PAPER

NJC
www.rsc.org/njc

Solvothermal synthesis of ultralong single-crystalline TiO_2 nanowires

Bao-Mei Wen,[ab] Chun-Yan Liu*[a] and Yun Liu[a]

[a] *Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, 100101, China. E-mail: cyliu@mail.ipc.ac.cn; Fax: +86-10-64879375; Tel: +86-10-64888179*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing, 100101, China*

Received (in Durham, UK) 22nd February 2005, Accepted 26th April 2005
First published as an Advance Article on the web 10th June 2005

Well-defined single crystalline TiO_2 nanowires with diameters of 20–50 nm mostly and lengths of up to a few millimeters have been successfully synthesized by a simple, low-cost solvothermal process using the mixed solvent aqueous NaOH–ethanol. The as-synthesized nanowires are structurally uniform, of high purity and show perfect crystallinity. The growth mechanism of the nanowires has been investigated by following the growth steps of the samples at various reaction stages. The solvent significantly influences the morphology and the crystallization behavior of the final products. This novel approach may be applied to the large-scale fabrication of some other oxide nanowires.

Introduction

Single-crystalline, one-dimensional nanostructures, such as nanotubes, nanorods, nanobelts and nanowires have stimulated intensive interest because of their unique applications in mesoscopic physics and the fabrication of nanoscale devices.[1–3] Among these one-dimensional nanostructures, in particular, nanowires play an important role as both interconnects and active components in fabricating nanoscale electronic and photonic devices.[4] Recently, many oxide nanowires were successfully synthesized by evaporating the desired commercial metal oxide powders at a high temperature.[5–7] However, a facile solution-phase synthesis for nanowires, which may provide a more promising approach in terms of cost and efficiency, has been less reported.

Titania is an n-type semiconductor and a typical photocatalyst, widely used as a catalyst support,[8] a photocatalyst,[9] in solar cells,[10] and in sensors,[11] attracting much attention from both fundamental and practical viewpoints. To explore novel approaches for nanostructured TiO_2 with various properties by controlling their size and morphology is of great interest. To date, a few methods have been developed to synthesize one-dimensional TiO_2 nanostructures. Kasuga *et al.*[12] prepared TiO_2 nanotubes by a sol–gel method. Kobayashi *et al.*[13] employed supramolecular assemblies to synthesize TiO_2 hollow fibers. However, single crystallinity of these nanostructures has not been confirmed so far. Recently, Liu *et al.*[14] synthesized single-crystalline anatase TiO_2 nanotubes with an unconstrained solution growth method by hydrolyzing TiF_4 under acidic conditions. Zhang *et al.*[15] fabricated single-crystalline anatase TiO_2 nanowires in anodic alumina membranes. Li and co-workers[16] synthesized single-crystalline TiO_2 nanowires with a mixed anatase and brookite structure by a hydrothermal method. Despite this, the challenge of synthetically controlling single crystallinity of ultralong anatase nanowires with high purity and high crystalinity has been met with only limited success.[17] Up to now, no reports have demonstrated the ability to control high purity, highly crystalline and ultralong single-crystalline nanowires of anatase TiO_2. Herein, we report a solvothermal route using the mixed solvent aqueous NaOH–ethanol to synthesize ultralong single-crystalline anatase TiO_2 nanowires with lengths of up to a few millimeters. To the best of our knowledge, the synthesis of TiO_2 nanowires by a solvothermal process using a mixed solvent has not been reported previously. In addition, this simple method has potential as a generic approach of synthesizing ultralong, high-purity single-crystalline semiconductor nanowires of other oxides.

Experimental

All chemicals were used as received without further purification. Degussa P25 powders (average particle size 30 nm and specific surface area of 50 $m^2\ g^{-1}$), sodium hydroxide (NaOH, A. R.), ethanol (C_2H_5OH, A. R.) were purchased from Beijing Chemical Factory. Doubly distilled deionized water was used during all the experiments.

