Self-assembly of highly oriented one-dimensional h-WO_3 nanostructures†

Zhanjun Gu, Ying Ma, Wensheng Yang,‡ Guangjin Zhang and Jiannian Yao*

Received (in Cambridge, UK) 20th April 2005, Accepted 26th May 2005
First published as an Advance Article on the web 24th June 2005
DOI: 10.1039/b505429j

A new self-assembled and highly oriented one-dimensional single-crystal nanostructure of WO_3 with hexagonal form was successfully prepared by a mild, solution-based colloidal approach.

One-dimensional (1-D) nanoscaled materials, such as nanotubes, nanowires and nanorods, have attracted intensive interest due to their novel physical properties and potential wide-ranging applications.[1] These 1-D systems can also be used as building blocks to assemble new generations of nanoscaled devices.[2] An important issue in the study and application of these one-dimensional materials is how to assemble them into highly integrated and hierarchically organized nanostructures. Many efforts have been made to assemble 1-D nanostructures and to optimize their properties.[3,4]

Among various metal oxides, WO_3 has been known to possess interesting properties that make it a promising candidate for wide-ranging applications in electrochromic or photochromic devices, secondary batteries, gas sensors and photocatalysts.[5–7] In particular, the hexagonal form of tungsten trioxide (h-WO_3) is of great interest owing to its well-known tunnel structure[8] and has been widely investigated, especially as an intercalation host for obtaining hexagonal tungsten bronzes M_xWO_3 ($M = Li^+, Na^+, K^+$, *etc.*) and a promising material for positive electrodes of rechargeable lithium batteries.[7] Recently, many efforts have been made to prepare one-dimensional tungsten oxides.[9–14] However, to the best of our knowledge, the synthesis of a one-dimensional single crystal nanostructure of h-WO_3 has not been reported to date. Moreover, although several oxide nanowires have been reported, there is no example of the assembly of the nanowires into an organized nanostructure. In this work, we first report the synthesis and characterization of a novel self-assembled nanostructure: oriented assemblies of h-WO_3 nanowires. The specific structure of the regular assembled h-WO_3 1D nanostructure may find applications in nanoelectronics and photonics.

In a typical synthesis, a colloidal white tungstic acid ($WO_3 \cdot xH_2O$) was used as the precursor which was prepared according to ref. 6. A certain amount of Li_2SO_4 and oxalic acid were added to the precursor, which act as structure-directing and disperse agents, respectively. This colloidal solution was put in a Teflon-lined stainless steel autoclave and heated at 180 °C for 2–24 h. After reaction, the autoclave was cooled to room temperature. Then a large white precipitate was filtered, washed sequentially with water and ethanol to remove ions possibly remnant in the final products, and dried at 60 °C.

In Fig. 1, a typical X-ray diffraction (XRD) pattern for our products is displayed. All peaks can be well indexed to the h-WO_3 phase (JCPDS card 33-1387, space group (SG) *P6/mm*, cell constants: $a = 7.298$ Å, $c = 3.899$ Å). The SEM images of as-prepared samples are shown in Fig. 2. The overall morphology of the samples, shown in Fig. 2a, indicates that there exists a great deal of uniform rod-like structures with diameter of 200–400 nm and length of 2.5–10 μm. Close observation (Fig. 2b and 2c) reveals that these rod-like products are actually composed of large numerous, highly aligned and closely packed nanowires. Furthermore, the nanowires in one bundle have similar diameter and length.

Transmission electron microscopy (TEM) provides further insight into the morphology and microstructural details of the h-WO_3 nanowire bundles. Fig. 3a shows the typical TEM image of one h-WO_3 nanowire bundle, suggesting good wire alignment and regular rod-like shape. A single nanowire with diameter about 5 nm can be clearly seen near from the bundle, as indicated with an arrow, which is probably separated from the bundle. These nanowires have a uniform diameter along their entire length and a narrow diameter distribution. The diameter of these uniform nanowires was about 5–15 nm and the length of the nanowires was up to 10 μm. The spacing of the lattice fringes was found to be about 0.636 nm and 0.391 nm, respectively, as shown in Fig. 3b.

