Research Article

Synthesis of Nb₂O₅ Nanorods by a Soft Chemical Process

Haiyan Luo,¹ Mingdeng Wei,^{1,2} and Kemei Wei²

¹ Institute of New Energy Technology and Nano-Materials, Fuzhou University, Fuzhou, Fujian 350002, China

² National Engineering Research Center for Chemical Fertilizer Catalyst, Fuzhou University, Fuzhou, Fujian 350002, China

Correspondence should be addressed to Mingdeng Wei, wei-mingdeng@fzu.edu.cn

Received 14 July 2009; Accepted 19 October 2009

Recommended by Sang-Hee Cho

Single crystalline Nb₂O₅ nanorods have been successfully synthesized by a soft chemical process, in which only metal Nb powder and water were used as the starting materials. The synthesized Nb₂O₅ nanorods are highly crystalline and their growth is along [001] direction. The diameter of the nanorods is found to be ca. 50 nm and their lengths up to several micrometers. Based on the experimental results of XRD, SEM, and TEM measurements, the possible mechanism for the formation of Nb₂O₅ nanorods was discussed.

Copyright © 2009 Haiyan Luo et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

1. Introduction

Since the discovery of carbon nanotubes in 1991 [1], one-dimensional (1D) nanomaterials including nanorods, nanotubes, nanowires, nanofibers, nanobelts, and nanoribbons have attracted much attention due to their physical and chemical properties different from those of bulk materials [2]. In the past decades, a large number of 1D oxide nanomaterial have been synthesized, such as TiO₂ [3], MnO₂ [4], ZnO [5], SnO₂ [6], VO_x [7], MoO₃ [8], Ga₂O₃ [9], Ta₂O₅ [10], In₂O₃ [11], and Nb₂O₅ [12]. Among them, Nb₂O₅ is an important semiconductor oxide with a wide band gap [13] and had been widely used in electrochromic devices [14], catalysts [15], chemical sensors [16], optical filters [17], solar cells [18], and lithium batteries [19]. As is well known, Nb₂O₅ has many polymorphic forms based on the octahedrally coordinated niobium atoms [20]. These polymorphs are identified with a variety of prefixes [21] such as B-Nb₂O₅ (PdF₃ rutile structure), H-Nb₂O₅ (ReO₃-type block, 3 × 3 or 3 × 5 octahedra), and N-Nb₂O₅ (ReO₃-type block, 4 × 4 octahedral). Among the niobium oxides, Nb₂O₅ is the most stable and exhibits the excellent chemical stability and corrosion resistance in both acid and base media [22]. So far, niobium oxide fibers have been prepared by using an electrospinning method [23]. Mozetič et al. [24] has synthesized Nb₂O₅ nanowires via a cold plasma treatment in the presence of a high neutral oxygen flux. Niobia-phase nanorods [25] were obtained by

the hydrothermal treatment of a niobium peroxo complex precursor at 140°C. Hu et al. [26] reported the synthesis of Nb₂O₅ nanocables using NbCl₅ as a precursor. Kobayashi et al. [27] prepared Nb₂O₅ nanotubes using the layered K₄Nb₆O₁₇ as a precursor, in which K₄Nb₆O₁₇ was formed at over 1050°C. Nb₂O₅ nanotubes have also been obtained using HF solution as a reactant [28]. Using amorphous Nb₂O₅ · nH₂O as a precursor, Nb₂O₅ nanorods [29] were formed at a high temperature. More recently, Nb₂O₅ nanobelts were synthesized by using a hydrothermal route [30]. To the best of our knowledge, however, the synthesis of niobium oxide with 1D nanostructure has not been reported by using a soft chemical process. Here, we first fabricated Nb₂O₅ nanorods starting from metal Nb powder by a soft chemical process, without templates or catalysts, and using only the raw material and water. Furthermore, the possible mechanism for the formation of nanorods was discussed according to the experimental results.

