

Synthesis of Needle-like and Flower-like Zinc Oxide by a Simple Surfactant-free Solution Method

Wei-Wei Wang and Ying-Jie Zhu*

State Key Laboratory of High Performance Ceramics and Superfine Microstructure,
Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China

(Received May 12, 2004; CL-040538)

Single-crystalline zinc oxide (ZnO) with needle-like and flower-like morphologies has been successfully synthesized by decomposition of $\text{Zn}(\text{OH})_4^{2-}$ in aqueous solution at 90 °C. The reaction temperature, reaction time, and zinc source are important factors in determining the phase and morphology of ZnO. When using zinc acetate as the zinc source at 90 °C for 90 min in an oil bath, ZnO with the needle-like morphology was obtained. Whereas using zinc nitrate as the zinc source, ZnO with flower-like morphology was produced.

Since the discovery of carbon nanotubes,¹ one-dimensional (1-D) nanomaterials have stimulated world wide interest because of their interesting properties that differ from those of the bulk or spherical nanoparticles of the same chemical composition^{2,3} and their potential applications as important components and interconnects in nanodevices.³⁻⁵

Zinc oxide (ZnO) is an important wide bandgap semiconductor with excellent properties and a variety of applications in catalysis,⁶ gas sensors,⁷ field effect transistors,⁸ resonators,⁹ and short-wave optics.^{10,11} Many efforts have been made to synthesize ZnO with various morphologies, the preparation methods used including template-confined methods,^{12,13} high-temperature methods,¹⁴⁻¹⁶ the hydrothermal process,¹⁷⁻¹⁹ and the solution-phase method using additives such as surfactants,²⁰ etc. Needle-shaped ZnO nanostructures were synthesized over NiO-coated Si substrate by a thermal evaporation of Zn powders at 500 °C in a chemical vapor deposition (CVD) reactor.²¹ However, to our knowledge, there have been no reports on the preparation of ZnO needles or flowers by the aqueous solution method without using any template or surfactant.

Here we demonstrate that needle-like and flower-like ZnO can be synthesized by simply decomposing $\text{Zn}(\text{OH})_4^{2-}$ in aqueous solution without using any surfactant or template at relatively low temperatures, which avoids the subsequent procedure for the removal of the surfactant or template.

Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), and sodium hydroxide (NaOH) were of analytical grade and used without further purification. In a typical experimental procedure, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ or $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in deionized water to form 0.13 M solution. Excess NaOH was dissolved in the above solution at room temperature by a magnetic stirrer ($[\text{NaOH}] = 1.3 \text{ M}$). A white precipitate occurred immediately but it was dissolved by further stirring. The above solution was heated by an oil bath at appropriate temperature for a certain time. Then the heating was terminated and the solution was allowed to cool to room temperature. The products were separated by centrifugation, washed with absolute ethanol three times, and dried at 60 °C in a vacuum. White powders were obtained.

X-ray power diffraction (XRD) patterns were recorded on a Huber G 670 diffractometer using graphite-monochromatized high-intensity $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.540598 \text{ \AA}$). The morphology of the products was characterized by transmission electron microscopy (TEM, JEOL JEM-2010, using an accelerating voltage of 200 kV). Samples were deposited on thin amorphous carbon films supported by copper grids from ultrasonically processed ethanol solutions of the products.

Figure 1 shows XRD patterns of six samples. Samples 1 and 2 were prepared for 30 min using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as the zinc source at 50 and 90 °C, respectively. One can see that both samples 1 and 2 consisted of a mixture of $\text{Zn}(\text{OH})_2$ and ZnO (Figures 1a and 1b). However, sample 3 prepared at 90 °C for 30 min using $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ as the zinc source was a single phase of well-crystallized ZnO with the hexagonal structure (JCPDS File No. 79-207, Figure 1c). This indicates that the type of zinc source has an influence on the formation of ZnO. Using $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as the zinc source, single phase of crystalline hexagonal ZnO could be produced by increasing the reaction time or the temperature (Figures 1d–1f). No characteristic peaks from $\text{Zn}(\text{OH})_2$ were observed. The overall reaction may be simplified as follows:

