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Synthesis of vanadium oxide nanotubes from V_2O_5 sols

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Abstract

Vanadium oxide nanotubes (VO_x-NTs) were prepared by using V_2O_5 sols as precursor for the first time with hexadecylamine (HDA) as structure-directing template via a modified sol–gel method followed by hydrothermal treatment. Structure and morphology of the nanotubes were investigated by XRD, SEM, HRTEM, TGA, FT-IR and XPS. The obtained nanotubes were found having outer diameters from 30 to 100 nm and inner diameters from 10 to 30 nm with length up to several micrometers. It is also confirmed that water molecules enter vanadium oxide layers together with structure-directing template and the low valence vanadium occurs in the VO_x-NTs.
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Keywords: V_2O_5 sols; Nanotubes; Synthesis; Characterization

1. Introduction

One-dimension nanostructure transition metal oxides represent a unique class of materials because of their redox activity, which is connected with outstanding electrochemical and catalytic properties. Among these materials, nanotubes are particularly attractive since they provide access to three different contract regions: inner and outer surface as well as the tubular ends. Since carbon nanotubes were discovered by Iijima in 1991 [1], much effort has been conducted on synthesizing nanotubes from materials with novel properties. Nanotubular materials are expected to have unusual characteristics amplified by their marked shape-specific and quantum size effects. The possibility of chemically modifying the outer and inner surfaces and edges also enhances the advantageous characteristics of nanotubes. The interest in nanotube materials thus stimulated researchers to extensively enlarge the range of inorganic nanomaterials, from carbon-based substances to a great many other inorganic materials [2–4]. The recently discovered vanadium oxide nanotubes (VO_x-NTs) [5] are especially interesting since vanadium oxides are widely applied in electrochemical devices and catalysis [6,7]. The easy access to large quantity of these products predestines them as potential candidates for wide investigation on the reaction of anisotropic reactivity and physical properties. Several types of vanadium precursors had been used in the synthesis of VO_x-NTs, such as $VO(OPr)_3$ [8] and NH_4VO_3 [9]. However, there has been no report on the synthesis of VO_x-NTs by using V_2O_5 sols as vanadium precursor until now. Preparation and structural characterization of the tubes will be described in detail in this paper.

2. Experimental

All chemicals were used without further purification. V_2O_5 sols were synthesized using a melt quenching method. Melting 10 g crystalline V_2O_5 power at 1073 K in a ceramic crucible keeping for 20 min results in a molten liquid. When the molten liquid was quickly poured into distilled water with stirring, a brownish solution was formed. The solution was allowed to heat to the boiling point and then cool to room temperature naturally. After filtration and aging for more than 7 days, brownish V_2O_5 sols were obtained. To 30 ml vanadium oxide sols, 1.100 g hexadecylamine (HDA) was added. After vigorous stirring for 2 h and aging for 2 days, the yellow suspension was put into a Teflon-lined autoclave with

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a stainless steel shell at 180 °C for 7 days. The obtained black product was washed with distilled water to remove the unreacted amine and decomposition product, finally dried in air at 80 °C in air for 7 h.

X-ray powder diffraction (XRD) pattern was done on a D/MAX-III powder diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å) and graphite monochrometer. The diffraction data were recorded for 2θ between 1.7° and 60°, with a resolution of 0.02°. Scanning electron microscopy (SEM) image was collected on a JSM-5610LV microscope operated at 20 kV. The morphologies and structures of the obtained products were observed through a JEOL JEM-2010F high resolution transmission electron microscope at an accelerating voltage of 200 kV. The Fourier transform infrared (FT-IR) instrument used was a Nicolet 60-SXB spectrometer from 400 to 3600 cm^{-1} with a resolution of 4 cm^{-1}. To determine water and organic content as well as overall stability, thermal gravity analysis was performed on a DTACN8078B2 from 30 to 990 °C at 10 °C/min. XPS spectra were recorded on a KRATOS XSAM800 spectrometer, using Mg Kα radiation (1253.6 eV) as the exciting source in high vacuum.

