A Novel Route to Prepare ZnO Nanotubes by Using Microwave Irradiation Method

Xiang-rong Kong,*[1] Yueqin Duan,[2] Peng Peng,[1] Chen Qiu,[1] Liyan Wu,[1] Lin Liu,[1] and Wenjun Zheng*[1]
[1]*Department of Materials, College of Chemistry, Nankai University, Tianjin 300071, P. R. China*
[2]*Nanomaterials & Nanotechnology Research Center, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin 300191, P. R. China*

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Well-crystallized zinc oxide nanoscale tubular structures have been prepared by using the microwave irradiation method which does not need any templates, seeds, and surfactants. The ZnO nanotubes have regular polyhedral shapes, hollow cores with diameters of 100–200 nm, lengths of 1–3 μm and wall thicknesses of 10–40 nm.

Nano-ZnO has been recognized as one of the promising nanomaterials in a broad range of high-technology applications, such as surface acoustic wave filters, photonic crystals, light-emitting diodes, photodetectors, optical modulator waveguides, varistors, gas sensors, and solar cells because of its unique electrical, optoelectronic, and luminescent properties, as well as high mechanical strength, thermal stability, chemical stability, and negative electron affinity.[1–14] Because the novel properties of nanomaterials depend on their size and shape, new synthetic strategies and better understanding of the growth mechanisms by which the size and shape of nanostructures can be easily tailored are key issues in nanomaterials chemistry.[10] In particular, nanotubes possess several different areas of contact (borders, inner and outer surfaces, and structured tube walls) that in principle can be functionalized in several ways such as the incorporation of nanorods in nanotubes and is more generally used as nanoscale host materials. Moreover, the tubular nanostructures might exhibit some interesting physical and chemical properties unattainable by other nanostructures and open up possibilities for various new application fields such as catalysis, intramolecular junctions, storage and release systems.[1]

During the past several years, various methods including chemical, electrochemical, and physical deposition techniques have been developed for the preparation of one-dimensional ZnO nanorods. However, ZnO nanotubes appear to be the most difficult to grow naturally, and the study on ZnO nanotubular is largely limited.[1–17] Recently, almost monodisperse nanoscale InGaP, InP, CdSe,[18] and TiO_2 nanotubes of good quality[19] have been prepared via direct microwave heating. To our best knowledge, ZnO nanotubes prepared by microwave irradiation (MWI) methods in aqueous solution have not been reported. In this study, we will report novel ZnO nanotubes prepared in aqueous solution at room temperature with the aid of MWI methods.

ZnO nanotubes were grown in 50 mL of an aqueous solution containing 0.05 M zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), and 0.08 M urea in a conventional reaction beaker for a limited time with fiercely stirring and then irradiated with a microwave oven (LGWD900(MG-5523SD), 900 W, 2450 GHz) at 180 W with 40 min. The resulting white precipitate was collected and washed with deionized water several times before being dried in an oven at 65 °C. Other samples were prepared similarly with the MWI method.

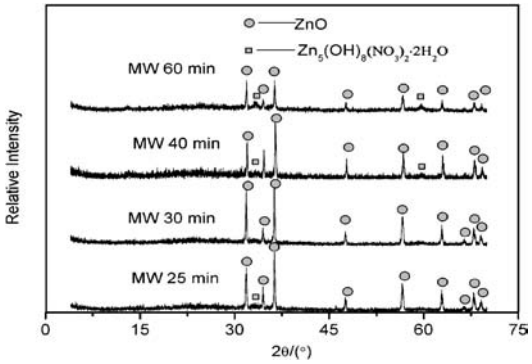

Figure 1. XRD patterns of the products at different reaction time (grown in 0.02 M Zn^{2+} + 0.04 M urea).

A typical XRD pattern is shown in Figure 1 (MWI 30 min) with all diffraction peaks well indexed to hexagonal phase ZnO (JCPDS No. 36-1451), indicating that the sample is wurtzite ZnO (space group $P63mc$, $a = 0.325$ nm and $c = 0.521$ nm). It can be seen from Figure 1 (MWI 25, 40, and 60 min) that the very weak peaks due to $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (JCPDS No. 24-1460) appear in addition to the ZnO peaks. That is to say, the samples are of mainly ZnO and a little $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$. According to previous literature,[20–22] the main process of urea hydrolyzation in the solution and other possible reactions in the solution are:

$$(NH_2)_2CO + 2H_2O \rightarrow 2NH_4^+ + CO_3^{2-} \quad (1)$$

$$(NH_2)_2CO + 3H_2O \rightarrow 2OH^- + 2NH_4^+ + CO_2 \quad (2)$$

$$2OH^- + Zn^{2+} \rightarrow ZnO_{(s)} + H_2O \quad (3)$$

$$Zn(NO_3)_2 + 2H_2O + 4Zn^{2+} + 8OH^- \rightarrow Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O \quad (4)$$

The different mol ratio of urea/Zn^{2+} has been observed to have an impact on the morphology and composition of samples. When the urea/$Zn^{2+} \geq 1$, $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ can be identified from Figure 2 S1 and S2. The diffraction peaks of $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ disappear when the mole ratio of urea/$Zn^{2+} < 1$.