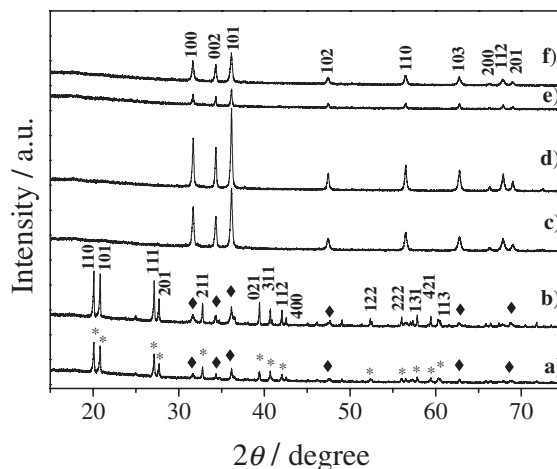
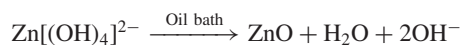


Figure 1. XRD patterns of six samples. a) Sample 1 and b) Sample 2. Samples 1 and 2 were prepared at 50 and 90 °C for 30 min in an oil bath, respectively. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used as the zinc source; c) Sample 3 prepared at 90 °C for 30 min. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was used as the zinc source; d) Sample 4 prepared at 120 °C for 30 min. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used as the zinc source; e) Sample 5 and f) Sample 6. Samples 5 and 6 were prepared at 50 and 90 °C for 90 min, respectively. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used as the zinc source; * $\text{Zn}(\text{OH})_2$; ♦ ZnO.



The morphologies of the samples were investigated by TEM and selected-area electron diffraction (SAED). Figures 2a–2c show TEM micrographs for sample 7 prepared at 90 °C for 90 min using $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ as the zinc source. One can see exclusively needle-like morphology of ZnO. The diameters of ZnO needles range from 40 to 460 nm and lengths from hundreds of nanometers to several micrometers. Figure 2b shows an individual ZnO needle with a diameter of ≈ 125 nm and lengths of ≈ 1.3 μm . The corresponding SAED pattern was shown in the inset of Figure 2b. The SAED patterns taken from different positions of an individual needle or from different needles were essentially the same, indicating that ZnO needles were single-crystalline in structure. The preferential growth direction of these needles was along the *c* axis of the crystal lattice.

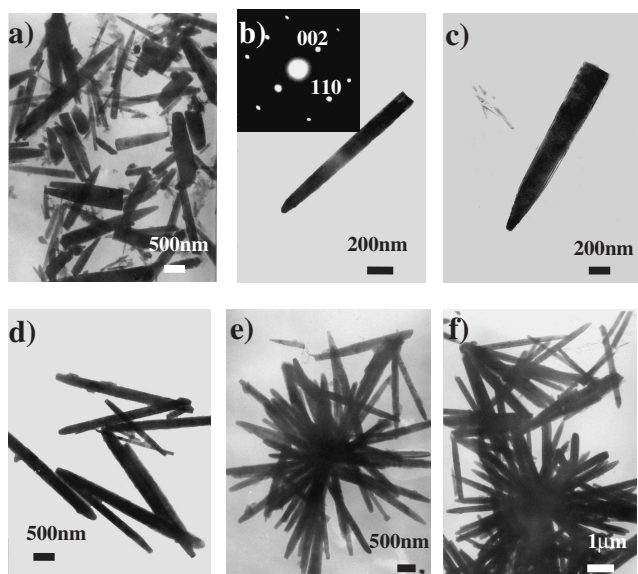


Figure 2. TEM micrographs of two as-prepared ZnO samples. a)–c) Sample 7 prepared at 90 °C for 90 min in an oil bath. $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was used as the zinc source; d)–f) Sample 6 prepared at 90 °C for 90 min. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was used as the zinc source. The inset of (b) is the corresponding SAED image.

When $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ instead of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was used as the zinc source, both flower-like (Figures 2e and 2f) and needle-like (Figure 2d) ZnO were obtained, indicating the influence of zinc source on the morphology of ZnO. The difference in the morphology of ZnO crystals by using different zinc source may be due to different role of CH_3COO^- and NO_3^- during the crystal growth. Similar morphologies have also been reported, for example, flower-like ZnO was obtained by hydrothermally treating $\text{Zn}[(\text{OH})_4]^{2-}$ precursor in water at 180 °C for 13 h;¹⁹ star-like ZnO was obtained by treating zinc acetate in water with the presence of PVA at 95 °C;²² mutipod-like ZnO whiskers were synthesized by hydrothermally treating a mixture of $\text{Zn}(\text{OH})_2$ and polyethylene glycol at 180 °C for 10 h.²³

In summary, single-crystalline ZnO with needle-like and flower-like morphologies has been successfully synthesized by decomposition of $\text{Zn}(\text{OH})_4^{2-}$ in aqueous solution at 90 °C using

zinc acetate or zinc nitrate as the zinc source and sodium hydroxide as both an alkali and a complexing reagent. This simple solution method does not need any surfactant. The reaction temperature, reaction time and zinc source are important factors in determining the phase and morphology of ZnO. The needle-like ZnO was obtained when using zinc acetate as the zinc source at 90 °C for 90 min in an oil bath. However, flower-like ZnO was produced using zinc nitrate as the zinc source. This synthetic method has advantages in terms of simplicity, low-temperature, low-cost and large-scale production of ZnO with various morphologies.

