synthesized ZnO also can be confirmed by ref 14. While the structure of Al remained unchanged during the process.

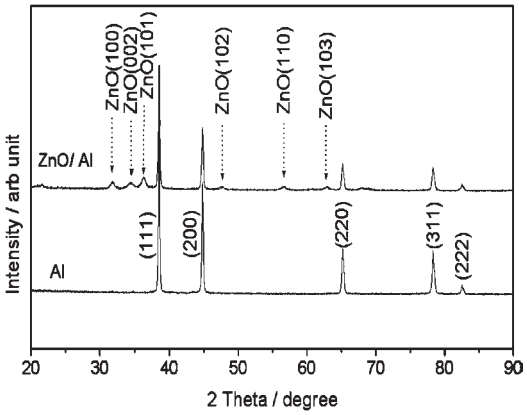

Figure 1. XRD patterns of Al and ZnO/Al samples synthesized from esterification at 80 °C for 24 h.

The morphology of the products was characterized using a transmission electron microscope (TEM, Hitachi H-800) with an accelerating voltage of 200 kV. Figure 2 shows the typical TEM images of Al and ZnO/Al samples prepared from esterification of zinc acetate on Al surface at 80 °C for 24 h. The lamella structure of Al with smooth surface can be observed from Figure 2a. Figure 2b shows the sample of ZnO/Al particles synthesized by esterification. From the picture, we can see that the deposited ZnO particles have been homogeneously distributed on the surface of Al particles, and they are spherical with size

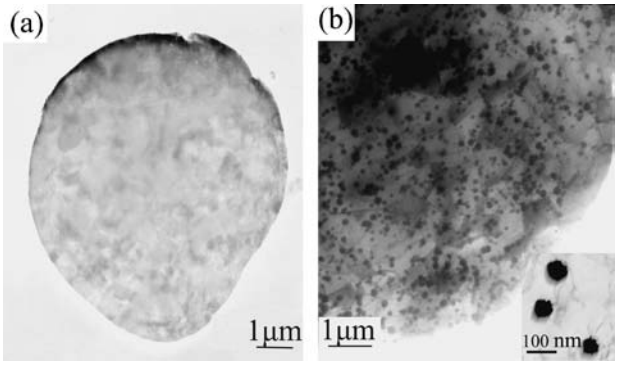

Figure 2. TEM images of (a) Al and (b) ZnO/Al samples prepared at 80 °C for 24 h.

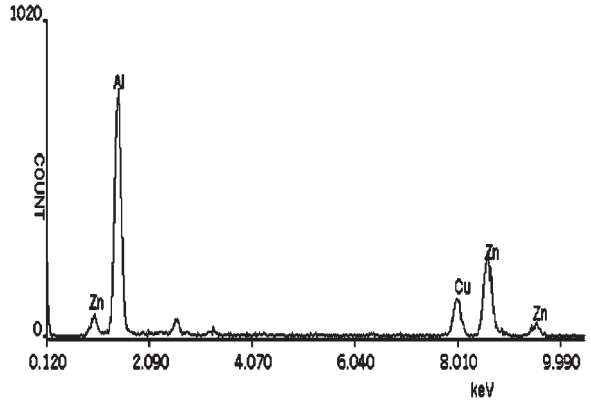

Figure 3. EDX spectrum of ZnO/Al prepared at 80 °C for 24 h.

close to 100 nm as the inset shown in Figure 2b. The chemical compositions of the nanoparticles were analysed 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. The results shown in Figure 3 illustrate 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 is about 1.5, which indicated the deposition of ZnO nanoparticles on Al surface. By varying the length of reaction time, we can also tailor the packing density of ZnO nanoparticles on Al surface.