3. Results and discussion

V_2O_5 sols have been used as vanadium precursor for the synthesis of VO_x-NTs. We prepared V_2O_5 sols via a melt quenching method. Compared to some other synthetic methods of V_2O_5 sols such as protonation of vanadate in aqueous solution, hydrolysis of vanadium alkoxides [10], the melt quenching procedure is more suitable for industrial purpose. Vanadium oxide in sol state enables to intercalate a much wider variety of inorganic and organic species than crystalline V_2O_5. So this synthetic method may provide more opportunities to obtain VO_x-NTs with more outstanding properties. For example, we successfully introduced poly(ethylene oxide) (PEO) into V_2O_5 sols [6], and then via the similar method obtained PEO modified VO_x-NTs, which were found having improved electrochemical performance. This result will be discussed in a forthcoming paper.

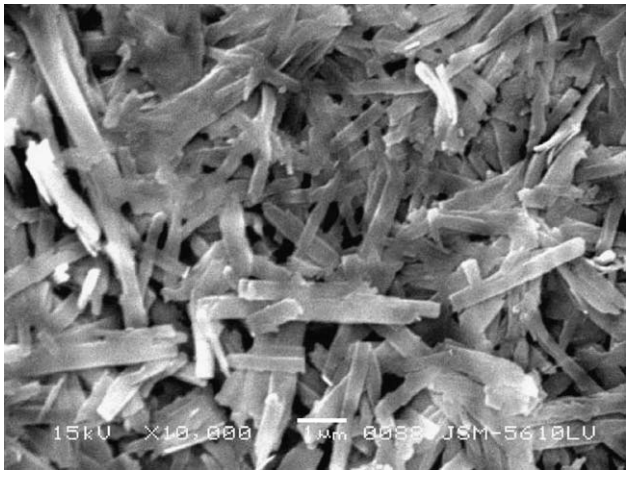

Fig. 1. SEM image of VO_x-NTs.

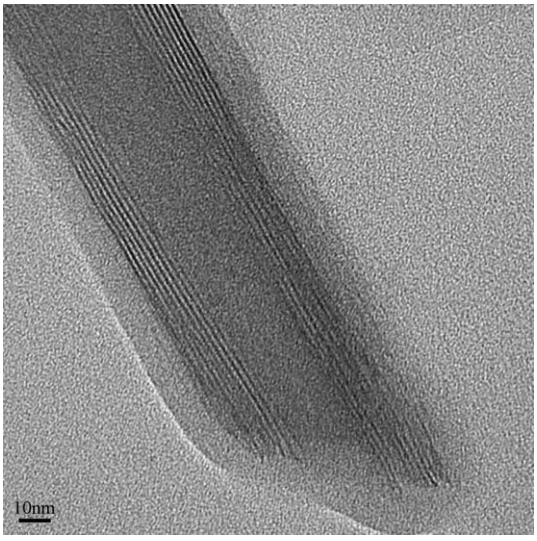

Fig. 2. HRTEM image of VO_x-NTs, showing the opened end.

The samples have a black color, indicating some vanadium in a 4+ oxidation state, because mixed-valent V (IV, V) oxides are generally black (e.g., V_6O_{13}). Microscopic images (Figs. 1–3) show the final product consisting majority of VO_x-NTs. Vanadium oxide nanotubes are frequently grown together in the form of bundles, but individual nanotube can also be observed, which can be confirmed by the HRTEM investigation. The external tube diameters fall between 30 and 100 nm and the internal diameters are between 10 and 30 nm. The lengths of nanotubes range from 1 to 5 μm. The nanotube in Fig. 2 was a typical vanadium oxide nanotube with opened end. As shown in Fig. 3, the walls of VO_x-NTs appear as alternating fringes of dark and bright contrast. The dark fringes represent the vanadium oxide layers while the

