Inorg. Chem. **2002**, *41*, 4996–4998

Inorganic Chemistry
Communication

Large-Scale Synthesis of Sodium and Potassium Titanate Nanobelts

Xiaoming Sun, Xing Chen, and Yadong Li*

Department of Chemistry, Tsinghua University, Beijing 100084, People's Republic of China

Received June 9, 2002

A low-temperature solution-based synthetic method was developed for the large-scale synthesis of one-dimensional nanostructures of alkali titanates. Two kinds of highly pure ribbonlike titanates were synthesized successfully in gram quantities without introducing any templates or catalysts. The structure and composition of the titanates were characterized by XRD, HRTEM, and EDX. The chemical and physical properties were preliminarily characterized, and some distinctive properties were observed.

In the past decade, one-dimensional (1D) nanostructures, such as nanotubes[1,2] and nanowires,[3−4] have attracted extraordinary attention for their novel physical properties and potential applications in constructing nanoscale electronic and optoelectronic devices. Recently, the discovery of semiconducting oxide nanobelts (ZnO, SnO_2, In_2O_3, CdO, Ga_2O_3, PbO_2) has initiated intense interest in such beltlike nanostructures.[5] There has been much speculation about the properties and potential application of these nanostructures; for example, they were considered candidates for fabrication of nanoscale devices. Up to now, considerable efforts have been focused on the synthesis of different compounds with this nanostructure, and several beltlike structures of compounds such as PbO,[6] Si,[7] Zn,[8] and Ge_3N_4 [9] have been reported. However, to the best of our knowledge, the beltlike microcrystals obtained were all based on a thermal evaporation/reaction process at a temperature usually in the range 1000−1400 °C. In this work, a simple solution synthetic method was used to fabricate beltlike nanostructures of titanates in gram quantities. Successful synthesis of such nanostructure in large scale will open up the possibilities of sufficient study of the physical and chemical properties of 1D nanomaterial systems.

Alkali titanates have attracted increasing attention[10−13] owing to their high photocatalytic activities, as well as interesting ion-exchange/intercalation properties. Their applications in photo cleavage of water,[14] photocatalysis,[15] and fuel cell electrolytes[16] were expected. In order to improve the functional properties such as photocatalytic activity or ion-exchange ability, it is highly desirable to control the size and morphology of the titanates.[17] Recently, nanosized TiO_2 powder has been used as a starting material for preparation of nanotubes.[18] In this paper, two kinds of titanate, ribbonlike potassium and sodium titanate, were synthesized.

The chemical reaction for the synthesis of the potassium titante ($K_2Ti_8O_{17}$) can be formulated as

$$8TiO_2 + 2KOH \rightarrow K_2Ti_8O_{17} + H_2O$$

In a typical procedure, 1.5 g of TiO_2 powder with an average diameter size of 4 nm prepared using the method reported[19] was dispersed in 40 mL of 4−10 mol/L KOH (A.R. grade) aqueous solution. The resulting suspension was stirred for 10 min and then transferred into a Teflon-lined stainless autoclave, sealed, and maintained at 160−180 °C for 48 h. The resulting white precipitate was filtered, washed with deionized water, and finally dried in a vacuum at 60 °C for 3 h.

---

* Author to whom correspondence should be addressed. E-mail: ydli@tsinghua.edu.cn.

(1) Krumeich, F.; Muhr, H. J.; Niederberger, M.; Bieri, F.; Schnyder, B.; Nesper, R. *J. Am. Chem. Soc.* **1999**, *121*, 8324.

(2) Tremel, W. *Angew. Chem., Int. Ed.* **1999**, *38*, 2175.

(3) (a) Duan, X. F.; Liber, C. M. *J. Am. Chem. Soc.* **2000**, *122*, 188. (b) Wu, Y. Y.; Yan, H. Q.; Huang, M.; Messer, B.; Song, J. H.; Yang, P. D. *Chem. Eur. J.* **2002**, *8*, 1260.

(4) Huang, M. H.; Mao, S.; Feick, H.; Yan, H. Q.; Wu, Y. Y.; Kind, H.; Wekber, E.; Tusso, R.; Yang, P. D. *Science* **2001**, *292*, 1897.

(5) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947−1949.

(6) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Appl. Phys. Lett.* **2002**, *80*, 309−311.

(7) Shi, W. S.; Peng, H. Y.; Wang, N.; Li, C. P.; Xu, L.; Lee, C. S.; Kalish, R.; Lee, S. T. *J. Am. Chem. Soc.* **2001**, *123*, 11095.

(8) Wang, Y. W.; Zhang, L. D.; Meng, G. W.; Liang, C. H.; Wang, G. Z.; Sun, S. H. *Chem. Commun.* **2001**, 2632.

(9) Gao, Y. H.; Bando, Y.; Sato, T. *Appl. Phys. Lett.* **2001**, *79*, 4565.