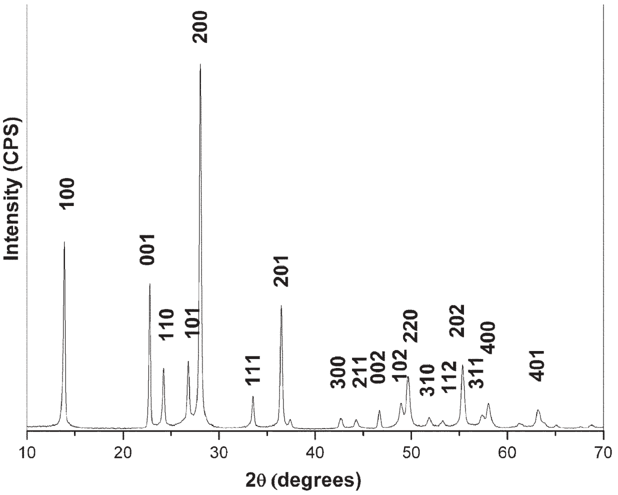

Fig. 1 XRD pattern of as-prepared products.

---

† Electronic Supplementary Information (ESI) available: Experimental details and additional SEM images. See http://dx.doi.org/10.1039/b505429j
‡ Present address: College of Chemistry, Jilin University, Changchun 130023, P. R. China.

Key Laboratory of Photochemistry, Centre for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, P. R. China. E-mail: jnyao@iccas.ac.cn; Fax: (+86)10-82616517; Tel: (+86)10-82616517
*jnyao@iccas.ac.cn

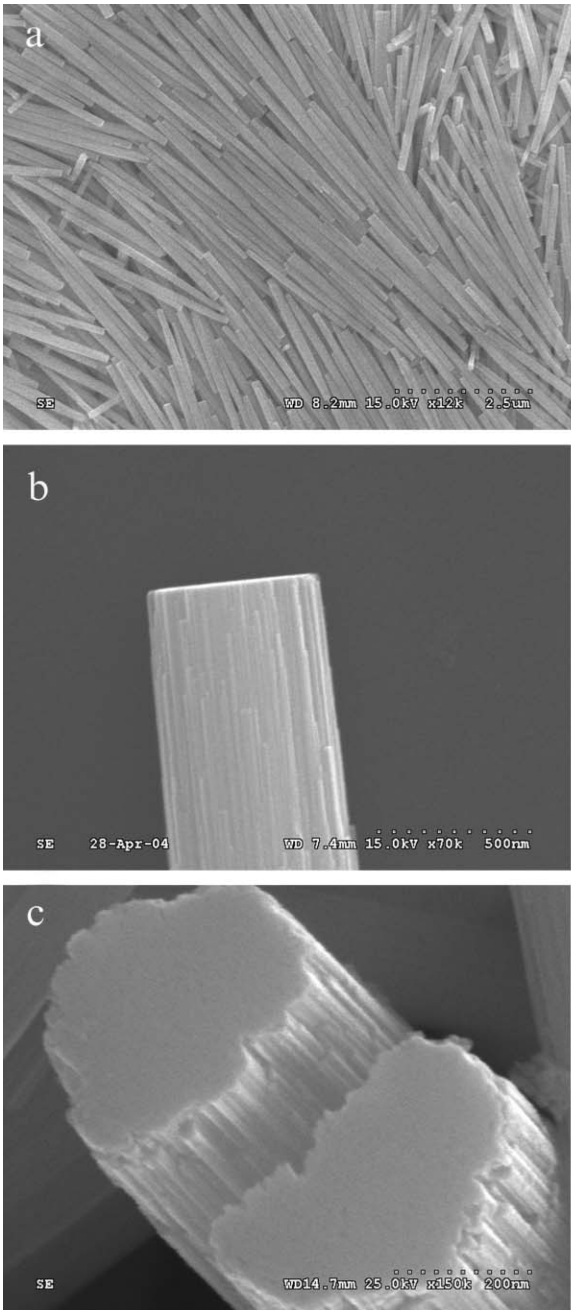

Fig. 2 SEM images of as-synthesized products. (a) Low magnification SEM micrograph of the rod-like h-WO_3 nanowire bundles. (b) and (c) High magnification SEM micrograph of side and top view of typical nanowire bundle.

