Synthesis of VO_x Nanotubes by Cooperation of Tetramethylammonium Hydroxide and Tetradecylamine in Short Duration

Yeqian Shen, Luming Peng,* Xuefeng Guo,* and Weiping Ding
Key Lab of Mesoscopic Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P. R. China

(Received June 24, 2009; CL-090594; E-mail: guoxf@nju.edu.cn, luming@nju.edu.cn)

A simple, rapid, and highly efficient method for the synthesis of uniform vanadium oxide nanotubes with the cooperation of tetramethylammonium hydroxide and tetradecylamine was successfully developed.

Nanotubular materials are expected to have unique characteristics amplified by their marked shape-specific and quantum size effects. Since the discovery of carbon nanotubes (CNT) in 1991 by Iijima,[1] the tubular-structured materials have been greatly explored, from carbon-based substances to a great many other inorganic materials.[2–4] Among them, vanadium compounds, especially VO_x nanotubes, have attracted special interests because of their outstanding structural flexibility combined with chemical and physical properties which are of interest for, e.g., the cathode materials for rechargeable lithium batteries[5–9] and heterogenous catalysts.[10–14]

Vanadium oxide nanotubes were first prepared by Nesper's group by a chimie douce approach.[15] Since then many groups have tried different methods to obtain vanadium nanotubes.[16–19] According to previous research, the most important step for the synthesis of VO_x nanotubes is the formation of a lamellar precursor with intercalated organic amines. The completely intercalated precursor will shorten the scrolling time to form the nanotubes during hydrothermal treatment. By the traditional procedure, the intercalation reaction is carried out by a time-consuming stirring method, and the obtained precursor still requires 7–10 days under 180 °C hydrothermal treatment. Here, we report a highly efficient and facile approach for VO_x nanotubes with uniform morphology by the cooperation of tetramethylammonium hydroxide (TMAOH) and tetradecylamine under ultrasonic treatment followed by a much shortened hydrothermal treatment. The ultrasonic treatment is a fast method for the delamination of layered materials in a diluted solution of TMAOH,[20] and the current method proves more efficient for the precursor formation. It represents a facile strategy for the VO_x nanotube synthesis.

In a typical procedure, 1.828 g (10 mmol) of V_2O_5 powder was added to a mixed solution of 16 mL of ethanol and 6 mL of H_2O, then 1.34 mL of TMAOH and 2.13 g of tetradecylamine was added to the beaker in turn. After vigorous magnetic stirring for 2 h, 15-mL of H_2O was added, and the mixture was continuously stirred for 4 h. The obtained light-orange suspension was treated for 40 min with ultrasonic (400 W) and then transferred into a Teflon-lined autoclave with a stainless shell. The hydrothermal reaction proceeded for 180 °C for 3 days. The obtained black precipitate was washed several times with distilled water and ethanol to remove the unreacted amine and other decomposited products and finally dried under vacuum at 60 °C for 6 h. VO_x nanotubes by traditional method were prepared for comparison.[20]

As shown in Figures 1a and 1b, both the SEM and TEM images prove that there are a large amount of nanotubes lying randomly and intersecting each other, without any other impurities. All the tubes are up to 3–4-μm long and have outer diameters about 60–70 nm and inner diameters from 20–25 nm. The tube walls consist of 6–8 crystalline vanadium oxide layers with amine molecules intercalated in between (Figure 1c), and the distance between the layers is about 2.89 nm (Figure 1c inset). Figure 1d shows the TEM image of VO_x nanotubes attained by the traditional hydrothermal treatment for 7 days without existence of TMAOH. There are many nanotubes; however, products with other morphologies (e.g., nanobelts) are found. The XPS data indicate the ratio of V^{5+} and V^{4+} in the nanotubes is around 1.80:1, thus the average valence of vanadium is about 4.64. In combination with the elemental analysis and DSC-TG results, the nominal composition of the nanotubes obtained is $VO_{2.47}[C_{14}H_{29}NH_3]_{0.25}[C_4H_{12}N]_{0.05}$.

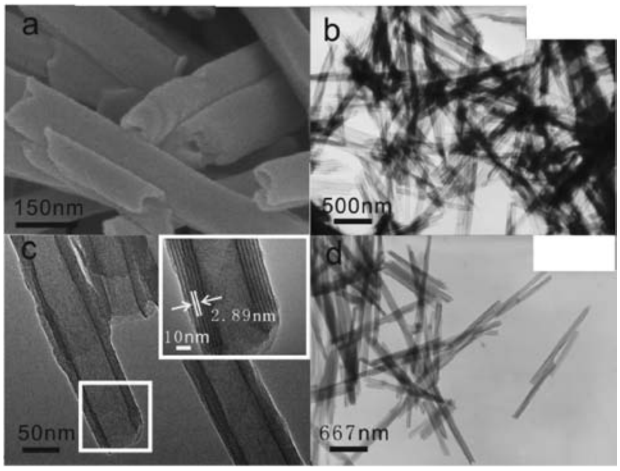

Figure 1. TEM and SEM images of the VO_x nanotube hydrothermally synthesized with TMAOH. a) SEM image, b) typical TEM image, c) HRTEM image, and d) TEM image of VO_x nanotubes by traditional hydrothermal treatment for 7 days.