Financial support from Chinese Academy of Sciences under the Program for Recruiting Outstanding Overseas Chinese (Hundred Talents Program) is gratefully acknowledged. We thank the Fund for Innovation Research from Shanghai Institute of Ceramics, Chinese Academy of Sciences and the fund from Shanghai Natural Science Foundation. We also thank Professor Jingtai Zhao and Haohong Chen for assistance in the XRD experiments.

References

- 1 S. Iijima, *Nature*, **354**, 56 (1991).
- 2 W. U. Huynh, J. J. Dittmer, and A. P. Alivisatos, *Science*, **295**, 2425 (2002).
- 3 X. Duan, Y. Huang, Y. Cui, J. Wang, and C. M. Lieber, *Nature*, **409**, 66 (2001).
- 4 S. Frank, P. Poncharal, Z. L. Wang, and W. A. de Heer, *Science*, **280**, 1744 (1998).
- 5 H. M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, *Science*, **292**, 1897 (2001).
- 6 D. Li and H. J. Haneda, *Chemosphere*, **51**, 129 (2003).
- 7 E. Comini, G. Faglia, G. Sberveglieri, Z. W. Pan, and Z. L. Wang, *Appl. Phys. Lett.*, **81**, 1869 (2002).
- 8 M. S. Arnold, P. Avouris, Z. W. Pan, and Z. L. Wang, *J. Phys. Chem. B*, **107**, 659 (2002).
- 9 X. D. Bai, P. X. Gao, Z. L. Wang, and E. G. Wang, *Appl. Phys. Lett.*, **82**, 4806 (2002).
- 10 V. A. L. Roy, A. B. Djurišić, W. K. Chan, J. Gao, H. F. Lui, and C. Surya, *Appl. Phys. Lett.*, **83**, 141 (2003).
- 11 P. X. Gao, Y. Ding, and Z. L. Wang, *Nano Lett.*, **3**, 1315 (2003).
- 12 H. Zhang, X. Y. Ma, J. Xu, J. J. Niu, and D. R. Yang, *Nanotechnology*, **14**, 423 (2003).
- 13 C. H. Liu, J. A. Zapien, Y. Yao, X. M. Meng, C. S. Lee, S. S. Fan, Y. Lifshitz, and S. T. Lee, *Adv. Mater.*, **15**, 838 (2003).
- 14 J. Y. Lao, Y. Huang, D. Z. Wang, and Z. F. Ren, *Nano Lett.*, **3**, 235 (2003).
- 15 Z. W. Pan, Z. R. Dai, and Z. L. Wang, *Science*, **291**, 1947 (2001).
- 16 H. Q. Yan, R. R. He, J. Pham, and P. D. Yang, *Adv. Mater.*, **15**, 402 (2003).
- 17 Z. Q. Li, Y. J. Xiong, and Y. Xie, *Inorg. Chem.*, **42**, 8105 (2003).
- 18 J. Zhang, L. D. Sun, C. S. Liao, and C. H. Yan, *Chem. Commun.*, **2002**, 262.
- 19 J. Zhang, L. D. Sun, J. L. Yin, H. L. Su, C. S. Liao, and C. H. Yan, *Chem. Mater.*, **14**, 4172 (2002).
- 20 A. P. A. Oliveira, J. F. Hochepped, F. Grillon, and M. H. Berger, *Chem. Mater.*, **15**, 3202 (2003).
- 21 T. Y. Kim, J. Y. Kim, S. H. Lee, H. W. Shim, S. H. Lee, E. K. Suh, and K. S. Nahm, *Synth. Met.*, **144**, 61 (2004).
- 22 R. V. Kumar, R. Elgamiel, Y. Kolytyn, J. Norwig, and A. Gedanken, *J. Cryst. Growth*, **250**, 409 (2003).
- 23 J. M. Wang and L. Gao, *J. Cryst. Growth*, **262**, 290 (2004).