These two planes could be well indexed as [100] and [001] of a h-WO_3 crystal, respectively, according to JCPDS card No.33-1387. The selected area electron diffraction (SAED) pattern shown in the inset of Fig. 3b could be indexed perfectly and supported the HRTEM results, indicating nanowire growth along the [001] direction. The perfect diffraction pattern and clear lattice fringes indicate that the nanowires are single crystals. In addition, the oriented arrangement of nanowires is confirmed by ED analysis, which shows only one set of diffraction patterns for an array of nanowires.

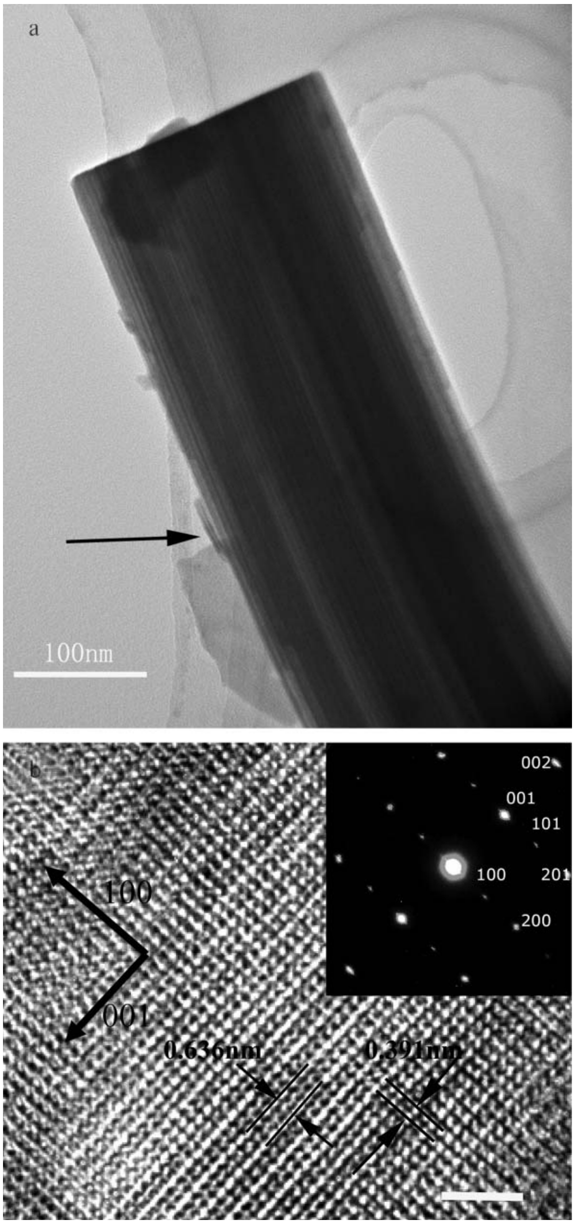

Fig. 3 (a) TEM observation of a typical h-WO_3 nanowire bundle. (b) HRTEM image of an individual tungsten oxide nanowire with growth direction [001]. Inset shows the electron diffraction pattern of h-WO_3, scale bar 2 nm.

To understand the formation process of the bundle structures, time-dependent experiments were carried out. When the reaction continued to 2 h, an examination of the intermediate products showed shuttle-like short bundles.(Fig. 4a) A long nanowire with rapid growth may act as a leader crystal in the centre of the bundles and some short nanowires closely connected parallel to the surface of the leading wire resulting in the bundle structure formation. The length of bundles could be varied by reaction time, but the diameter of individual nanowires in each bundle showed weak time dependence. After reaction for 24 h, single-crystalline h-WO_3 bundles with a flat tip end had readily formed with the diameter of 200–400 nm and length of 5–10 μm. (Fig. 4b) When we further prolonged the reaction time, the length of the bundle did not appear to increase.