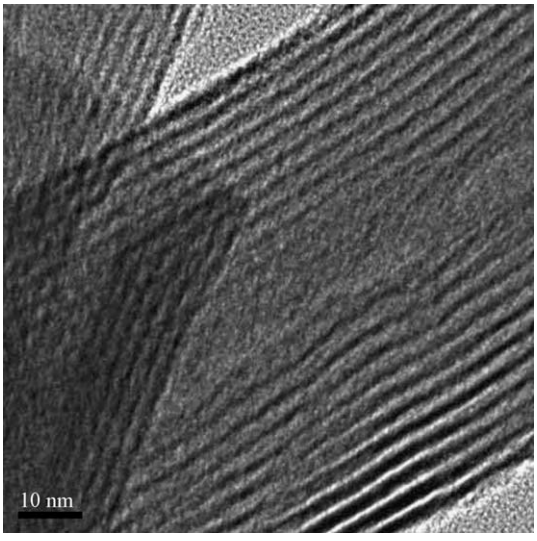

Fig. 3. HRTEM image of VO_x-NTs, indicating the layered structure of VO_x-NTs.

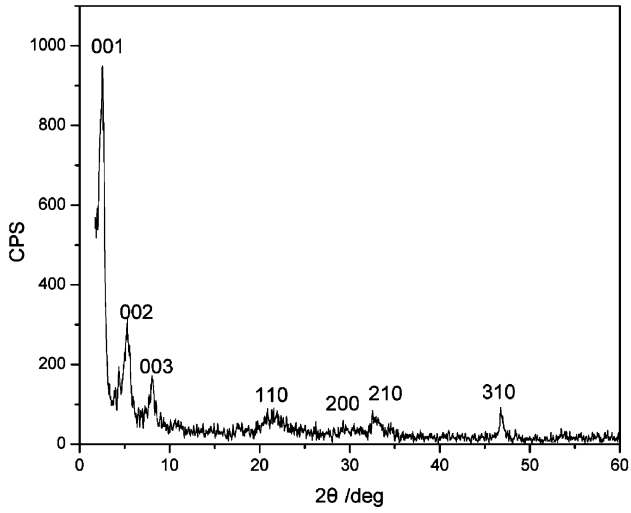

Fig. 4. XRD pattern of VO_x-NTs.

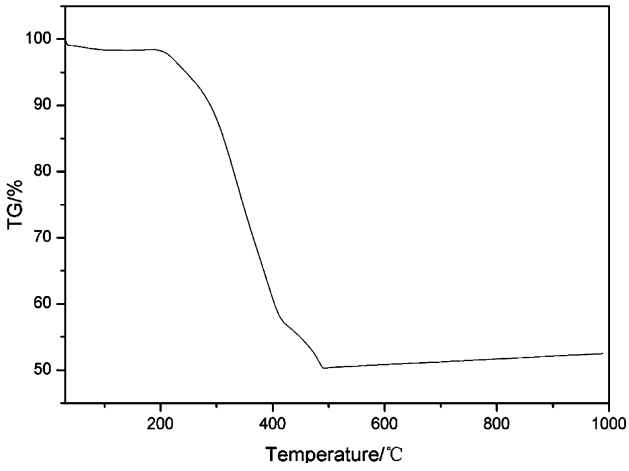

Fig. 6. TGA curve of VO_x-NTs.

bright fringes represent organic molecules that are intercalated between vanadium oxide layers.

