

Self-Assembling Vanadium Oxide Nanotubes by Organic Molecular Templates

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Vanadium oxide nanotubes were synthesized as the main product by hydrothermal self-assembling from ammonium metavanadate (NH_4VO_3) and organic molecules as structure-directing templates. Several kinds of templates including primary amines ($\text{C}_n\text{H}_{2n+1}\text{NH}_2$), α,ω -diamines ($\text{H}_2\text{N}[\text{CH}_2]_n\text{NH}_2$), and quaternary ammonium salt (CTAB) were demonstrated to be appropriate for the formation of nanotubes. The morphologies and structures of the nanotubes were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), and thermal gravimetric analysis (TGA). The nanotubes were found forming together with the layered structures and the sheetlike structures. On the basis of the growth mechanism of WS_2 nanotubes proposed by our group, a possible rolling mechanism was proposed, which might be a suitable general formation mechanism for types of nanotubes from lamellar structures.

Introduction

Since the carbon nanotubes were discovered in 1991,¹ considerable effort has been placed on the synthesis of different kinds of nanotubes. Many types of nanotubes such as WS_2 , MoS_2 , InS , NbS_2 , TaS_2 nanotubes,² BN, BCN nanotubes,³ NiCl_2 nanotubes,⁴ and organic nanotubes⁵ have been reported. Recently, Nesper and co-workers synthesized the novel vanadium oxide nanotubes (VO_x -NT) in a sol-gel reaction followed by hydrothermal treatment from vanadium alkoxide precursors and primary amines.⁶ Due to the potential applications in electrochemical devices and catalytic applications, this representative of oxidic nanotubes attracted much attention. Furthermore, this type of nanotube was easily accessible as a pure product in gram quantities

by low-temperature, soft chemistry synthesis, so this provided a promising approach to nanotube study.

However, as we know there are only a few reports on exploring the formation mechanism of these kinds of nanotubes. Obviously, the formation mechanisms will be a significant breakthrough for nanotube synthetic methods, which may open fascinating possibilities for further chemical and physical explorations of nanostructures and hold promise for possible applications. As is known, most of the synthesized nanotube materials commonly possessed lamellar structures. A series of significant work done by Mallouk and co-workers on lamellar structures, in which lamellar sheets, tubular structures, and rolling phenomena were observed,⁷ gave us inspiration. Our group recently proposed a novel growth mechanism called the “rolling mechanism” from the study on WS_2 nanotubes.⁸

Herein we report a high-yielding low-cost facile synthesis of vanadium oxide nanotubes by hydrothermal reaction from NH_4VO_3 and structure-directing templates. One of our aims

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in this area is to develop general synthetic methods and explore the formation mechanism of nanotubes. We found that nanotubes formed together with the layered structures and the sheetlike structures, which seemed in accord with the growth process of WS₂ nanotubes. Here we propose a rolling mechanism of vanadium oxide nanotubes by hydrothermal self-assembling from ammonium metavanadate (NH₄VO₃) and organic molecules as structure-directing templates, which suggested that the rolling mechanism of vanadium oxide nanotubes should be a kind of general formation mechanism of nanotubes from lamellar structures and may develop into a general synthetic method for preparing nanotubes from lamellar structures.

Experimental Section

Preparation. The vanadium oxide nanotubes were synthesized under hydrothermal conditions. All chemicals were purchased from Beijing Chemical Reagents Company and used without further purification. NH₄VO₃ was mixed with the structure-directing templates in a molar ratio of 2:1 under stirring. The resulting mixture was then adjusted to a specific pH (9–12 or 4–6) under vigorous stirring. The coprecipitation was formed and the resultant suspension was then transferred into a Teflon-lined autoclave with a stainless steel shell. The autoclave was kept at 180 °C for more than 3 days and then allowed to cool to room temperature naturally. The final product was washed with deionized water several times and then dried at 70 °C under vacuum for 6–8 h.

X-ray Powder Diffraction. Powder X-ray diffraction (XRD) experiments of all the products were conducted on a Bruker D-8 Advance X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$).

Transmission Electron Microscopy. The morphologies and structures of the synthesized products were observed through a Hitachi-800 transmission electron microscopy (TEM) operated at 200 KV and a JEOL JEM-2010F transmission electron microscope operated at 200 KV.

Thermal Analysis. The samples were heated to 700 °C at a rate of 20 deg/min, under a nitrogen atmosphere on a TA instruments TGA2050.

Thermal Stability Characterization. Thermal stability characterization of products was carried out in a conventional tube furnace. The as-prepared vanadium nanotubes were placed in a quartz boat. The quartz boat was placed in the hot zone inside the quartz tube and heated to 500 °C at a constant rate. Then the temperature was kept constant for 2 h and then cooled to room temperature. All the heating processes were carried out under a nitrogen atmosphere (99.9%).