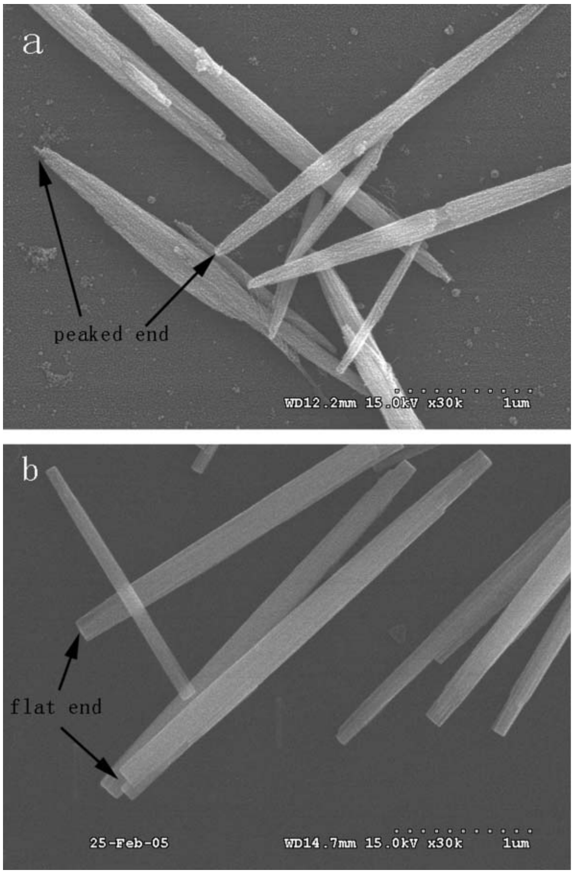

Fig. 4 SEM images of intermediate products. (a) 2 h. (b) 24 h.

Regarding the growth process, it is believed that $H_2C_2O_4$ plays a crucial rule in ensuring the formation of h-WO_3 nanowire bundles, which can generate sufficient amounts and sizes of colloidal particles as WO_3 cluster nuclei for subsequent hydrothermal growth.[6,18] Without $H_2C_2O_4$, only irregularly aggregated nanorods have been generated from untreated precursor solution after reaction for 24 h at 180 °C (see supporting information†). Furthermore, the sulfate also plays an important role in determining the crystal structure and morphology. When the experiment was conducted in the absence of Li_2SO_4, only irregular nanoparticles of WO_3 were obtained. Results from the XRD characterization showed that these nanoparticles were a mixture of orthorhombic and monoclinic phases of WO_3. When 0.1 g Li_2SO_4 was added to 15 ml colloidal tungstic acid solution, bundles of orthorhombic WO_3 nanowire and a few irregular particles were generated. With increased amounts of sulfate added, the hexagonal phase become gradually dominant. WO_3 with pure hexagonal phase and complete rod morphology could be obtained by adding about 0.5 g Li_2SO_4. Excess amounts of the sulfate had no obvious effect on the rod shape and crystal form.† Other inorganic salts, such as NaCl, KCl, LiBr and $NaNO_3$, have been used in this work, but only irregular WO_3 particles were obtained. Based on the above experimental results, we speculate that sulfate may preferentially adsorb onto the faces parallel to the *c* axis of the WO_3 nanocrystal, leading to preferential growth along the *c* axis.[15,16] In the meantime, a certain amount of Li^+ is required as stabilizing ions for the hexagonal and triangular tunnels in the formation of h-WO_3.[14,15]

Consequently, together with the previous discussion, the formation mechanism for the bundle of the h-WO_3 nanowires is speculated as follows: (1) In the synthetic process, sulfate may act as a capping agent to kinetically control the growth rate of different crystal faces through selective absorption and desorption. (2) Small amounts of h-WO_3 particles may be first formed around one white tungstic acid colloidal particle under hydrothermal conditions. (3) These particles serve as seeds for further growth. In the initial reaction stage, some h-WO_3 seeds rapidly grow along the *c* axis of the h-WO_3 unit cell and act as "leader crystals" to the initial template for the growth of subsequent nanowires parallel to the leader crystal. Continuous growth of the secondary nanowires led to the final h-WO_3 nanowire bundles. After a long reaction time, the secondary nanowires gradually grew at the end of the leader wire resulting in a flat tip end.[17]