Typical SEM images of the prepared products are shown in Figure 3. Figure 3 S1 reveals that ZnO nanotubes have regular polyhedral shapes, hollow cores with diameters of 100–200 nm, lengths of 1–3 μm, and wall thicknesses of 10–40 nm. It can be seen that some of the nanotubes appear straight. Figure 3 S2 shows that ZnO nanotubes have regular polyhedral shapes, hollow cores with diameters of 400 nm, lengths over several micrometres and wall thicknesses of 25–100 nm. Detailed SEM analysis revealed that the nanotubes had distinctive hollow cores with well defined polyhedral shapes. Most of the open ends of the nanotubes are found to have typical hexagonal shapes pro-

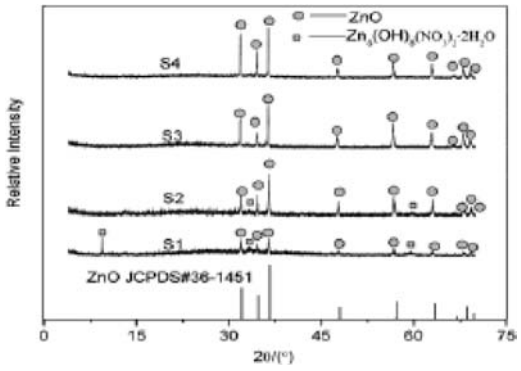

Figure 2. XRD patterns of the products MWI 40 min at different reaction concentration. (S1): 0.05 M Zn^{2+} + 0.08 M urea, (S2): 0.02 M Zn^{2+} + 0.04 M urea, (S3): 0.02 M Zn^{2+} + 0.02 M urea, (S4): 0.05 M Zn^{2+} + 0.02 M urea.

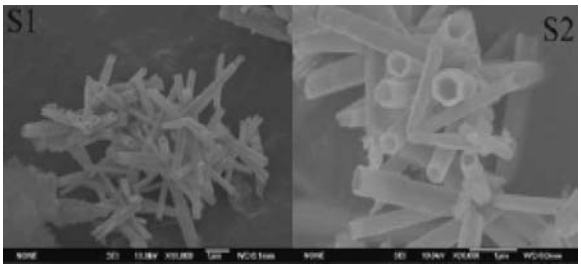

Figure 3. SEM images of the products at different reaction concentration (The scale bar is 1 μm). (S1): 0.05 M Zn^{2+} + 0.08 M urea, (S2): 0.02 M Zn^{2+} + 0.03 M urea.

viding strong evidence of the [001] growth direction (the *c* axis) of the hexagonal ZnO nanotubes.

As to the formation mechanism of the zinc oxide nanotubes, the nuclei at proper nucleation sites and unidirectional growth of the nuclei are key factors responsible for it.[23] Additionally, there is no center of inversion in the wurtzite crystal structure and, therefore, an inherent asymmetry along the *c* axis is present which allows the anisotropic growth of the crystal along the [001] direction. Accordingly, the most stable crystal habit is a hexagon elongated along the *c* axis.[16] The observed hexagonal end of the nanotubes is thus reflected by of its hexagonal nanostructure. However, we could not disaffirm that the $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ can be concomitantly formed with ZnO according to above discussion. According to our SEM results (not shown here), ZnO nanotubes were not found in samples prepared when the mole ratio of urea/Zn^{2+} < 1. Microwave is an electromagnetic wave composed of both electronic and magnetic field components, which give both the irradiation effects and the nonirradiation effects.[24] The water of crystallization and hydroxy group (OH) of layered $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ can absorb MWI energy,[25] and thus unbalanced energy converts the layered product into the tubular ZnO nanostructure. However, further investigations have to be carried out to understand in more detail the formation mechanism during the MWI process, thermal stability, catalytic property of the present ZnO nanotubes.