In a typical synthesis, 0.5 g of commercial Degussa P25 powder was mixed with aqueous 10 M NaOH and absolute ethanol with a volume ratio of 1 : 1. Then 20 mL of the mixed solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave. The autoclave was maintained at 170–200 °C under autogenous pressure for 24 h and then cooled to room temperature naturally. The obtained sample was filtered off, washed several times with dilute HCl aqueous solution and deionized water until the pH value of the washing solution was about 7, and dried at 60 °C for 12 h in air.

X-Ray powder diffraction (XRD) analysis was used to determine the phases of the products. The morphologies of the products were viewed by transmission electron microscopy (TEM). The XRD analysis was performed using a Rigaku DMAX-2000 X-Ray diffractometer with Cu-Kα radiation ($\lambda = 1.54056$ Å) at a scanning rate of 0.02 ° s^{-1} in 2θ ranging from 20 to 80°. The TEM and SAED images were recorded on a JEOL JEM-CX200 microscope at an acceleration voltage of 160 kV. The TEM samples were prepared by dropping an alcohol suspension of sample powders on a Formvar coated copper grid and allowing the alcohol evaporate at room temperature. The HRTEM images were obtained on a Philips CM200/FEG microscope at an acceleration voltage of 200 kV.

DOI: 10.1039/b502604k

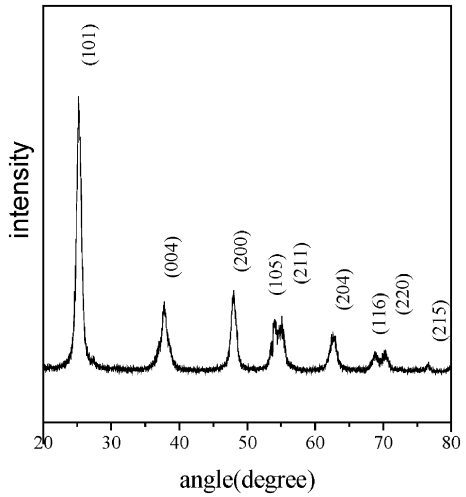

Fig. 1 XRD pattern of the synthesized TiO_2 nanowires.

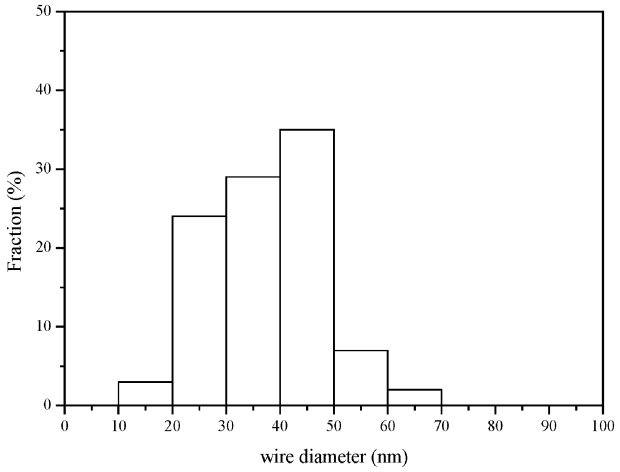

Fig. 3 Histogram of the diameter distribution of the synthesized TiO_2 nanowires.

Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern of the synthesized TiO_2 nanowires. All of the peaks can be readily indexed to the pure anatase phase with lattice constants $a = 3.7806$ Å, $c = 9.4977$ Å, which are basically in agreement with the reported values (JCPDS No. 21-1272). No characteristic peaks of other impurities were observed, which indicated that the product had high purity.