In conclusion, uniform h-WO_3 nanowire bundles were synthesized successfully *via* a mild, solution-based colloidal approach. The possible growth mechanism was also studied. With the ordered arrangement and well known 1D tunnel structure, the h-WO_3 nanowire bundles may be important materials for advanced electronics for nanodevices and for storage containers, such as gas sensors or lithium batteries. We expect that this facile solution-based colloidal approach for the formation of interesting highly oriented 1D nanostructures should be worth further exploration for other metal or semiconductor systems.

This work was supported by National Natural Science Foundation of China (No.50221201, 90301010, 20373077, 20471062), the Chinese Academy of Sciences and the National Research Fund for Fundamental Key Projects No.973.

Notes and references

1 (*a*) Y. N. Xia, P. Y. Yang, Y. G. Sun, Y. Y. Wu, B. Mayer, B. Gates, Y. D. Yin, F. Kim and H. Yan, *Adv. Mater.*, 2003, **15**, 353; (*b*) G. R. Patzke, F. Krumeich and R. Nesper, *Angew. Chem. Int. Ed.*, 2002, **41**, 2446.
2 (*a*) Y. Huang, X. F. Duan, Q. Q. Wei and C. M. Lieber, *Science*, 2001, **291**, 630; (*b*) B. Q. Wei, R. Vajtai, Y. Jung, J. Ward, R. Zhang, G. Ramanath and P. M. Ajayan, *Chem. Mater.*, 2003, **15**, 1598.
3 Y. C. Zhu, Y. Bando, D. F. Xue and D. Golberg, *Adv. Mater.*, 2004, **16**, 831.
4 H. Qi, C. Y. Wang and J. Liu, *Adv. Mater.*, 2003, **15**, 411.
5 X. L. Li, T. J. Lou, X. M. Xiao and Y. D. Li, *Inorg. Chem.*, 2004, **43**, 5442.
6 T. He, Y. Ma, Y. A. Cao, X. L. Hu, H. M. Liu, G. J. Zhang, W. S. Yang and J. N. Yao, *J. Phys. Chem. B*, 2002, **106**, 12670.
7 M. Hibino, W. Han and T. Kudo, *Solid State Ionics*, 2000, **135**, 61.
8 W. Han, M. Hibino and T. Kudo, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 933.
9 Y. B. Li, Y. Bando and D. Golberg, *Adv. Mater.*, 2003, **15**, 1294.
10 G. Gu, B. Zheng, W. Q. Han, S. Roth and J. Liu, *Nano Lett.*, 2002, **2**, 849.
11 K. Lee, W. S. Seo and J. T. Park, *J. Am. Chem. Soc.*, 2003, **125**, 3408.
12 X. L. Li, J. F. Liu and Y. D. Li, *Inorg. Chem.*, 2003, **42**, 921.
13 X. W. Lou and H. C. Zeng, *Inorg. Chem.*, 2003, **42**, 6169.
14 X. Wang and Y. D. Li, *J. Am. Chem. Soc.*, 2002, **124**, 2880.
15 G. R. Patzke, A. Michailovski, F. Krumeich, R. Nesper, J. D. Grunwaldt and A. Baiker, *Chem. Mater.*, 2004, **16**, 1126.
16 A. Michailovski, F. Krumeich and G. R. Patzke, *Helv. Chim. Acta*, 2004, **87**, 1029.
17 Y. Z. Jin, Y. Q. Zhu, R. L. D. Whitby, N. Yao, R. Ma, P. C. P. Watts, H. W. Kroto and D. R. M. Walton, *J. Phys. Chem. B.*, 2004, **108**, 15572.
18 I. Bedja, S. Hotchandani and P. V. Kamat, *J. Phys. Chem.*, 1993, **97**, 11064.