Results and Discussion

Synthetic Method. The main approach to obtaining vanadium oxide nanotubes and some other nanotubes was self-assembling with use of organic molecules as structure-directing agents for the assembly of inorganic precursors at the template–solution interface. The interaction between organic molecules and inorganic precursors could be coordinative interactions,⁹ electrostatic interactions,¹⁰ or even

hydrogen bonding.¹¹ This method has opened a way to controlled synthesis for template-based periodic inorganic structures.

Although there have been some reports on the synthesis of vanadium oxide nanotubes based on this method,⁶ in our process the self-assembling method was further developed. First, our process was a high-yielding low-cost route to the synthesis of vanadium oxide nanotubes. The inorganic precursor we employed was NH₄VO₃ instead of the vanadium triisopropoxide. The bulk of the products in gram quantities could be obtained without the requirement of delicate equipments and in our experiment the starting materials could be mostly translated to the final products. The yield of the vanadium oxide nanotubes was estimated to be about 80% from repeats of the typical synthetic process and TEM observations of the samples from different batches of synthesis. Second, all the reactions of the preparation process were carried out in the aqueous solution. An organic solvent such as absolute ethanol was normally used for dissolving the organic molecules. In our process, all the samples could be obtained with water as solvent. Third, various amine molecules and surfactants could be used as templates in our process including primary amines (C_nH_{2n+1}NH₂), α,ω -diamines (H₂N[CH₂]_nNH₂), and quaternary ammonium salt (CTAB), which offered perspectives for more flexible structures. Moreover, there are not such limits in the chain lengths as predicated.^{6a} For example, we could use $n = 6$ in the case of aliphatic α,ω -diamines templates while in the vanadium alkoxide route,⁶ the chain length could only extend from $n = 14$ to 20. It is notable that the structure of the nanotubes obtained from NH₄VO₃ and 1,6-hexamethylenediamine seemed to be special and interesting and further experiments are being performed.

Morphology and Structure of Vanadium Oxide Nanotubes. The final products consisted almost exclusively of vanadium oxide nanotubes (Figure 1). Nanotubes were obtained successfully with primary amines (Figure 1a), α,ω -diamines (Figure 1b), and quaternary ammonium (Figure 1c). The typical nanotube length was about 2 μm while the length could range from 0.3 to 8 μm . The diameter ranged from 30 to 100 nm. Lengths and diameters of the nanotubes depended on the conditions of the preparation, such as different template molecules, concentration, and reaction time. For example, prolonging reaction time could obtain more long tubes. The tube walls consist of 3–10 vanadium oxide layers. As shown in Figure 2, the nanotube, which was a typical nanotube from octadecylamine and NH₄VO₃, had an open end and an outer diameter of approximately 70 nm. The walls appear as alternating fringes of dark and bright contrast. According to the structure model of vanadium oxide nanotubes,⁶ the dark fringes represent the vanadium oxide layers, between which the template molecules were embedded. The distance between the layers varied with the length of the templates. The layer distances were calculated from the d

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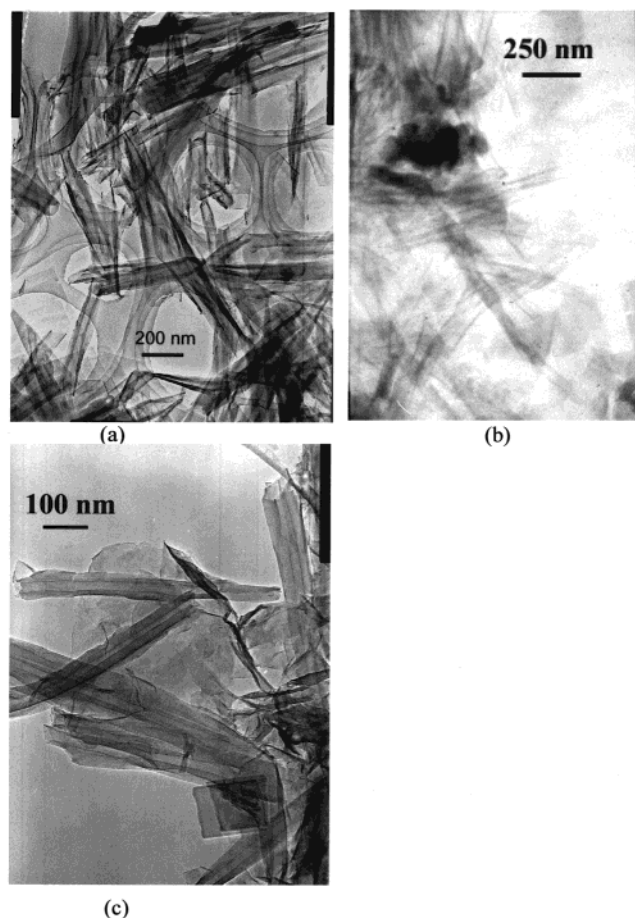


