Templateless Hydrothermal Synthesis of Aligned ZnO Nanorods

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Aligned single crystalline ZnO nanorods with sharp end were synthesized hydrothermally starting from metallic zinc powders; investigations reveal that only metal powders can give rise to nanorods under suitable conditions.

The research area of one-dimensional (1D) nanomaterials is very active recently because of their unique properties and wide potentials in nanodevices.[1] Although a large number of 1D nanomaterials have been isolated,[2] fabrication of 1D nanomaterial arrays is still a paramount challenge. Many methods have been reported including the famous vapor–liquid–solid or vapor–solid growth techniques and methods employing templates such as porous aluminum oxide or lyotropic liquid crystals.[3] The vapor techniques usually require special equipments and high temperatures, and the template method often encounters difficulties of prefabrication and postremoval of the templates and usually results in impurities. Hence, further development of synthetic methods is required. Substantial recent studies have indicated that hydrothermal route is a powerful and promising strategy for preparing 1D nanomaterials, such as nanowires and nanotubes, but mostly without any orientatianal order.[4] For its simple procedure and low cost, it would be desirable to use hydrothermal reactions for the synthesis of arrayed nanowires if ever possible.

Extensive efforts have been focused on zinc oxide nanomaterials with controllable morphologies because of its wide bandgap feature and various applications. Oriented ZnO nanowire or nanorods have been reported by high temperature technique or template methods.[5] Solution routes were also developed to make 1D ZnO nanostructures under the assistance by surfactant or polymers.[6] Recently, Yang's group reported a mild method for ZnO nanowire arrays using nanoparticles as seeds.[7] We have successfully prepared large area free-standing titanate and anatase nanowire arrays with aspect ratios up to 20000 by simple templateless hydrothermal method using metallic Ti powders as the starting reagent.[8] To extend this method for other anisotropic nanowire arrays, zinc oxide nanorod arrays were prepared using H_2O_2 as the oxidant.

The zinc oxide nanorods were prepared by using metallic zinc powder (100 mesh, Aldrich) as the raw material. Typically, 0.4 g of Zn powder and 14 mL of H_2O were mixed in a Teflon vessel without stirring. Then 1 mL of H_2O_2 (35%) was injected. The mixture was sealed and hydrothermally reacted at 220 °C for two days. The reaction can be expressed as:

$$Zn + H_2O_2 \rightarrow ZnO + H_2O$$

Indicated by this equation, this process is environmentally benign without any additive and by-product and also avoids impurities. The reaction produced a light yellow precipitate that was separated by decanting the solution, washed by distilled water, and dried at room temperature. The product was characterized by powder X-ray diffraction (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM).

The XRD pattern was recorded on a Riguku D/MAX-2200 Ultima diffractometer equipped with a monochromated Cu Kα radiation. The XRD profile (Figure 1A) confirmed that the ZnO nanorods are hexagonal wurtzite structure ($P6_3mc$, $a = 3.2495$, $c = 5.2069$ Å). All the peaks could be well indexed without any impurity. The SEM observation was performed on a Philips XK30-FEG model operating at a maximum accelerating voltage of 30 kV. The SEM image (Figure 1B) reveals that the product is composed of aligned hexagonal pencil-like nanorods with nearly uniform diameters. The energy dispersive X-ray analysis shows a 1:1 Zn:O composition within an experimental error that is consistent with stoichiometric ZnO, revealing that the nanorods are composed of pure ZnO. The sample was further characterized by TEM on a JEM-3011 model operating with a 300 keV electron beam. Figure 2 shows the TEM and HRTEM images and ED pattern of a single nanorod. The nanorod is 5 µm in length and 45–200 nm in diameter with one sharp end of 20 nm, showing the aspect ratio up to 110. The HRTEM im-