Fig. 2(a)–(c) show overviews of TEM images of the synthesized TiO_2 nanowires. There are several important features for these nanowires. First, the nanowires are ultralong with lengths of up to a few millimeters. Second, the diameters of the nanowires almost entirely range from 20 to 50 nm (Fig. 3). Third, all nanowires are structurally uniform. Such characteristics are very significant for future nanowire device fabrication. The electron diffraction image (inset in Fig. 2(c)) was recorded perpendicularly to the long axis of the nanowire. The diffraction spots were indexed for the [010] zone axis of single-crystal anatase phase, which confirmed that the nanowires grew preferably along the [001] direction.

High-resolution transmission electron microscopy (HRTEM) images (Fig. 4) showed nanowires with well-defined structure. The fringes parallel to the nanowire axis corresponded to an interplanar distance of about 0.35 nm. This fringe spacing is a characteristic of the anatase crystal phase in the (101) plane. The clear lattice fringes further confirm the nanowires are single-crystalline and the structure is perfect.

To understand the role of NaOH and ethanol in the synthetic process, we changed the concentration of NaOH, and the volume ratio of ethanol to water, respectively, keeping all other conditions unchanged. We found that the ratio of ethanol to water was important for the formation of nanowires, the volume ratio of 1 : 1 for ethanol–water being most suitable for the synthesis of ultralong nanowires. Although a slight increase or decrease in the amount of ethanol did not seriously affect the formation of nanowires, a small amount of ethanol or its absence was not favorable for forming ultralong single-crystalline TiO_2 nanowires, with some short and wide flake-like structures instead being obtained. The presence of ethanol at a high concentration not only can cause the polarity of the solvent to change but also strongly affects zeta potential values of reactant particles, and increases solution viscosity. Fig. 5 shows a TEM image of the products in the absence of ethanol. In our experiments, a very low or high concentration of NaOH was not suitable for forming nanowires.

In order to elucidate the growth process of single-crystal TiO_2 nanowires, we followed the growth steps of the samples at various reaction stages by TEM. Fig. 6(a) shows a TEM image of the sample obtained for 4 h at 200 °C, which displayed flake-like structures. The XRD pattern (Fig. 6(e)) indicated that the sample was composed of titanate. We could suppose that, in our experiments, these titanate flakes were not stable in the present reaction conditions, and had a tendency to decompose into TiO_2. During the reaction process, the folded flakes rupture into many smaller flake pieces along the fold axis due to the phase transition, in which seeds are generated *in situ* through a solid-solid phase transition. The ruptured TiO_2 flakes served as the seeds for the growth of nanowires. The TEM image of the sample reacted for 8 h clearly displayed several short nanowires from the flakes (Fig. 6(b)). A small amount of seeds could dissolve in the solution used as the feed for the continuous growth of nanowires. Fig. 6(c) shows the early morphology of the as-prepared nanowires reacted for 12 h. When reacted for 16 h (Fig. 6(d)), the morphology of the sample resembled that of the sample reacted for 24 h. It is known that solvent plays an important role in determining the crystal morphology.[18–20] Solvents with different physical and chemical properties can influence the solubility, reactivity, and diffusion behavior of the reactants; in particular, the polarity

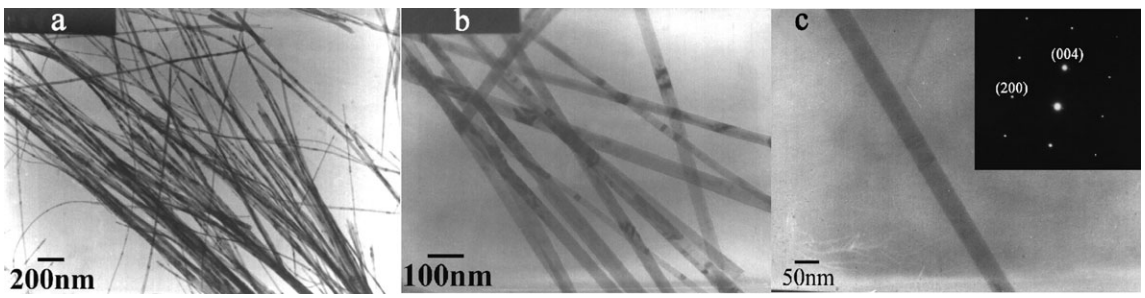

Fig. 2 TEM images of the synthesized TiO_2 nanowires by solvothermal treatment for 24 h at 200 °C. (a) Low-magnification, (b) higher magnification, and (c) an individual nanowire, the inset shows the corresponding SAED pattern taken along the [010] zone axis.