To investigate the effects of TMAOH and ultrasonic treatment in the synthesis, three different methods were used to prepare the precursors before hydrothermal treatment. The TEM images and SAXRD patterns of the three precursors are shown in Figures 2a–2c. Precursor-A was obtained by the conventional method with only tetradecylamine as the template. It has a sheet-like morphology and its SAXRD pattern proves a layered structure with a layer distance of ca. 3.28 nm (Figure 2a). When a small amount of TMAOH was added, precursor-B was formed featuring larger nanosheets. The corresponding SAXRD pattern shows two groups of reflection peaks, from which the distances between the layers can be calculated as 3.28 and 2.94 nm (Figure 2b), respectively. When both TMAOH and ultrasonic treatment were introduced, precursor-C was obtained. Figure 2c

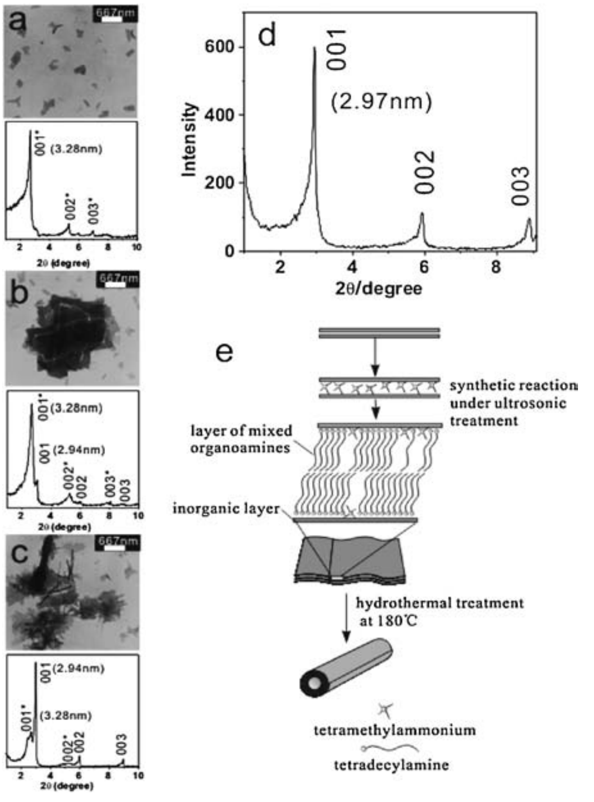

Figure 2. (a)–(c) TEM images and SAXRD patterns of the three different precursors intercalated with tetradecylamine: (a) precursor-A obtained without TMAOH and ultrasonic treatment, (b) precursor-B obtained with TMAOH but without ultrasonic treatment, and (c) precursor-C obtained with both TMAOH and ultrasonic treatment (the precursor of the VO_x nanotube). (d) The SAXRD pattern of the VO_x nanotubes by hydrothermal treating the precursor-C for 3 days. (e) The mechanism proposed for the current preparation of VO_x nanotube.

shows there are increased amount of large nanosheets in precursor-C, some of which scrolled. Two groups of peaks can also be observed in the SAXRD pattern, while the reflection peaks at $2\theta = 3.0$, 6.0, and 9.0° corresponding to a layer distance of ca. 2.94 nm are much stronger than the other reflections. The SAXRD pattern of VO_x nanotubes, obtained by hydrothermally treating the precursor-C for 3 days, depicts three reflections indexed as (00*l*), characteristic of well-ordered lamellar systems (Figure 2d). The most intense reflection appears at $2\theta = 2.94°$, corresponding to a layer distance of 2.97 nm, which matches well with the HRTEM images. The observed layer distance is smaller than twice the calculated maximum length of the tetradecylamine, which implies that large tilt angles must be present and results in a decrease of the distance from 3.28 to 2.97 nm due to the transformation from nanosheets to nanotubes.