2. Experimental

A soft chemical process was developed to prepare Nb₂O₅ nanorods. In a typical procedure, 0.1 g of the commercial metal Nb powder was dispersed into 40 mL distilled water and stirred, then transferred into a 50 mL Teflon-lined autoclave, and kept in an oven at 200°C for 3 to 30 days. The final products were washed with distilled water and then dried in the air.

FIGURE 1: SEM images of (a) raw material Nb and the products synthesized at 200°C for different reaction times (b) 3, ((c), (d)) 15, and ((e), (f)) 30 days.

Scanning electron (SEM) and transmission electron microscopy (TEM) were taken on a Philip-XL30 instrument and a JEOL 2010 instrument, respectively. X-ray diffraction (XRD) pattern was recorded on a PANalytical X'Pert spectrometer using the Co $K\alpha$ radiation ($\lambda = 1.78897 \text{ \AA}$) and the data would be changed to Cu $K\alpha$ data.

3. Results and Discussion

Figure 1 shows the SEM images of the raw Nb powder and the products obtained at 200°C for different reaction times. It clearly shows that the SEM morphology of the products is entirely different from the raw material Nb metal powder. Only particles with different sizes were detected in the raw material, as shown in Figure 1(a). After the raw Nb

metal powder was treated in H_2O at 200°C for 3 days, a large number of sheet-like and nanorod-like products were observed, as depicted in Figure 1(b). With increasing reaction time, numerous nanorods with a bundle-like structure were formed and the sheet-like products disappeared, as depicted in Figures 1(c)–1(f). It can also be found that the length of these nanorods increased significantly with reaction time. These nanorods lie close to each other and their lengths up to several micrometers.

The morphologies of the product can be further confirmed by TEM measurements. Figure 2(a) clearly shows a single nanorod obtained at 200°C for 30 days. The diameter of the nanorod is found to be ca. 50 nm. Figure 2(b) is a high-resolution TEM image and clearly reveals that the formed nanorods are single crystalline. The lattice fringes correspond

FIGURE 2: The TEM images of the product synthesized at 200°C for 30 days: (a) low magnification, and (b) high magnification (inset, SAED).

FIGURE 3: The XRD pattern of the product synthesized at 200°C for 30 days (●: Orthorhombic Nb_2O_5 ; ▼: Cubic Nb).

to a d -spacing of 0.393 and 0.315 nm, respectively. The typical selected area electron diffraction (SAED) taken from a single nanorod is shown in Figure 2b (inset). The pattern exhibits broadened and strong spots along the growth direction of the nanorods which can be attributed to the essentially asymmetric 1D nature of the long and thin nanorods. These results also indicate that the growth of nanorods is along [001] direction.

XRD measurement was used to identify the crystalline structure of the product, as shown in Figure 3. Besides raw Nb metal, the main phase detected was Nb_2O_5 which could be indexed to Nb_2O_5 (JPCDS 27-1313) with an orthorhombic structure. This result is in agreement with the TEM observations. Based on the experimental results of XRD, SEM, and TEM measurements, a possible model for the formation of Nb_2O_5 nanorods is suggested as follows: (i) the surface of the metal Nb powder was oxidized by oxygen in water under the hydrothermal conditions, and the sheet-like products were formed; (ii) the sheet-like products were splitted in order to release strong stress and lower the total

energy, and then the nanorods were formed. Therefore, the formation of bundle-like structure can be contributed to the fact that the splitting of the sheets-like products is complete.

In the present work, metal Nb powder was used as a starting material and reacted with water under the hydrothermal conditions to yield single crystalline Nb_2O_5 nanorods. Although the purity of Nb_2O_5 nanorods in the final product is still to be improved, the synthetic route is very simple, in which templates or catalysts were not introduced into the reaction system. Comparing with the normal hydrothermal process, such a synthetic route took a long reaction time. This might be related to that the hydrothermal reaction was accelerated in the presence of templates or catalysts.

4. Conclusions

In summary, single crystalline Nb_2O_5 nanorods were successfully synthesized by a soft chemical process, in which the metal Nb powder and water were used as the precursors. The synthesized nanorods are highly crystalline and their growth direction is along [001]. The diameter of the nanorods is found to be ca. 50 nm and their lengths up to several micrometers. Furthermore, the work is underway to optimize the process and increase purity of nanorods in the product. Compared with other synthetic routes, no any catalysts or templates were introduced into the reaction system. We believe that the synthetic route of Nb_2O_5 nanorods from the metal Nb powder has the potential to prepare 1D nanostructural metal oxides.