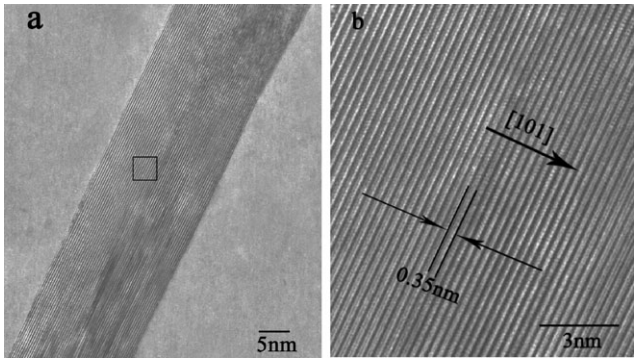

Fig. 4 (a) HRTEM image of an individual nanowire. (b) The corresponding HRTEM image of the local plane of the nanowire from (a). The fringes with a spacing of 0.35 nm correspond to (101) planes.

Fig. 5 TEM image of the products without ethanol for 24 h at 200 °C.

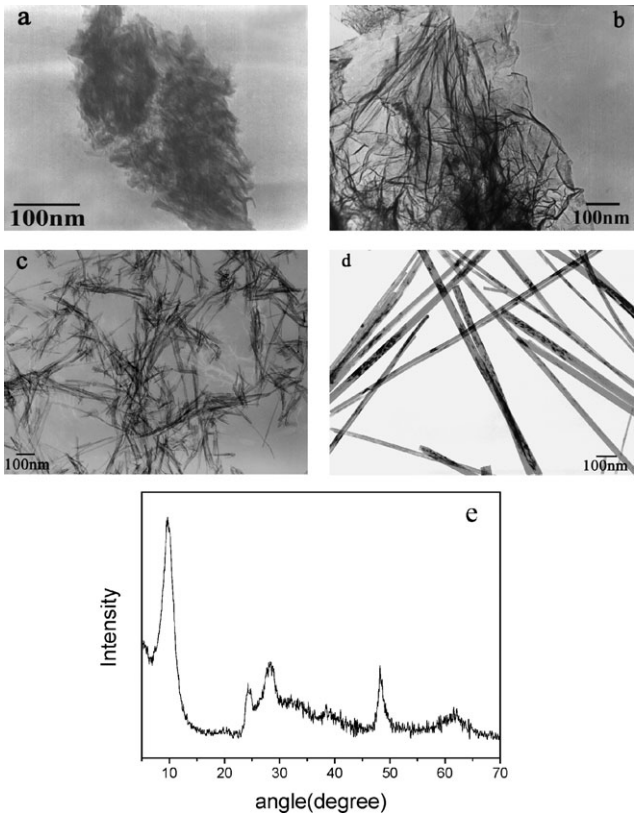

Fig. 6 TEM images of the samples obtained by solvothermal treatment at 200 °C at different growth times: (a) 4 h, (b) 8 h, (c) 12 h, (d) 16 h; (e) XRD pattern of the polycrystalline titanate flakes from (a).