Figure 1. Representative TEM images of vanadium oxide nanotubes with lengths ranging from 0.4 to 3.2 μm . The nanotube materials were obtained from (a) NH_4VO_3 and octadecylamine, (b) NH_4VO_3 and CTAB, and (c) NH_4VO_3 and 1,6-hexamethylenediamine.

values of the (00 l) reflections of XRD patterns over a small angle range, which matched well with HRTEM images.

In the case of octadecylamine as the template, it was worthy to note that there were two kinds of layered distances, which could be identified by the power X-ray diffraction pattern of the vanadium oxide nanotubes (Figure 2b). The peak (\circ) with the highest intensity at $2\theta = 2.15$ corresponding to a d value of 4.2 nm reflects one kind of layer distance and the peak (\bullet) with the highest intensity at $2\theta = 2.51$ corresponding to a d value of 3.4 nm reflects the other kind of layer distance. Two types of layer distances could even be found in one nanotube as indicated in Figure 2a. The layer distances of nanotubes were smaller than twice the calculated maximum lengths of the templates, which implies that overlap of the alkyl chains and/or tilt angles must be present. The difference in the layer distances may be attributed to the difference in the overlap or/and tilt angles.

1,6-Hexamethylenediamine was also used as a template to synthesize vanadium oxide nanotubes successfully. As shown in Figure 3, the layer distance of vanadium oxide nanotubes from NH_4VO_3 and 1,6-hexamethylenediamine was unexpectedly large. The layer distance of 4.9 nm identified in Figure 3a was much more than twice the calculated maximum lengths of 1,6-hexamethylenediamine. The peak with highest intensity at $2\theta = 1.81$ corresponding to a d

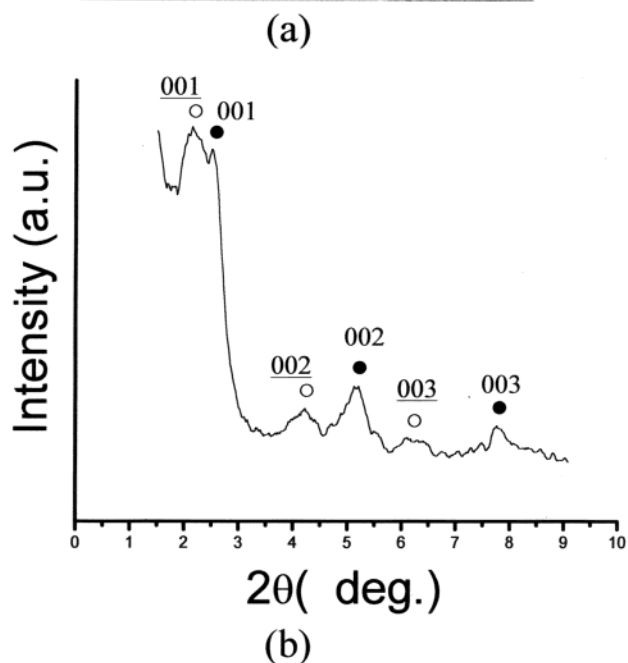
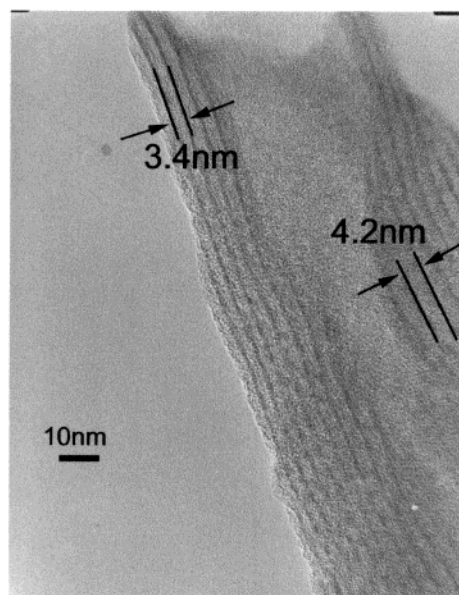


Figure 2. The structure of vanadium oxide nanotubes from NH_4VO_3 and octadecylamine: (a) High-resolution TEM images of the vanadium oxide nanotubes, indicating the multisheet structure of the tube walls with two kinds of layer distances. (b) Powder X-ray diffraction pattern of the vanadium oxide nanotubes. Two sets of 00 l reflections (\circ and \bullet) represented two kinds of layer distances separately. The peak (\circ) with the highest intensity at $2\theta = 2.15$ corresponding to a d value of 4.2 nm reflect the layer distance of 4.2 nm and the peak (\bullet) with the highest intensity at $2\theta = 2.51$ corresponding to a d value of 3.4 nm reflected the other kind of layer distance of 3.4 nm.

value of 4.9 nm confirmed the large layer distance (Figure 3b). Although the model for this nanotube was not completely clear, the possible reason for this large distance can be described: The large distance was contributed to the long chain combined from several (more than 3) 1,6-hexamethylenediamine molecules one by one. The combination might be through hydrogen bonding ($-\text{N}-\text{H}\cdots\text{N}-$).