Acknowledgments

This work was financially supported by the National High Technology Research and Development Program ("863") and Ministry of Education under Grant nos. 2007AA05Z438 and 200803860004, Science and Technology Program from Fujian Province (nos. 2008J0332, 2007HZ0005-1), and the startup funds from the Ministry of Education and Fuzhou University.

References

- [1] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, no. 6348, pp. 56–58, 1991.
- [2] Y. Cui, Q. Wei, H. Park, and C. M. Lieber, "Nanowire nanosensors for highly sensitive and selective detection of biological and chemical species," *Science*, vol. 293, no. 5533, pp. 1289–1292, 2001.
- [3] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, and K. Niihara, "Titania nanotubes prepared by chemical processing," *Advanced Materials*, vol. 11, no. 15, pp. 1307–1311, 1999.
- [4] X. Wang and Y. Li, "Selected-control hydrothermal synthesis of α - and β - MnO_2 single crystal nanowires," *Journal of the American Chemical Society*, vol. 124, no. 12, pp. 2880–2881, 2002.
- [5] W. I. Park, J. S. Kim, G.-C. Yi, and H.-J. Lee, "ZnO nanorod logic circuits," *Advanced Materials*, vol. 17, no. 11, pp. 1393–1397, 2005.
- [6] H. Huang, O. K. Tan, Y. C. Lee, M. S. Tse, J. Guo, and T. White, "In situ growth of SnO_2 nanorods by plasma treatment of SnO_2 thin films," *Nanotechnology*, vol. 17, no. 15, pp. 3668–3672, 2006.
- [7] M. Wei, H. Sugihara, I. Honma, M. Ichihara, and H. Zhou, "A new metastable phase of crystallized $\text{V}_2\text{O}_4 \cdot 0.25\text{H}_2\text{O}$ nanowires: synthesis and electrochemical measurements," *Advanced Materials*, vol. 17, no. 24, pp. 2964–2969, 2005.
- [8] H. Luo, M. Wei, and K. Wei, "A new metastable phase of crystallized $\text{MoO}_3 \cdot 0.3\text{H}_2\text{O}$ nanobelts," *Materials Chemistry and Physics*, vol. 113, no. 1, pp. 85–90, 2009.
- [9] J. Zhang, F. Jiang, Y. Yang, and J. Li, "Catalyst-assisted vapor-liquid-solid growth of single-crystal Ga_2O_3 nanobelts," *Journal of Physical Chemistry B*, vol. 109, no. 27, pp. 13143–13147, 2005.
- [10] H. A. El-Sayed and V. I. Birss, "Controlled interconversion of nanoarray of Ta dimples and high aspect ratio Ta oxide nanotubes," *Nano Letters*, vol. 9, no. 4, pp. 1350–1355, 2009.
- [11] A. J. Chiquito, A. J. C. Lanfredi, R. F. M. de Oliveira, L. P. Pozzi, and E. R. Leite, "Electron dephasing and weak localization in Sn doped In_2O_3 nanowires," *Nano Letters*, vol. 7, no. 5, pp. 1439–1443, 2007.
- [12] K. Sayama, H. Sugihara, and H. Arakawa, "Photoelectrochemical properties of a porous Nb_2O_5 electrode sensitized by a ruthenium dye," *Chemistry of Materials*, vol. 10, no. 12, pp. 3825–3832, 1998.
- [13] K. Hara, T. Horiguchi, T. Kinoshita, K. Sayama, H. Sugihara, and H. Arakawa, "Highly efficient photon-to-electron conversion with mercurochrome-sensitized nanoporous oxide semiconductor solar cells," *Solar Energy Materials and Solar Cells*, vol. 64, no. 2, pp. 115–134, 2000.