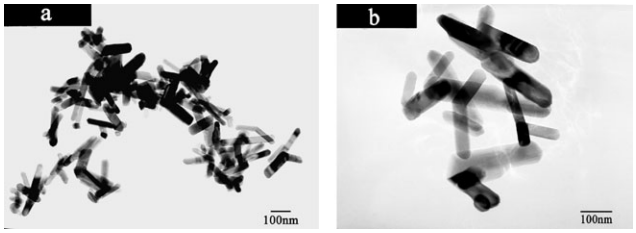

Fig. 7 TEM images of the synthesized TiO_2 nanorods using chloroform instead of ethanol: (a) low-magnification, (b) higher magnification.

and coordinating ability of solvent can influence the morphology and the crystallization behavior of the finial products. The diameters of the nanowires were mainly defined by the size of the ruptured flakes, and the formation of ultralong nanowires may arise from the slow nucleation rate and the very fast growth rate. We substituted chloroform for ethanol, kept the other reaction conditions unchanged, and found that the obtained samples showed rodlike morphology (Fig. 7). This further confirms that the solvent plays a key role.

Conclusions

Solvothermal synthesis is an important technology for the preparation of nanowires at relatively low temperature. Under the pressure generated by solvothermal reactions, as-prepared nanowires are well crystallized. Moreover, the solvents have important effects on the crystal morphology of the final product. This synthetic method may be applied to the large-scale fabrication of some other oxide nanowires.

Acknowledgements

The authors gratefully acknowledge the support of the 863 project and National Natural Science Foundation of China (90306003, 90406024).

References

1 J. Hu, T. W. Odom and C. M. Lieber, *Acc. Chem. Res.*, 1999, **32**, 435.
2 G. R. Patzke, F. K. Krumeich and R. Nesper, *Angew. Chem., Int. Ed.*, 2002, **41**, 2446.
3 Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim and H. Yan, *Adv. Mater.*, 2003, **15**, 353.
4 Y. Xia and P. Yang, *Adv. Mater.*, 2003, **15**, 351.
5 Z. W. Pan, Z. R. Dai and Z. L. Wang, *Science*, 2001, **291**, 1947.
6 Z. L. Wang and Z. W. Pan, *Adv. Mater.*, 2002, **14**, 1029.
7 Z. R. Dai, J. L. Gole, J. D. Stout and Z. L. Wang, *J. Phys. Chem. B*, 2002, **106**, 1274.
8 S. Matsuda and A. Kato, *Appl. Catal.*, 1983, **8**, 149.
9 G. Dagan and M. Tomkiewics, *J. Phys. Chem.*, 1993, **97**, 12651.
10 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissö, J. Salbeck, H. Spreitzer and M. Graetzel, *Nature*, 1998, **395**, 583.
11 A. M. Azad, L. B. Younkman and S. A. Akbar, *J. Am. Ceram. Soc.*, 1994, **77**, 481.
12 T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino and K. Niihara, *Langmuir*, 1998, **14**, 3160.
13 S. Kobayashi, K. Hanabusa, N. Hamasaki, M. Kimura and H. Shirai, *Chem. Mater.*, 2000, **12**, 1523.
14 S. M. Liu, L. M. Gan, L. H. Liu, W. D. Zhang and H. C. Zeng, *Chem. Mater.*, 2002, **14**, 1391.
15 X. Y. Zhang, L. D. Zhang, W. Chen, G. W. Meng, M. J. Zheng and L. X. Zhao, *Chem. Mater.*, 2001, **13**, 2511.
16 Y. X. Zhang, G. H. Li, Y. X. Jin, Y. Zhang, J. Zhang and L. D. Zhang, *Chem. Phys. Lett.*, 2002, **365**, 300.
17 T. Ohno, K. Sarukawa and M. Matsumura, *New J. Chem.*, 2002, **26**, 1167.
18 A. Sclafani and J. M. Herrman, *J. Phys. Chem.*, 1996, **100**, 13655.
19 E. Stathatos, P. Lianos, F. Del Monte, D. Levy and D. Tsiourvas, *Langmuir*, 1997, **13**, 4295.
20 S. T. Martin, H. Herrmann and M. R. Hoffmann, *J. Chem. Soc., Faraday Trans.*, 1994, **90**, 3323.