Formation of Vanadium Oxide Nanotubes. Layered structures employed for the synthesis of vanadium oxide nanotubes were obtained with NH_4VO_3 and suitable organic

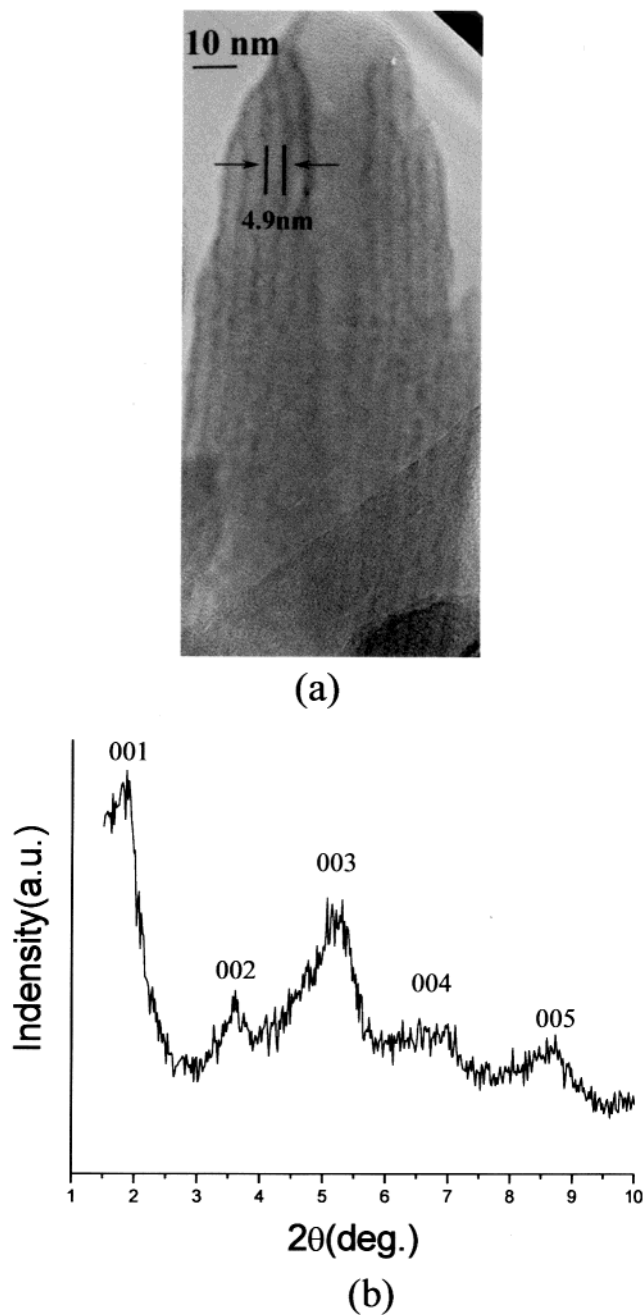


Figure 3. The structure of vanadium oxide nanotubes from NH_4VO_3 and octadecylamine: (a) High-resolution TEM images of the vanadium oxide nanotubes, indicating the multishell structure of the tube walls with unexpectedly large layer distances of 4.9 nm. (b) Powder X-ray diffraction pattern of the vanadium oxide nanotubes. The peak with the highest intensity at $2\theta = 1.81$ corresponding to a d value of 4.9 nm reflected the layer distance of two concentric single shells of the multishell structure of the tube wall.

surfactants, which also acted as nanotube structure templates. The artificial lamellas were based on the co-condensation mechanism of anionic inorganic (VO_3^- in our process) with organic molecules.¹² Under certain conditions, the interlayer

interaction of this kind of lamellar intercalates could be diminished from the edges. Then, the rolling of the layers into the tubules should take place. Where did the driving force for rolling of the lamellar sheets come from? The hydrothermal treatment should be a suitable explanation and there was some evidence. Heidenreich et al. have noted that severe bending of graphite sheets commonly occurs at high temperature.¹³ More recently, curling graphitic networks have been observed under electron beam irradiation.¹⁴ These suggested the possibility of the rolling process of the lamellar inorganic-surfactant mesostructures under hydrothermal treatment or other proper conditions.