In summary, well-crystallized nanoscale zinc oxide tubular structures have been prepared. This will open a new and quick way suitable for large scale-up production to produce nonlamellar semiconductor compound nanotubes. The novelty and the unique features of the ZnO nanotubes will have wide applications in optics and optoelectronics as well as in biology. Further research is under progress in our laboratory.

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References

1 X.-P. Shen, A.-H. Yuan, Y.-M. Hu, Y. Jiang, Z. Xu, Z. Hu, H. B. Jia, D. P. Yu, *Nanotechnology* **2005**, *16*, 2039.
2 J.-J. Wu, S.-C. Liu, C.-T. Wu, K.-H. Chen, L.-C. Chen, *Appl. Phys. Lett.* **2002**, *81*, 1312.
3 X.-H. Zhang, S.-Y. Xie, Z.-Y. Jiang, X. Zhang, Z.-Q. Tian, Z.-X. Xie, R.-B. Huang, L.-S. Zheng, *J. Phys. Chem. B* **2003**, *107*, 10114.
4 Y. J. Xing, Z. H. Xi, Z. Q. Xue, X. D. Zhang, J. H. Song, R. M. Wang, J. Xu, Y. Song, S. L. Zhang, D. P. Yu, *Appl. Phys. Lett.* **2003**, *83*, 1689.
5 J. Q. Hu, Q. Li, X. M. Meng, C. S. Lee, S. T. Lee, *Chem. Mater.* **2003**, *15*, 305.
6 Y. J. Xing, Z. H. Xi, X. D. Zhang, J. H. Song, R. M. Wang, J. Xu, Z. Q. Xue, D. P. Yu, *Solid State Commun.* **2004**, *129*, 671.
7 X. Y. Kong, Y. Ding, Z. L. Wang, *J. Phys. Chem. B* **2004**, *108*, 570.
8 X. Kong, X. Sun, X. Li, Y. Li, *Mater. Chem. Phys.* **2003**, *82*, 997.
9 H. Kim, W. M. Sigmund, *J. Mater. Res.* **2003**, *18*, 2845.
10 Q. Li, V. Kumar, Y. Li, H. Zhang, T. J. Marks, R. P. H. Chang, *Chem. Mater.* **2005**, *17*, 1001.
11 H. Yu, Z. Zhang, M. Han, X. Hao, F. Zhu, *J. Am. Chem. Soc.* **2005**, *127*, 2378.
12 H. W. Liang, Y. M. Lu, D. Z. Shen, B. H. Li, Z. Z. Zhang, C. X. Shan, J. Y. Zhang, X. W. Fan, G. T. Du, *Solid State Commun.* **2006**, *137*, 182.
13 Y. Sun, D. J. Riley, M. N. R. Ashfold, *J. Phys. Chem. B* **2006**, *110*, 15186.
14 J. Zhang, L. D. Sun, C. S. Liao, C. H. Yan, *Chem. Commun.* **2002**, 262.
15 X. H. Kong, Y. D. Li, *Chem. Lett.* **2003**, *32*, 1062.
16 L. Vayssieres, K. Keis, A. Hagfeldt, S.-E. Lindquist, *Chem. Mater.* **2001**, *13*, 4395.
17 Y. Sun, G. M. Fuge, N. A. Fox, D. J. Riley, M. N. R. Ashfold, *Adv. Mater.* **2005**, *17*, 2477.
18 J. A. Gerbec, D. Magana, A. Washington, G. F. Strouse, *J. Am. Chem. Soc.* **2005**, *127*, 15791.
19 Y. A. Wang, J. J. Yang, J. W. Zhang, H. J. Liu, Z. J. Zhang, *Chem. Lett.* **2005**, *34*, 1168.
20 R. J. M. J. Vogels, J. T. Kloprogge, P. A. Buining, D. Seykens, J. B. H. Jansen, J. W. Geus, *J. Non-Cryst. Solids* **1995**, *191*, 38.
21 W. H. R. Shaw, J. J. Bordeaux, *J. Am. Ceram. Soc.* **1955**, *77*, 4729.
22 J. T. Kloprogge, L. Hickey, R. Trujillano, M. J. Holgado, M. S. S. Román, V. Rives, W. N. Martens, R. L. Frost, *Cryst. Growth Des.* **2006**, *6*, 1533.
23 R. M. Wang, Y. J. Xing, J. Xu, D. P. Yu, *New J. Phys.* **2003**, *5*, 115.
24 *Microwave Chemistry (in Chinese)*, ed. by Q. H. Jin, Science Press, Beijing, **1999**.
25 K. J. Rao, B. Vaidhyanathan, M. Ganguli, P. A. Ramakrishnan, *Chem. Mater.* **1999**, *11*, 882.

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