(10) Sasaki, T.; Kooli, F.; Iida, M.; Michiue, Y.; Takenouchi, S.; Yajima, Y.; Izumi, F.; Chakounakos, B. C.; Watanabe, M. *Chem. Mater.* **1998**, *10*, 4123.

(11) Masaki, N.; Uchida, S.; Yamane, H.; Sato, T. *Chem. Mater.* **2002**, *14*, 419.

(12) Masaki, N.; Uchida, S.; Sato, T. *J. Mater. Sci.* **2000**, *35*, 3307.

(13) Tomiha, M.; Masaki, N.; Uchida S.; Sato, T. *J. Mater. Sci.* **2002**, *37*, 2341.

(14) Uchida, S.; Yamamoto, Y.; Fujishiro, Y.; Watanabe, A.; Ito, O.; Sato, T. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3229.

(15) Choy, J. H.; Lee, H. C.; Jung, H.; Huang, S. J. *J. Mater. Chem.* **2001**, *11*, 2232.

(16) Corcoran, D. J. D.; Tunstall, D. P.; Irvine, J. T. S. *Solid State Ionics* **2000**, *136−137*, 297.

(17) Masaki, N.; Uchida, S.; Sato, T. *J. Mater. Chem.* **2002**, *12*, 305.

(18) Sun, X. M.; Chen, X.; Li, Y. D. Novel Thermally Stable and Ion-Exchangeable Titanate Nanotubes. Submitted to *J. Phys. Chem. B.*

(19) Wang, C.; Deng, Z. X.; Li, Y. D. *Inorg. Chem.* **2001**, *40*, 5210.

10.1021/ic0257827 CCC: $22.00

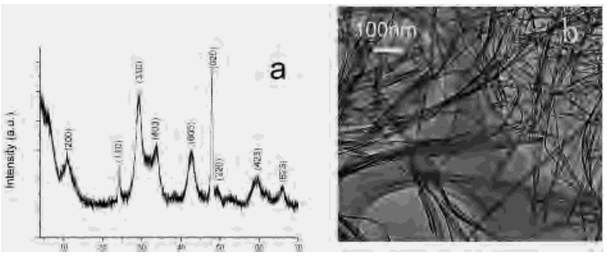

Figure 1. (a) A XRD pattern of $K_2Ti_8O_{17}$. (b) A typical TEM image of bulk $K_2Ti_8O_{17}$.

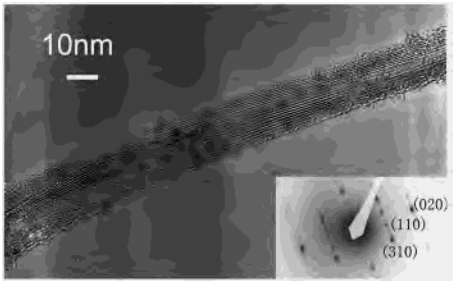

Figure 2. A HRTEM image of $K_2Ti_8O_{17}$ nanobelts. Inset: Electron diffraction recorded along the ⟨001⟩ zone axis indicates the growth direction along the (010) direction.

The crystal structures of the products were characterized with powder X-ray diffraction (XRD) using a Brucker D8-advance X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). All of the reflections of the XRD pattern in Figure 1a can be indexed to a pure monoclinic phase of $K_2Ti_8O_{17}$ [space group *C*2/*m*(12), JCPDS 84-2057]. This XRD data indicates that the reaction was complete under the current synthetic conditions. The peak of (020) was higher and far narrower than other peaks in the reflections, implying the high orientation of this nanostructure.

The morphology of the synthesized potassium titanates was characterized with a transmission electron microscope (TEM, Hitachi H800) and a high-resolution transmission electron microscope (HRTEM, JEOL-2010F), both operated at 200 keV. A typical TEM image (Figure 1b) showed that the products consisted of a large quantity of uniform ribbonlike bent and twisted $K_2Ti_8O_{17}$ several micrometers in length and tens of nanometers in width and thickness. Analysis of a number of belt-like structures with different widths reveals that the average width-to-thickness ratio is in the range 3−10. The HRTEM image recorded on individual $K_2Ti_8O_{17}$ (Figure 2) provided further insight into the nanostructure. The selected area electron diffraction (SAED) patterns (inset in Figure 2) recorded perpendicular to the growth axis of the single nanowire could be indexed to the [001] zone axis of the belt and thus suggests that they grow along the [010] direction, which was consistent with the result of XRD, in which the reflection of (020) is higher and far narrower. The energy-dispersive X-ray (EDX) analysis on the titanate showed the existence of only K, Ti, and O with a K/Ti atomic ratio of 1:4.

A thermal evaporation method to synthesize this nanostructure has been further developed, since it was first proposed by Z. L. Wang et al.[5] Later, SnO_2 nanobelts were even synthesized with the yield as high as 20−30%.[20] Herein, the solution-based synthesis method we proposed provides a new approach to the synthesis of this 1D nanostructure. This method is simple without delicate equipment, and the reaction conditions are mild, as the reaction temperature decreased to 160 °C. The starting materials could be mostly translated to the final products, and the yield was estimated to be more than 95% from repeats of a typical synthetic process and TEM observations of the samples from different batches of synthesis. Furthermore, this method can be easy to scale up. Our experiment results indicated that about 15 g of products can be obtained at one time using a Teflon-lined stainless autoclave with 300 mL capacity, which makes it possible to develop this method in large-scale synthesis for industrial application.