The above scheme for the formation of the vanadium oxide nanotube, which has been named the “rolling mechanism”, could be divided into three main steps: (1) The surfactant molecules condensed into aggregations with VO_3^- to form lamellar structures. (2) When treated under hydrothermal conditions, the condensation process continued and brought out more ordered lamellar assemblies. (3) These lamellar sheets became loose at the edges and then rolled into themselves to finally form vanadium oxide nanotubes. The above process is outlined in Figure 4.

To confirm the rolling mechanism, we designed and carefully performed a series of experiments under the same conditions except for hydrothermal reaction time. Our experiment results were in good agreement with those of the rolling mechanism. The coexistence of nanotubes and unrolled lamellar structures (Figure 5) could be seen from the products whose reaction time was not long enough. It could be seen that the vanadium oxide nanotubes coexisted with large plates, which suggested the link between the nanotubes and lamellar structure intermediates and corresponded well to the rolling mechanism. Moreover, some plates were found curling at their edges (Figure 6c), which could be considered being in the initial stage of rolling. Figure 6 (a \rightarrow b \rightarrow c \rightarrow d, e) might be considered the forming process of vanadium oxide nanotubes observed under TEM and HRTEM. The amorphous precursor was obtained by mixture and coprecipitation and the lamellar structure could be seen from this yellow precursor (Figure 6a). Under hydrothermal treatment, the amorphous precursor became crystallized ordered layered structures (Figure b). Then, the layer began to roll (Figure 6c). Finally, the nanotubes formed after hydrothermal treatment for enough time (Figure 6d,e).

The most direct evidence for the rolling mechanism was the presence of intermediates of ordered layered structures (Figure 7). Layered vanadium compounds have been widely studied over the past decades. Vanadium pentoxide (V_2O_5) can be regarded as a layered structure in which VO_5 square pyramids are connected by sharing corners and edges and thereby form the layers.¹⁵ Several types of layered polyoxovanadates have also been reported, which were built of mixed valence polyoxovanadate planes made of VO_5 pyramids and/

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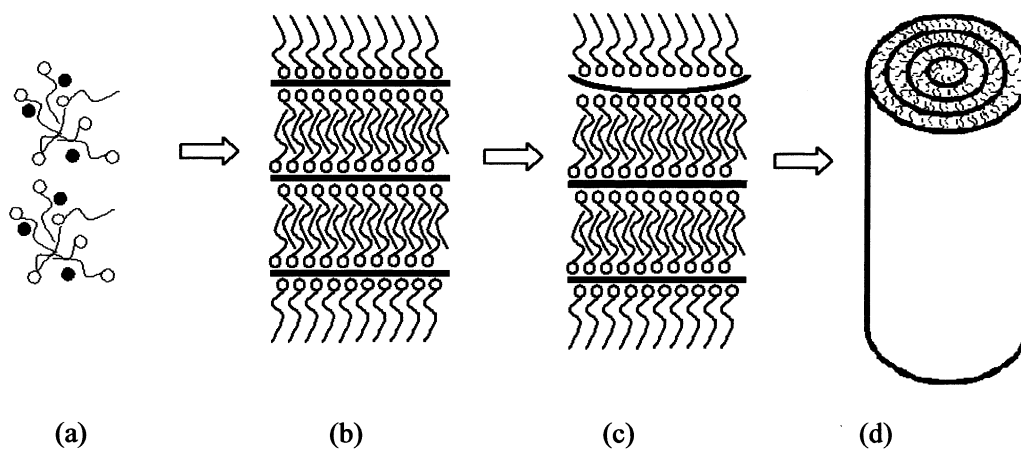


Figure 4. Schematic presentation of the whole rolling mechanism for the formation of the vanadium oxide nanotubes: (a) the mixture of the NH_4VO_3 and the template molecules, (b) layered structures formed through the hydrothermal treatment, (c) the beginning stage of the rolling process, and (d) the formed nanotubes.

