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Cost-saving synthesis of vanadium oxide nanotubes

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Abstract

The synthesis of vanadium oxide nanotubes has been achieved by using V_2O_5 as vanadium oxide precursor. Due to its low cost, high yield and ease of handling, the synthesis starting from V_2O_5 provides an advantageous access to large quantity of the tubular vanadium oxide nanotubes.

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In recent years, nanoscale one-dimensional materials have attracted much attention due to their remarkable physicochemical properties and their great potential for nanodevices [1]. The outstanding structural versatility of vanadium oxides and their derivatives has been receiving significant attention especially with respect to applications in catalysis and as electrochemical devices [2–3]. Recently, Nesper and co-workers synthesized the novel vanadium oxide nanotube in a sol–gel reaction followed by hydrothermal treatment from vanadium alkoxide precursors and primary amines [4–5]. Here, we synthesize the vanadium oxide nanotubes by using a similar method but with V_2O_5 as the precursor.

The main approach to prepare vanadium oxide nanotubes and some other nanotubes was with use of organic molecules as structure-directing agents. The interaction between organic molecules and inorganic precursors could be coordinative interactions, electrostatic interactions, or even hydrogen bonding. This method has opened a way to controlled synthesis for template-based periodic inorganic structures. Although there were some reports on the synthesis of vanadium oxide nanotubes based on this method, the template-directing method have been further developed in our present work. First, the inorganic precursor we employed was V_2O_5 instead of the vanadium triisopropoxide. The bulk of the products in gram quantities could be obtained in high yield without the requirement of delicate equipments. The yield of the vanadium oxide nanotubes was estimated to be $75 \sim 85\%$ from different batches of synthesis, and examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The actual yield varies from batch to batch depending on the conditions selected for the preparation, e.g. concentration, hydrothermal treating time, and type of template. Second, the time of hydrothermal treatment decreased from seven to four days. The hydrothermal treatment was normally at 180 °C for seven days. In our work, the hydrothermal pretreatment at 140 °C for 24 h following three-day hydrothermal treatment at 180 °C was made. Third, organic solvents, i.e. absolute ethanol or hexane, were normally used for dissolving the organic molecules or washing the products. In our experiment, all the reactions of the synthetic process were carried out in aqueous solution. Moreover, the products were normally dried at 80 °C for one day under vacuum. In our work, the products were dried at 70 °C for 6 h at ambient condition. Therefore, our process is a high-yield, low-cost and easy-handling route to the synthesis of vanadium oxide nanotubes.

The X-ray diffraction (XRD) pattern of vanadium oxide nanotubes (Fig. 1) shows the low-angle reflection peaks, which are characteristic for the well-ordered layered

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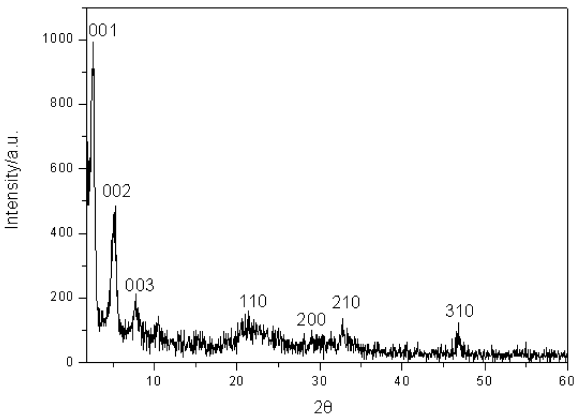

Fig. 1. XRD pattern of vanadium oxide nanotubes.

structures. The peak with the highest intensity at the low diffraction angle reflects the distance between the vanadium oxide layers. The *d* value of the 001 peak is 3.53 nm and bigger than the *d* value (3.20 nm) reported by R. Nesper, [4] which can attribute to the difference between synthesized methods.

The final products consist mainly of vanadium oxide nanotubes (Fig. 2). Vanadium oxide nanotubes are frequently grown together in the form of bundles. The typical nanotube length is about 4 μm while the length could range from 1 to 10 μm. The diameter ranges from 30 to 100 nm. Lengths and diameters of the nanotubes depend on the conditions of the preparation, such as different template molecules, concentration and reaction time [4]. The nanotube walls consist of 3–10 vanadium oxide layers. The prepared nanotube has an open end and inner diameters of about 45 nm and outer diameters of about 80 nm (Fig. 3).