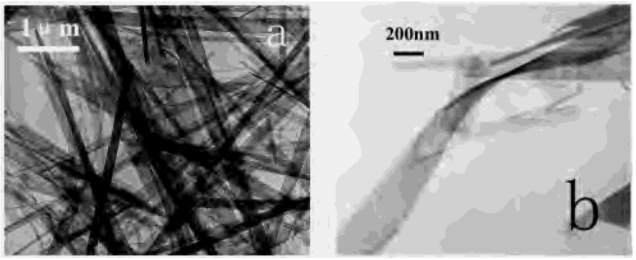

Figure 3. (a) A typical TEM image of sodium titanate. (b) TEM image of a twisted beltlike sodium titanate.

In order to explore the possibility for synthesis of other kinds of nanobelts using this method, we expanded it to the synthesis of sodium titanate due to the similarity of their crystal structure and chemical properties. The beltlike sodium titanates were prepared successfully under similar conditions, except that NaOH was used instead of KOH. The characterization of the final products by XRD and TEM indicated the beltlike structure of sodium titanates. The effect of the reaction time was also studied. When the reaction was terminated after 2 days, some poorly crystallized fibrous products were obtained; when it was terminated after more than 10 days, uniform and well-crystallized beltlike sodium titanates were obtained. Elongating the reaction time could lead to the improvement of crystallization and the size of the nanostructure.

A typical TEM image (Figure 3a) exhibited exclusively beltlike structures. The titanate was long, smooth, and uniform. Each belt has an unchanged width along its entire length, and the typical widths of the belts are in the range 100−500 nm. No particle or ripples were observed at the ends or edges of the nanostructures. A twisted belt (Figure 3b) showed that the thickness of the nanostructure was about 30 nm and the width-to-thickness ratios were about 10 nm. EDX analysis on different individual nanobelts indicated the identical atomic Na/Ti ratio of 1:2. Thermal gravity analysis (TGA, TA instruments, TGA 2050) indicated that water was completely removed at 700 °C, while the corresponding XRD pattern indicated the identical pattern with starting material. So it contains no crystallization water molecule. The reaction

---

(20) Hu, J. Q.; Ma, X. L.; Shang, N. G.; Xie, Z. Y.; Wong, N. B.; Lee, C. S.; Lee, S. T. *J. Phys. Chem. B* **2002**, *106*, 3823.

might be formulated as

$$4TiO_2 + 2NaOH \rightarrow Na_2Ti_4O_9 + H_2O$$

When the sample was heated to 900 °C, a mixture of $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$ formed, which supported our proposal. It is notable that the as-prepared beltlike sodium titanate may be a new phase. Its standard XRD pattern is not available in the ICDD PDF-2 database (sets 1−50 plus 70−88). The further solution of the crystal structure of the sodium titanate is under investigation.

Preliminary characterization on the sodium titanate showed some distinctive properties. To our knowledge, the titanate nanostructures reported herein are the first ion-exchangeable nanobelts prepared and characterized. The sodium ions in the titanate nanostructures are exchangeable for a variety of inorganic cations with respect to structural degradation. Photoluminescence of the potassium titanate was first observed at room temperature with the excitation wavelength of 401 nm and emission wavelength of 612 nm. The chemiluminescence was detected on the potassium titanate at 270 °C, which is 140 °C lower than for TiO_2 nanopowders.[21] These results show that this kinds of titanate nanobelts may be promising materials in selective catalysis, photocatalysis, gas sensors, and so on.

In summary, we have exploited a low-temperature solution-based method to large-scale synthesis of titanate 1D nanostructures. Two kinds of highly pure ribbonlike titanates were synthesized successfully in gram quantities. We believe that this solution synthetic route, based on simple reactions with no participation of catalysts or templates, requiring no expensive equipment, and ensuring higher purity and uniformity of the products, will greatly reduce the production cost and offer great opportunity for large-scale synthesis of such 1D nanostructured materials.

Acknowledgment. This work was supported by the NSFC (20025102, 50028201, 20151001), the Foundation for the Author of National Excellent Doctoral Dissertation of P. R. China, and the state key project of fundamental research for nanomaterials and nanostructures. We would also like to thank Prof. Zhang X. R. and Dr. Zhang Z. Y. for chemiluminescence characterization.

Supporting Information Available: Two electron microscopic images, two EDX analysis spectra, and an XRD pattern. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0257827

---

[21] Zhu, Y. F.; Shi, J. J.; Zhang, Z. Y.; Zhang, C.; Zhang, X. R. *Anal. Chem.* **2002**, *74*, 120.