With the cooperation of TMAOH and tetradecylamine under ultrasonic treatment for a short time of 40 min, the layered V_2O_5 was effectively delaminated and began to scroll. One possible reason for the accelerated intercalation reaction rate is the microstreaming effect. When a solid–liquid mixture is treated ultrasonically, acoustic cavitations occur. The cavitation bubbles undergo unsymmetric collapse near an extended liquid–solid interface and causes "in-rush" of the liquid into the solid, which pushes the organic molecules into the V_2O_5 layers.[21,22] The other possible reason is the presence of TMA^+, which has a smaller size than tetradecylamine and more easily resides in the interlayer region of the V_2O_5 material. It is known that the intercalation products have the capability for re-intercalation of other either smaller or larger molecules, so a light pathway is proposed as shown in Figure 2e. The layered vanadium pentoxide is quickly delaminated by the TMA^+ under ultrasonic treatment, and the TMA^+ enlarges the distance between the layers, which makes it easier for the larger tetradecylamine molecule to intercalate into the layers and form a lamellar compound, so the aging time is shortened. During both the ultrasonic treatment and the hydrothermal treatment, partial decomposition of amines promotes the reduction of some V^{5+} species to V^{4+} species, which may lead to a curvature of the inorganic structure. So the vanadium oxide sheets can readily start to scroll both ends of the layers at the same time. The binding sheets have the possibility to close perfectly, leading to cylinder morphologies.

In summary, vanadium nanotubes with uniform morphology have been successfully prepared via a hydrothermal synthesis. The cooperation between TMA^+ and $C_{14}H_{29}NH_3{}^+$ under ultrasound for the delamination of layered vanadium oxide is a more efficient procedure than the ones used before. Thin VO_x nanosheet can be formed easily, and the followed scrolling procedure under hydrothermal treatment requires a shorter period of time. This new approach to the synthesis of VO_x nanotubes opens up a range of possible applications in the preparation of nanocomposites with novel properties and morphologies.

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References

1 S. Iijima, *Nature* **1991**, *354*, 56.
2 Y. Feldman, E. Wasserman, D. J. Srolovitz, R. Tenne, *Science* **1995**, *267*, 222.
3 N. G. Chopra, R. J. Luyken, K. Cherrey, V. H. Crespi, M. L. Cohen, S. G. Louie, A. Zettl, *Science* **1995**, *269*, 966.
4 Y. R. Hacohen, E. Grunbaum, R. Tenne, J. Sloan, J. L. Hutchison, *Nature* **1998**, *395*, 336.
5 J. S. Braithwaite, C. R. A. Catlow, J. D. Gale, J. H. Harding, *Chem. Mater.* **1999**, *11*, 1990.
6 J. Dai, S. F. Y. Li, Z. Gao, K. S. Siow, *Chem. Mater.* **1999**, *11*, 3086.
7 Y. Wang, K. Takahashi, H. Shang, G. Cao, *J. Phys. Chem. B* **2005**, *109*, 3085.
8 S. Nordlinder, L. Nyholm, T. Gustafsson, K. Edström, *Chem. Mater.* **2006**, *18*, 495.
9 C. O'Dwyer, V. Lavayen, C. Clavijo-Cedeño, C. M. Sotomayor Torres, *Phys. Status Solidi B* **2008**, *245*, 2102.
10 G. C. Bond, S. F. Tahir, *Appl. Catal.* **1991**, *71*, 1.
11 E. A. Mamedov, V. C. Corberan, *Appl. Catal., A* **1995**, *127*, 1.
12 L. Krusin-Elbaum, D. M. Newns, H. Zeng, V. Derycke, J. Z. Sun, R. Sandstrom, *Nature* **2004**, *431*, 672.
13 W. Chen, Q. Xu, Y. S. Hu, L. Q. Mai, Q. Y. Zhu, *J. Mater. Chem.* **2002**, *12*, 1926.
14 X.-W. Chen, Z. Zhu, M. Hävecker, D. S. Su, R. Schlögl, *Mater. Res. Bull.* **2007**, *42*, 354.
15 F. Krumeich, H.-J. Muhr, M. Niederberger, F. Bieri, B. Schnyder, R. Nesper, *J. Am. Chem. Soc.* **1999**, *121*, 8324.
16 X. Chen, X. Sun, Y. Li, *Inorg. Chem.* **2002**, *41*, 4524.
17 W. Chen, J. Peng, L. Mai, Q. Zhu, Q. Xu, *Mater. Lett.* **2004**, *58*, 2275.
18 F. Sediri, N. Gharbi, *J. Phys. Chem. Solids* **2007**, *68*, 1821.
19 L. I. Vera-Robles, A. Campero, *J. Phys. Chem. C* **2008**, *112*, 19930.
20 Y. Cui, Z. Liu, M. Wang, K. Ooi, *Chem. Lett.* **2006**, *35*, 740.
21 L. Liu, Z. Zhou, C. Peng, *Electrochim. Acta* **2008**, *54*, 434.
22 L. Peng, J. Yu, J. Li, Y. Li, R. Xu, *Chem. Mater.* **2005**, *17*, 2101.