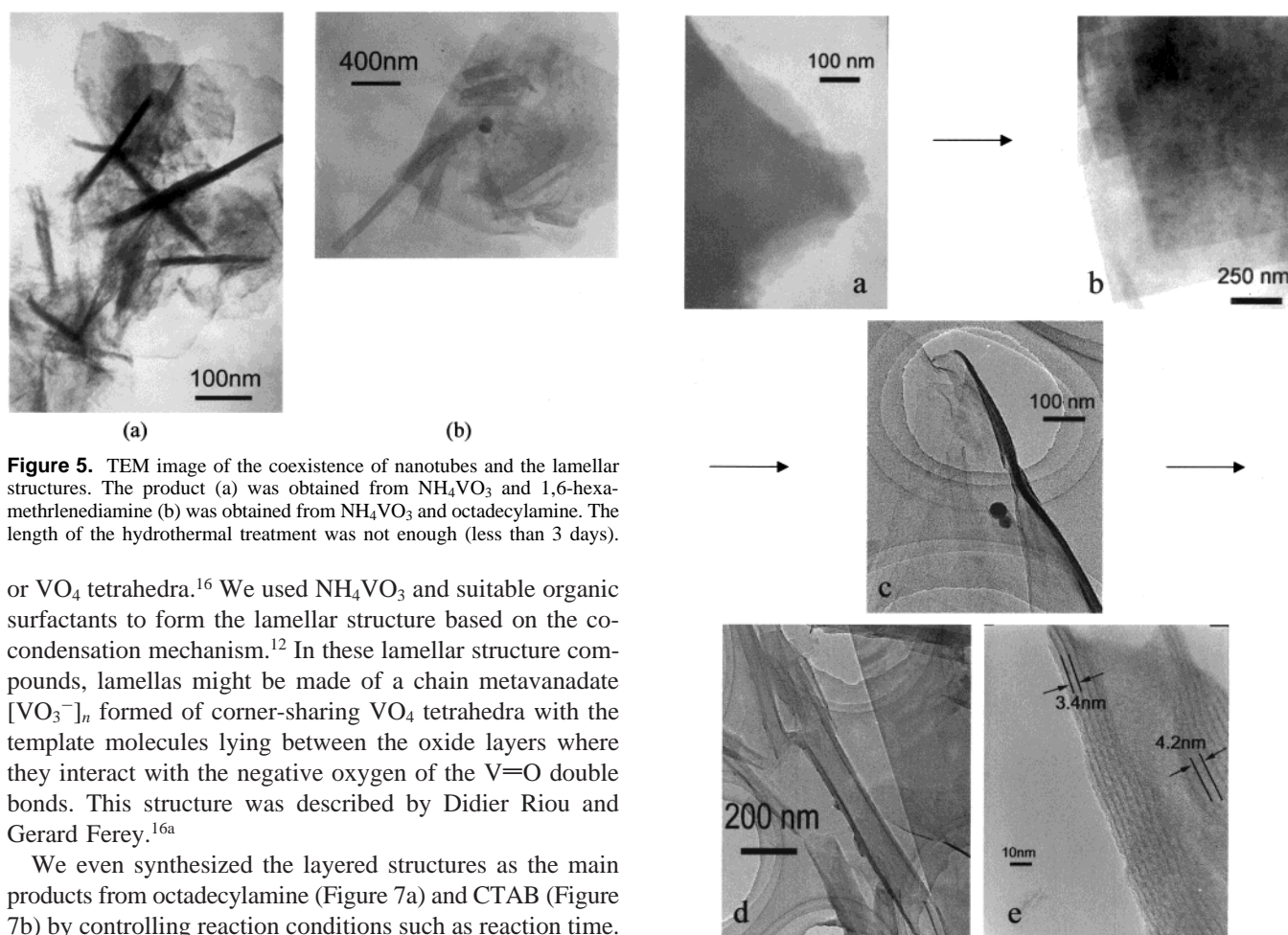


Figure 5. TEM image of the coexistence of nanotubes and the lamellar structures. The product (a) was obtained from NH_4VO_3 and 1,6-hexamethylenediamine (b) was obtained from NH_4VO_3 and octadecylamine. The length of the hydrothermal treatment was not enough (less than 3 days).

or VO_4 tetrahedra.¹⁶ We used NH_4VO_3 and suitable organic surfactants to form the lamellar structure based on the co-condensation mechanism.¹² In these lamellar structure compounds, lamellas might be made of a chain metavanadate $[\text{VO}_3^-]_n$ formed of corner-sharing VO_4 tetrahedra with the template molecules lying between the oxide layers where they interact with the negative oxygen of the $\text{V}=\text{O}$ double bonds. This structure was described by Didier Riou and Gerard Ferey.^{16a}

We even synthesized the layered structures as the main products from octadecylamine (Figure 7a) and CTAB (Figure 7b) by controlling reaction conditions such as reaction time. These ordered layered structures were confirmed by the 001 reflections of XRD patterns. The layered distance of the lamellar structures from octadecylamine was 0.90 nm back calculated from the peak with the highest intensity at $2\theta = 9.82$ corresponding to a d value of 0.90 nm and the distance from CTAB was 0.56 nm. The two kinds of layered distances of lamellar structures were both smaller than those of the