The nanotubes 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}). The ESR spectrum at room temperature for vanadium oxide nanotubes is shown in Fig. 4. It exhibits a single line without apparent hyperfine structure. This is the typical feature

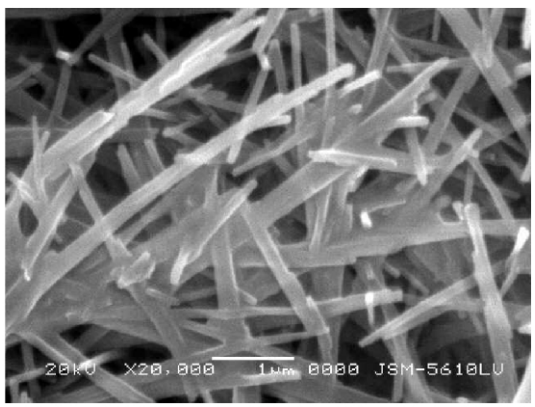

Fig. 2. SEM pattern of vanadium oxide nanotubes.

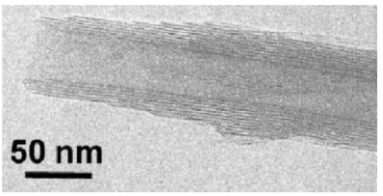

Fig. 3. TEM pattern of vanadium oxide nanotubes.

observed for interacting V^{4+} ions. It indicates that the paramagnetic centers are close enough ($d < 0.7$ nm) to allow spin–spin interactions. The value for g_{iso} calculated from this spectrum is 1.961, which is coincide with the value (1.962) for $[VO(H_2O)_5]^{2+}$ reported elsewhere [6]. Therefore, the black material is paramagnetic and show a semimetallic conductivity, presumably due to mixed valence vanadium centers, which also indicates that the vanadium oxide nanotubes have certain fraction of vanadium (IV) besides vanadium (V). The determination of the fraction of Vanadium (IV) in vanadium oxide nanotubes is underway.

In conclusion, in addition to the well-known synthesis of vanadium oxide nanotubes starting with a vanadium (V) alkoxide, an alternative route has been found, which utilizes V_2O_5 as vanadium sources. In this route, the time of hydrothermal treatment has been decreased and all the reactions of the synthetic process are carried out in the aqueous solution. Therefore, our process provides the possibility of a coat-saving scaling up of the nanotube preparation procedure, due to its low cost, high-yield and ease of handling.

1. Experimental

10 mmol V_2O_5 (99.5%) and 10 mmol 1-hexadecylamine (purchased from ACROS ORGANICS Company) was mixed with 5 ml distilled water. After stirring for 1 h, to the orange solution, 15 ml distilled water was added. The mixture was allowed to hydrolyze under vigorous stirring for 48 h. The resulting suspension was then transferred into

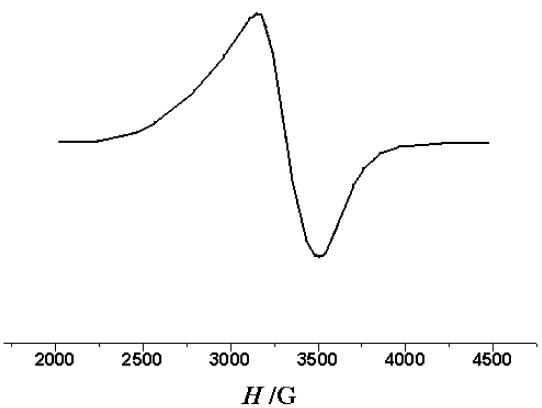

Fig. 4. ESR spectrum of vanadium oxide nanotubes.

a Teflon-lined autoclave with a stainless steel shell. The autoclave was kept at 140 °C for 24 h and then at 180 °C for three days, which was allowed to cool to room temperature naturally. The final black product was washed with distilled water and dried at 70 °C for 6 h.

XRD experiments were done on a HZG4/B-PC X-ray diffractrometer with Co K_α radiation and graphite monochrometer. SEM image was collected by employing a JSM-5610LV scanning electron microscope operated at 20 kV. TEM image was taken in a JEOL JEM-2010F microscope operated at 200 kV. ESR spectroscopy was recorded on JEOL JES-FE1XG ESR SPECTROMETER. Microwave frequency is 9.233 GHz, power is 10 mW.

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