- [14] B. Varghese, S. C. Haur, and C.-T. Lim, " Nb_2O_5 nanowires as efficient electron field emitters," *Journal of Physical Chemistry C*, vol. 112, no. 27, pp. 10008–10012, 2008.
- [15] K. Tanabe, "Catalytic application of niobium compounds," *Catalysis Today*, vol. 78, no. 1–4, pp. 65–77, 2003.
- [16] M. E. Gimon-Kinsel and K. J. Balkus Jr., "Pulsed laser deposition of mesoporous niobium oxide thin films and application as chemical sensors," *Microporous and Mesoporous Materials*, vol. 28, no. 1, pp. 113–123, 1999.
- [17] I. Sieber, H. Hildebrand, A. Friedrich, and P. Schmuki, "Formation of self-organized niobium porous oxide on niobium," *Electrochemistry Communications*, vol. 7, no. 1, pp. 97–100, 2005.
- [18] R. Jose, V. Thavasi, and S. Ramakrishna, "Metal oxides for dye-sensitized solar cells," *Journal of the American Ceramic Society*, vol. 92, no. 2, pp. 289–301, 2009.
- [19] M. Wei, K. Wei, M. Ichihara, and H. Zhou, " Nb_2O_5 nanobelts: a lithium intercalation host with large capacity and high rate capability," *Electrochemistry Communications*, vol. 10, no. 7, pp. 980–983, 2008.
- [20] A. F. Wells, *Structural Inorganic Chemistry*, Oxford Science, Oxford, UK, 5th edition, 1984.
- [21] B. M. Gatehouse and A. D. Wadsley, "The crystal structure of the high temperature form of niobium pentoxide," *Acta Crystallographica*, vol. 17, no. 12, pp. 1545–1554, 1964.
- [22] S. Venkataraj, R. Drese, Ch. Liesch, O. Kappertz, R. Jayavel, and M. Wuttig, "Temperature stability of sputtered niobium-oxide films," *Journal of Applied Physics*, vol. 91, no. 8, pp. 4863–4871, 2002.
- [23] P. Viswanathamurthi, N. Bhattarai, H. Y. Kim, D. R. Lee, S. R. Kim, and M. A. Morris, "Preparation and morphology of niobium oxide fibres by electrospinning," *Chemical Physics Letters*, vol. 374, no. 1–2, pp. 79–84, 2003.
- [24] M. Mozetič, U. Cvelbar, M. K. Sunkara, and S. Vaddiraju, "A method for the rapid synthesis of large quantities of metal oxide nanowires at low temperatures," *Advanced Materials*, vol. 17, no. 17, pp. 2138–2142, 2005.
- [25] E. R. Leite, C. Vila, J. Bettini, and E. Longo, "Synthesis of niobia nanocrystals with controlled morphology," *Journal of Physical Chemistry B*, vol. 110, no. 37, pp. 18088–18090, 2006.
- [26] W. Hu, Y. Zhao, Z. Liu, and Y. Zhu, " $\text{NbS}_2/\text{Nb}_2\text{O}_5$ nanocables," *Nanotechnology*, vol. 18, no. 9, pp. 1–5, 2007.
- [27] Y. Kobayashi, H. Hata, M. Salama, and T. E. Mallouk, "Scrolled sheet precursor route to niobium and tantalum oxide nanotubes," *Nano Letters*, vol. 7, no. 7, pp. 2142–2145, 2007.
- [28] C. Yan and D. Xue, "Formation of Nb_2O_5 nanotube arrays through phase transformation," *Advanced Materials*, vol. 20, no. 5, pp. 1055–1058, 2008.
- [29] Y. Zhou, Z. Qiu, M. Lü, A. Zhang, and Q. Ma, "Preparation and spectroscopic properties of Nb_2O_5 nanorods," *Journal of Luminescence*, vol. 128, no. 8, pp. 1369–1372, 2008.
- [30] M. Wei, Z.-m. Qi, M. Ichihara, and H. Zhou, "Synthesis of single-crystal niobium pentoxide nanobelts," *Acta Materialia*, vol. 56, no. 11, pp. 2488–2494, 2008.