Figure 6. The forming process of $\text{VO}_x\text{-NT}$: (a) TEM image of the lamellar-structured, periodic assembly of surfactant and VO_3^- of the precursor obtained by coprecipitation. This precursor was amorphous. (b) TEM image of the ordered layered structure after hydrothermal treatment for 1.5 days. The layered structure could be confirmed by the XRD pattern (Figure 4b). (c) HRTEM image of the beginning stage of the rolling process obtained after hydrothermal treatment for 2.5 days. (d and e) HRTEM image of the formed nanotube after hydrothermal treatment for 4.5 days.

corresponding nanotubes, perhaps because the interaction of templates had not finished yet. Although the ordered layered structures from 1,6-hexamethylenediamine were not sepa-

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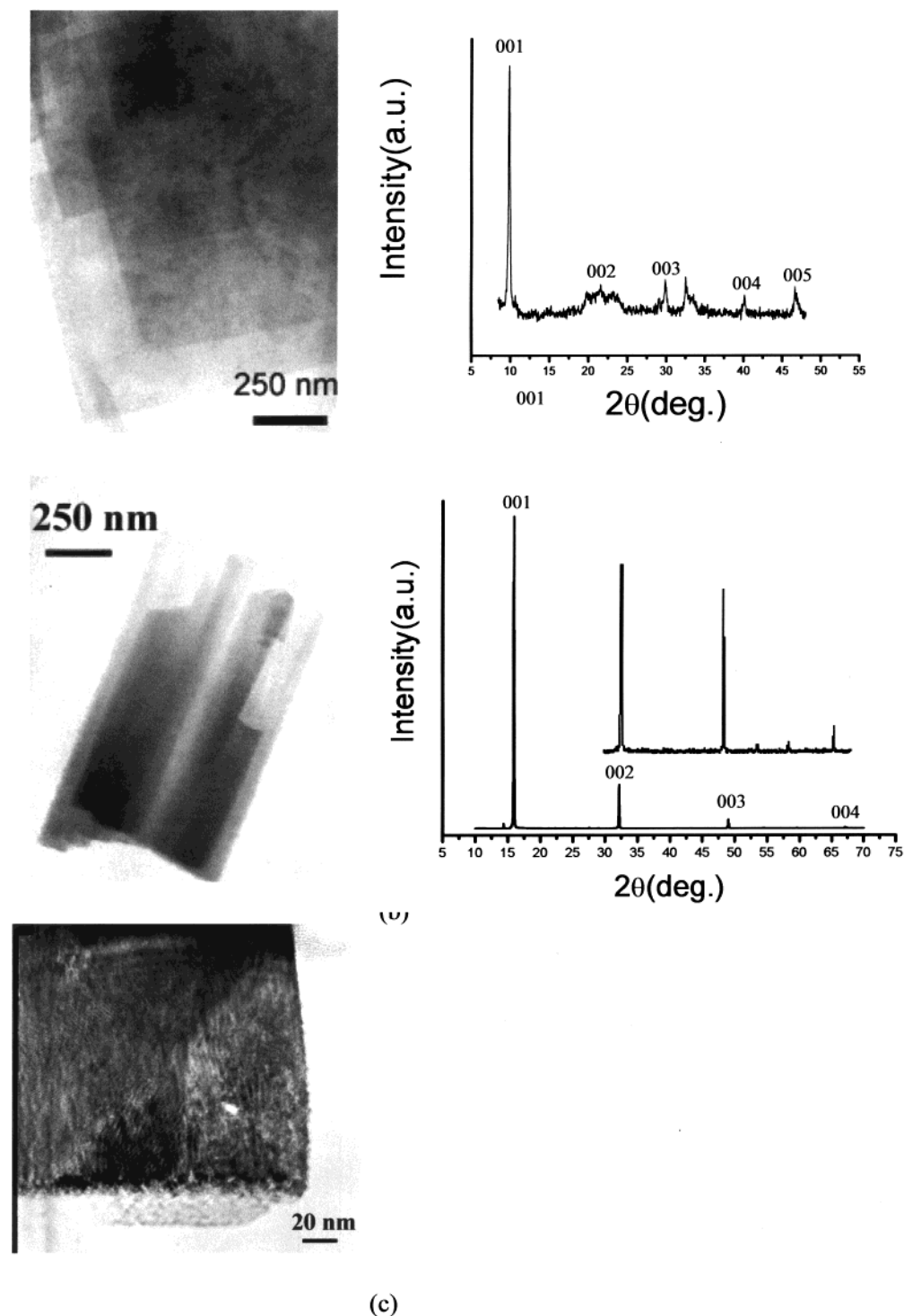


Figure 7. The intermediates of the rolling process, ordered layered structures: (a) from NH_4VO_3 and octadecylamine, (b) from NH_4VO_3 and CTAB, and (c) from NH_4VO_3 and 1,6-hexamethylenediamine. The $00l$ reflections of XRD patterns confirmed the layered structures. The layered structures in a and b were synthesized as the main products, while those in c formed together with nanotubes.

rated, we also found this structure under transmission electron microscopy while observing the nanotubes from NH_4VO_3 and 1,6-hexamethylenediamine (Figure 7c). To solve their further crystal structure, single-crystal X-ray diffraction is needed and this work is underway.