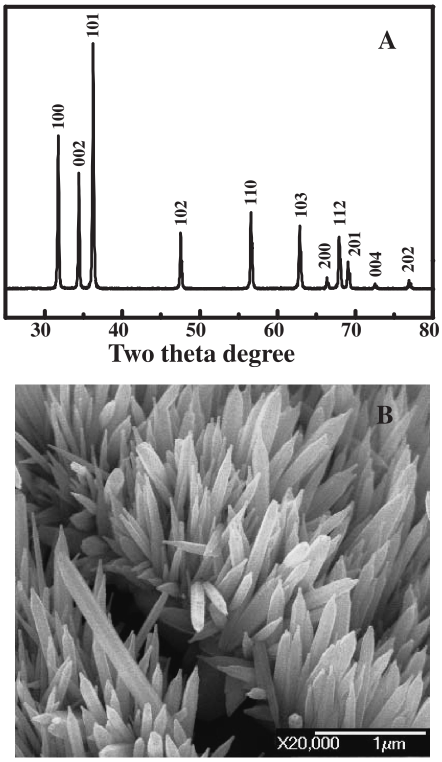

Figure 1. XRD pattern (A) and SEM image (B) of ZnO nanorod arrays.

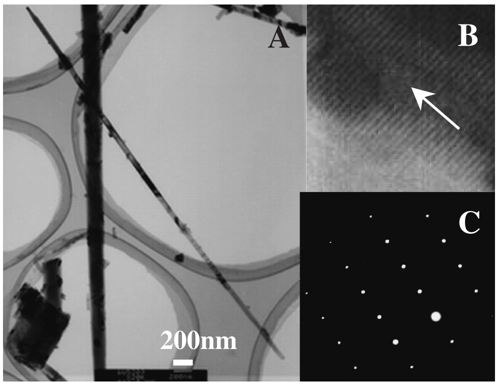

Figure 2. TEM (A) and HRTEM (B) images and ED pattern of a single ZnO nanorod with the arrow showing the growing direction.

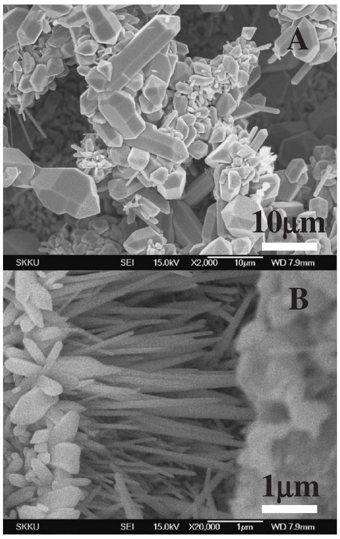

Figure 3. SEM images of ZnO produced by using zinc foil: (A) on the surface of the foil, (B) nanorods in the crack of the foil.

age shows clear lattice fringes with the interval distance of 2.6 Å between adjacent planes, corresponding to the distance between two [002] lattice planes, disclosing the single crystal feature. This also confirms that [001] is the preferred growth direction for ZnO nanorods.

To our knowledge, array structures of 1D nanomaterials were seldom reported from seedless or templateless hydrothermal reactions. As the case observed in our previous titanate nanowire arrays, the key is using metal powder as the raw material. The same reaction was also carried out by using zinc foil in place of zinc powder. Large micron size crystals formed on the surface of the foil (Figure 3A). However, aligned nanorods grow between the cracks which were generated during the reaction (Figure 3B). This is because of the rough surface of the cracks, which is similar to stacked metal powders. The reaction is also sensitive to temperature. Below 220 °C, the product contains unreacted zinc metal. The nanorods grow randomly at higher temperature. These investigations indicate that the growth of ZnO nanorods is kinetic control. That is, the involved reactions must occur in compatible rates in order to form the nanorods into arrays. Li has also hydrothermally prepared randomly grown ZnO nanorods with nearly 100 nm in diameters from zinc metal using cetyltrimethylammonium bromide (CTAB) to control the morphology.[8] This method generated flammable H_2 gas. The CTAB also contaminates the environment. Our strategy is a green method and produces thinner nanorods with sharp ends. Furthermore, our result suggests that nanorod array patterns may be produced by modifying the surface by planting metal particles.

In summary, a simple templateless hydrothermal method was developed for ZnO nanorod arrays by using metallic zinc powder as the reagent and H_2O_2 as the oxidant. The simple route avoids impurities and is environmentally benign. The nanorods are single crystalline that have pencil-like morphology with sharp ends. The formation of zinc oxide nanorod arrays is influenced by the reaction temperature and the form of zinc metal.