Further experiment was performed by increasing the reaction temperature from 80 to 100 °C, and the results were shown in Figure 4. From Figure 4a, we can see that no individual ZnO particles were obtained on the surface of Al particles, and further magnification of the particle was shown in Figure 4b, which distinctly illustrated the existence of ZnO thin films on the Al particle margin. The EDX analysis gave an evidence of Zn on the Al surface and the weight ratio is about 7.90 wt %, which is rather lower than former experiment. It might contribute to the difference between the thickness of the films and size of particles. The thickness of the films is about 30–40 nm from the Al particle margin, as shown in Figure 4b, however, the size of deposited ZnO particles is about 100 nm. In our experiment, the temperature is relatively lower than that in the reference[14] for the purpose of obtaining composite materials rather than individual ZnO nanoparticles in solution. These results revealed that when crystal growth was feasible on Al surface, temperature plays a key role on the conformation of deposited ZnO owing to the effect of temperature on the activation energy of reaction. Therefore, by varying the temperature of reaction, the conformation of

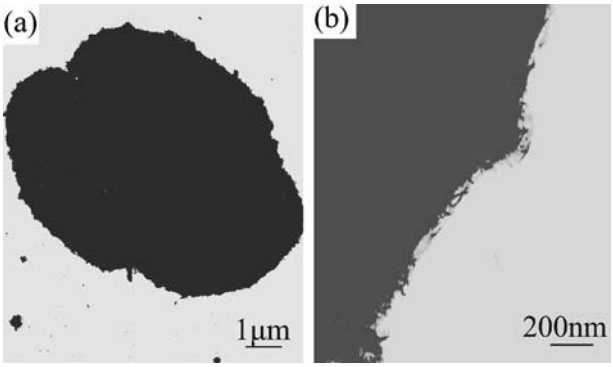

Figure 4. TEM images of ZnO/Al sample prepared at 100 °C for 24 h with (a) low magnification and (b) high magnification.

ZnO deposited on Al particles could be controlled. Since esterification between metal acetate and ethanol under solvothermal condition could be used to synthesize various metals and oxides, it is expected that this method could be used to synthesize other ceramic/metal and ceramic/ceramic composite materials with tunable structures. Moreover, the results hint us that this structure opening a possibility to tailor the properties of composite materials as a functional device.

References

1 J. M. Tsay, M. Pflughoefft, L. A. Bentolila, S. Weiss, *J. Am. Chem. Soc.* **2004**, *126*, 1926.
2 Z. Hao, J. Li, Z. L. Wang, J. P. Liu, S. H. Sun, *Nano Lett.* **2004**, *4*, 187.
3 I. A. Banerjee, L. T. Yu, H. Matsui, *Proc. Natl. Acad. Sci. U.S.A.* **2003**, *100*, 14678.
4 C. J. Zhong, M. M. Maye, *Adv. Mater.* **2001**, *13*, 1507.
5 D. Dorfs, A. Eychmüller, *Nano Lett.* **2001**, *1*, 663.
6 K. P. Velikov, A. V. Blaaderen, *Langmuir* **2001**, *17*, 4779.
7 G. Maayan, R. Neumann, *Chem. Commun.* **2005**, 4595.
8 Y. Kobayashi, V. Salgueiriño-Maceira, L. M. Liz-Marzán, *Chem. Mater.* **2001**, *13*, 1630.
9 J. Q. Hu, Q. Li, X. M. Meng, C. S. Lee, S. T. Lee, *Chem. Mater.* **2003**, *15*, 305.
10 Z. J. Jiang, C. Y. Liu, *J. Phys. Chem. B* **2003**, *107*, 12411.
11 F. Caruso, R. Caruso, H. Mohwald, *Science* **1998**, *282*, 1111.
12 L. H. Lu, A. Wohlfart, H. Parala, A. Birkner, R. A. Fischer, *Chem. Commun.* **2003**, 40.
13 S. W. Woo, W. M. Sigmund, *Chem. Commun.* **2003**, 780.
14 H. C. Du, F. L. Yuan, S. L. Huang, J. L. Li, Y. F. Zhu, *Chem. Lett.* **2004**, *33*, 770.

Published on the web (Advance View) March 11, 2006; DOI 10.1246/cl.2006.370