From the X-ray diffraction pattern of VO_x-NTs (Fig. 4), two sets of diffraction patterns are actually observed: the (00*l*) series corresponding to a well-ordered layer structure and the (*hk*0) series corresponding to the two dimensional structure of the VO_x layers which form the walls of VO_x-NTs. The peak with the highest intensity at $2\theta = 2.52°$, corresponding to the *d* value of 3.51 nm, reflects the distance between the vanadium oxide layers in the nanotubes. According to literature [11], intercalated long chain alkylamines (number of carbon atoms >12) lay perpendicular to the oxide planes and the basal distance should be similar to the length of amine chain. The length of the carbon chain in hexadecylamine is 3.3 nm, smaller than the layer spacing of VO_x-NTs. This could be attributed to the intercalation of water molecules. Water molecules together with organic template could be intercalated into VO_x layers in aqueous solution, and thereby the distance between VO_x layers is enlarged. Contrasted to the (00*l*) set, the (*hk*0) set can be indexed on the basis of a square lattice with $a = 0.615$ nm.

The FT-IR spectrum of VO_x-NTs (Fig. 5) has strong absorptions at 2956, 2919, 2850 and 1468 cm^{-1}, which could be assigned respectively to the stretching and bending modes of the different C−H vibrations in the hexadecylamine template. Two absorption bands at 3426 and 1637 cm^{-1}, which could be attributed to the stretching and bending modes of O−H vibrations, respectively, confirms the intercalation of water molecules into VO_x layers of VO_x-NTs. Absorption bands between 400 and 1000 cm^{-1} could be indexed to various (group) vibrations of V−O type. There were three major bands at 1001, 574 and 498 cm^{-1} and two week bands at 790 and 721 cm^{-1}. The band at 1001 cm^{-1} could be signed to the V=O vibration in compared with crystalline V_2O_5. The shift of V=O

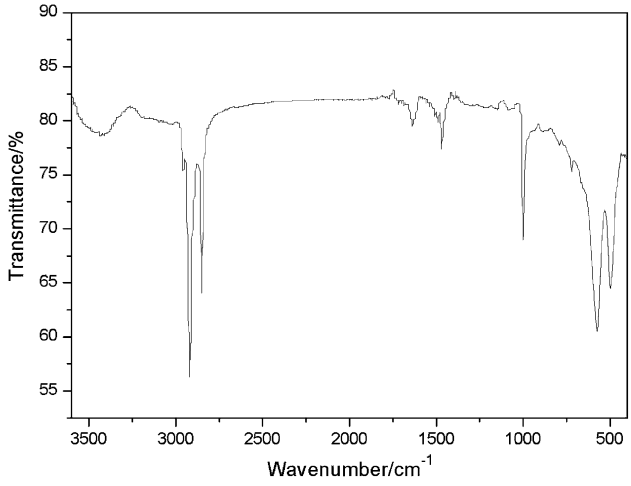

Fig. 5. FT-IR spectrum of VO_x-NTs.

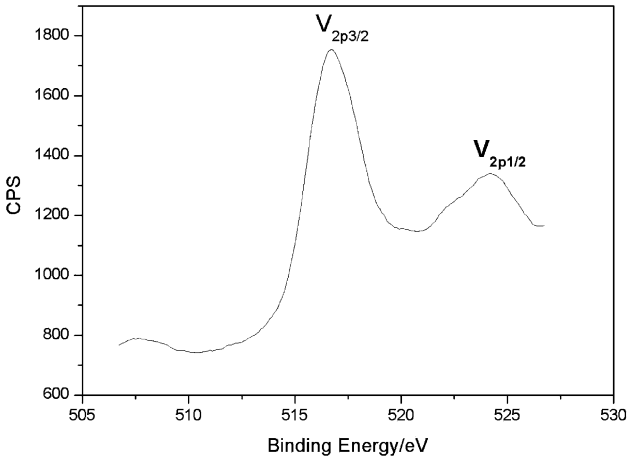

Fig.7. V2p core-level spectrum of VO_x-NTs.