The thermal stability of the vanadium oxide/organic molecule nanotubes was also characterized to further comprehend the formation process of the nanotubes. According

to the thermal gravity analysis (TGA) plots (Figure 8), the weight loss began at about 260°C and continued until about 500°C . The total weight loss of the vanadium oxide nanotubes from NH_4VO_3 and octadecylamine was about 63% (Figure 8a), from which the estimated molecular ratio of vanadium to temperate molecule is 2:1. From Figure 8b of nanotubes from NH_4VO_3 and 1,6-hexamethylenediamine, the ratio was about 1:1 estimated from the total weight loss of

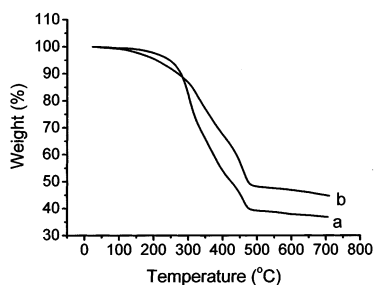


Figure 8. TGA plots of as-prepared vanadium oxide nanotubes. The product (a) was obtained from NH_4VO_3 and octadecylamine (b) was obtained from NH_4VO_3 and 1,6-hexamethylenediamine.

55%. The molecular ratios were in good agreement with the model stated above: Two octadecylamine molecules overlapped and about four 1,6-hexamethylenediamine molecules combined one by one.

When the nanotubes were destroyed by heat treatment, it could be expected based on the “rolling mechanism” that the tubular structures cracked to form nanobelts, or unrolled to form large plates. In fact, after being heated at 500 °C for 2 h under a nitrogen atmosphere, the tubular structures of vanadium oxide nanotubes disappeared, which was confirmed by low-angle X-ray diffraction patterns and mostly transferred to large plates (Figure 9). A few nanobelts were also found. This provided evidence for the “rolling mechanism” indirectly.

The rolling mechanism may present a general method for preparing nanotubes from lamellar structures. Our group has now synthesized several types of nanotubes from lamellar structures as well as WS_2 nanotubes and vanadium oxide nanotubes, which further strengthens our growth mechanism. We developed a low-temperature hydrothermal reduction method and successfully synthesized Bi nanotubes from the layered structures of α -bismuth.¹⁷ Recently, we successfully synthesized layer structured titanate nanotubes.¹⁸ On the basis of these experiments and the fully demonstrated rolling mechanism, we believe that it would be possible to prepare other novel nanotube materials with varying electrical, magnetic, optical, and optoelectric properties from lamellar structures under proper experimental conditions.

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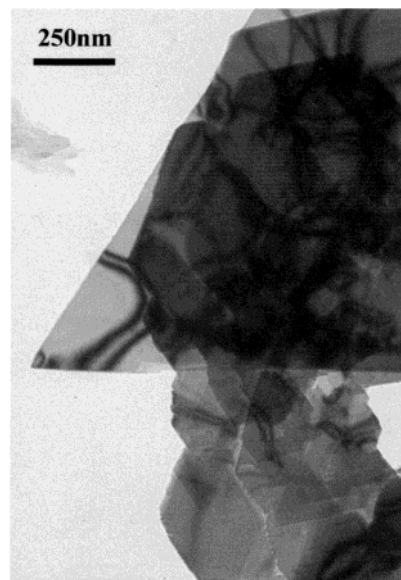


Figure 9. Representative TEM images of the large plates obtained from the heat treatment of as-prepared vanadium oxide nanotubes. The nanotubes were prepared from NH_4VO_3 and 1,6-hexamethylenediamine, and then heated at 500 °C for 2 h under a nitrogen atmosphere.

Conclusions

A self-assembling process assisted by organic molecules has been developed to prepare vanadium oxide nanotubes. Varying organic molecules are expected to be used as structure-directing templates, which may open a facile synthetic method to flexible structures of nanotubes, and the length, diameter, and layer distance of the nanotubes can be controlled by choosing different templates and proper experimental conditions.

The rolling mechanism has been demonstrated to be a general formation mechanism of nanotubes from lamellar structures. On the basis of the rolling mechanism, other types of nanotubes with varying structures may be fabricated under proper conditions. Moreover, this self-assembling process may be extended to preparing other nanostructures, such as mesoporous materials.

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