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References

1 a) G. R. Patzke, F. Krumeich, and R. Nesper, *Angew. Chem., Int. Ed.*, **41**, 2446 (2002). b) J. Hu, T. W. Odom, and C. M. Lieber, *Acc. Chem. Res.*, **32**, 435 (1999). c) N. I. Kovtyukhova and T. E. Mallouk, *Chem.—Eur. J.*, **8**, 4355 (2002). d) Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kin, and H. Yan, *Adv. Mater.*, **15**, 353 (2003). e) D. Appell, *Nature*, **419**, 553 (2002).

2 C. N. R. Rao, F. L. Deepak, G. Gundiah, and A. Govidara, *Prog. Solid State Chem.*, **31**, 5 (2003).

3 a) A. L. Prieto, M. Martin-Gonzalez, J. Kenyani, R. Grosky, T. Sands, and A. M. Stacy, *J. Am. Chem. Soc.*, **125**, 2388 (2003). b) M. S. Sander, A. M. Prieto, R. Gronsky, T. Sands, and A. M. Stacy, *Adv. Mater.*, **14**, 665 (2002). c) Y. Zhang, G. Li, Y. Wang, B. Zhang, W. Song, and L. Zhang, *Adv. Mater.*, **14**, 1227 (2002). d) C. Schonenberger, B. M. I. van der Zander, L. G. J. Fokkink, M. Henny, C. Schmid, M. Kruger, A. Bachtold, R. Huber, and U. Staufer, *J. Phys. Chem. B*, **101**, 5497 (1997). e) H. Yang, Q. Shi, B. Tian, Q. Lu, F. Gao, S. Xie, J. Fan, C. Yu, B. Tu, and D. Zhao, *J. Am. Chem. Soc.*, **125**, 4724 (2003). f) L. Huang, H. Wang, Z. Wang, A. Mitra, D. Zhao, and Y. Yan, *Chem. Mater.*, **14**, 876 (2002). g) L. Huang, H. Wang, Z. Wang, A. Mitra, K. N. Bozhilov, and Y. Yan, *Adv. Mater.*, **14**, 61 (2002).

4 a) W. Wang and Y. Li, *J. Am. Chem. Soc.*, **124**, 2880 (2002). b) A. Xu, Y. Fang, L. You, and H. Liu, *J. Am. Chem. Soc.*, **125**, 1494 (2003). c) B. Liu and H. C. Zeng, *J. Am. Chem. Soc.*, **125**, 4430 (2003). d) Y. Li, J. Wang, Z. Deng, Y. Wu, X. Sun, D. Yu, and P. Yang, *J. Am. Chem. Soc.*, **123**, 9904 (2001). e) M. Cao, C. Hu, G. Peng, Y. Qi, and E. Wang, *J. Am. Chem. Soc.*, **125**, 4982 (2003). f) J. L. Fulton and M. M. Hoffman, U. S. Patent 6316377 B1. g) X. Wang and Y. Li, *Angew. Chem., Int. Ed.*, **41**, 4790 (2002). h) Y. Li, Y. Ding, and Z. Wang, *Adv. Mater.*, **11**, 847 (1999).

5 Y. K. Tseng, C. J. Huang, H. M. Cheng, I. N. Lin, K. S. Liu, and I. C. Chen, *Adv. Funct. Mater.*, **13**, 811 (2003).

6 B. Liu and H. C. Zeng, *Chem. Mater.*, **20**, 4196 (2004); B. Cheng and E. T. Samulski, *Chem. Commun.*, **2004**, 986.

7 L. E. Greene, M. Law, J. Goldberger, F. Kim, J. C. Johnson, Y. Zhang, R. J. Saykally, and P. Yang, *Angew. Chem., Int. Ed.*, **42**, 3031 (2003).

8 Y. Zhao, U. H. Lee, M. Suh, and Y. U. Kwon, *Bull. Korean Chem. Soc.*, **25**, 1341 (2004).

9 X. M. Sun, X. Chen, Z. X. Deng, and Y. D. Li, *Mater. Chem. Phys.*, **78**, 99 (2002).

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