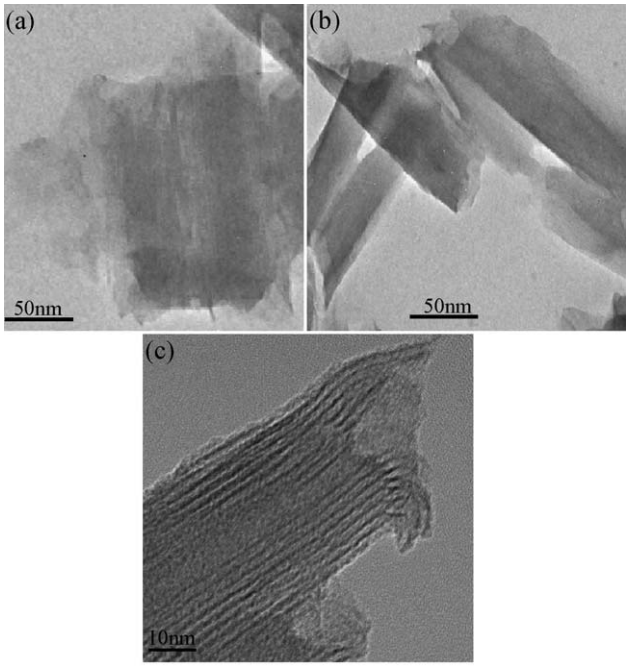

Fig. 8. HRTEM image of (a) lamellar structures, (b) beginning period of the rolling progress and (c) VO_x-NTs with defects.

vibration to lower wavenumber may be associated with increased vanadium content in lower oxidation states; it also may be attributed to some additional bonding either to the oxygen or to the vanadium at the vacant bonding position following the intercalation of the organic component [12]. Other bands are difficult to be indexed. Significant changes for the V—O—V vibrations indicate a considerable rearrangement of the vanadium oxide structure took place when the VO_x-NTs were formed.

The thermal stability of the VO_x-NTs was studied by thermal gravity analysis in air atmosphere. For the template-containing VO_x-NTs, the thermal gravity curve (Fig. 6) shows only one major loss of 47.4 % weight between 180 and 486 °C, this corresponds to the decomposition of residual organic templates and the loss of water between vanadium oxide layers. With the increasing of temperature, there was a gain in mass that be related to the oxidation of vanadium in lower oxidations by oxygen concomitant with the conversion to crystalline vanadium pentoxide.

Studying from the color, the FT-IR spectrum and the TGA curve of VO_x-NTs, it could be concluded that the oxidation states of vanadium in VO_x-NTs could not all be the same as that in crystalline vanadium pentoxide. XPS analysis was carried out in order to obtain some information about the oxidation state of the vanadium element. For the as-synthesized VO_x-NTs, the maximum of the $V2p_{3/2}$ peak is located at 156.70 eV (Fig. 7), which is quite similar to that of V (IV). This confirms that a great proportion of vanadium in lower oxidation states.

Although the formation mechanism of the VO_x-NTs stays an open question, it is obvious that HDA plays a role as structure-directing template in the formation of nanotubes. In the synthesis of the VO_x-NTs from V_2O_5 sols, the amine was directly intercalated into vanadium oxide layers, forming van der Waals intercalation between the organic molecules and the inorganic spices [11] during the aging progress. We propose that HDA molecules co-condensed with anionic inorganic clusters in the sols to form lamellar structures (Fig. 8a). During the hydrothermal treatment, these lamellar sheets started to roll up (Fig. 8b) and finally formed well-developed VO_x-NTs (Fig. 2). Additionally, the nanotubes with some defects can be observed in Fig. 8c, whose formation reason still need to be further investigated.

4. Conclusions

Vanadium oxide nanotubes have been synthesized successfully by using vanadium oxide sols as vanadium precursor via a hydrothermal method. The obtained product has a well-ordered layer structure and tubule-like morphology. A structure rearrangement progress to the vanadium oxide took place during the formation of VO_x-NTs, and a great proportion of vanadium in lower oxidation states was obtained.

Acknowledgements

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