Low-temperature Hydrothermal Synthesis of Orthorhombic Vanadium Pentoxide Nanowires

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Orthorhombic V_2O_5 single-crystalline nanowires with diameters of 30–50 nm, and lengths up to hundreds of micrometers, which was by far the longest 1-D nanostructure of vanadium oxide been fabricated, were synthesized on a large scale through a template-free mild and direct hydrothermal reaction between $VOSO_4{\cdot}xH_2O$ and $KMnO_4$. The ability of the oxidizing agent was testified to be the decisive factor in the successful fabrication of as-obtained ultralong orthorhombic V_2O_5 single-crystalline nanowires, which might be a superior cathode material for the lithium ion batteries.

Vanadium oxide and derived compounds are receiving significant attention recently because of their structural versatility combined with chemical and physical properties.[1] A variety of binary vanadium oxides with the general formula VO_{2+x} ($0 \leq x \leq 0.33$), such as V_2O_5, V_2O_3, V_6O_{13}, VO_2 etc., have been synthesized because of their outstanding properties and potential applications as catalysts, chemistry sensors, high-energy density lithium ion batteries, and electrochemical and optical devices.[2–5]

In recent years, great attention has been focused on synthesis and applications of nanostructured materials, and one of the most dynamic research areas is on the synthesis of one-dimensional (1-D) nanostructures, such as nanowires, nanorods, nanobelts, and nanotubes. In the past decades, the fabrication of vanadium oxide 1-D nanostructures has been researched intensively. A variety of methods, such as thermal evaporation, surfactant-assisted solution, and hydrothermal/solvothermal synthesis, have been developed to prepare vanadium oxide 1-D nanostructures.[6–9] For instance, nanowires of V_2O_5 have been synthesized by polycondensation of vanadic acid, which involves ion exchange between Na^+ from sodium metavanadate solutions and H^+ ions in a resin.[10] V_2O_5 nanorods and nanowires have been fabricated using a reverse-micelle technique by Pinna et al.[11] Nesper and co-workers have developed a novel soft-chemistry synthetic method of a fundamentally new type of vanadium oxide nanotubes (VO_x-NTs) involving an amine with long alkyl chains as a molecular, structure-directing template.[12,13] Cao et al. have made lots of efforts on the synthesis and electrochemical study of V_2O_5 nanorod/nanotube arrays.[14] Li et al. have fabricated various vanadium oxide 1-D nanostructures and studied their application as ethanol sensor materials and magnetic properties.[15,16] However, all these synthetic methods of vanadium oxide 1-D nanostructures are either based on the transformation of V^{5+}-contained precursors during reaction or through a complex and lengthy route. To the best of our knowledge, the simple direct hydrothermal synthesis of V_2O_5 1-D nanostructures from reagents with the oxidation state of vanadium at +4 has rarely been reported before.

Herein, we report the fabrication of orthorhombic V_2O_5 nanowires through a simple mild template-free hydrothermal synthetic method using $VOSO_4{\cdot}xH_2O$ as precursors. The length of as-obtained orthorhombic V_2O_5 nanowires reached up to hundreds of micrometers, which was by far the longest 1-D nanostructure of vanadium oxide that had been fabricated. The ability of the oxidizing agent was found to be the decisive factor in the successful fabrication of the as-obtained ultralong orthorhombic V_2O_5 nanowires.

All the reagents were of analytical grade and were used without further purification. In a typical synthetic procedure of orthorhombic V_2O_5 nanowires, 10 mmol of $VOSO_4{\cdot}xH_2O$ and 5 mmol of $KMnO_4$ were dissolved in 40-mL of distilled water and stirred magnetically for 30 min to get good homogeneity. Nitric acid was added dropwise under stirring until the final pH of the solution was about 1–2. The resulting clear solution was then transferred into a 50-mL Teflon-lined stainless steel autoclave. The autoclave was maintained at 160 °C for 24 h. After cooling to room temperature on standing, the yellow precipitates were filtered off, washed with distilled water and anhydrous alcohol for several times, and dried in vacuum at 80 °C for 12 h.

XRD patterns of the final products were recorded by using a Philiphs X'Pert Super diffractometer with graphite monochromatized Cu Kα radiation ($\lambda = 1.54178$ Å) in the 2θ range of 5–80°. The morphology of the products was examined by a field emission scanning electron microscope (JEOL JSM-6300F, 15 kV). The TEM images were obbained with a Hitachi 800 transmission electron microscope with the accelerating voltage of 200 kV. The samples used for characterization were dispersed in absolute ethanol and were ultrasonicated before TEM and FESEM tests.

The XRD pattern of the typical product was given in Figure 1. All the diffraction peaks could be indexed as the orthorhombic phase of V_2O_5 in agreement with literature values (JCPDS card 85-0601) with calculated lattice constants $a = 3.563$, $b = 11.516$, $c = 4.374$ Å. The particle size of as-prepared V_2O_5 samples was estimated to be around 40 nm by Debye–Scherre formula. No impurity phases such as $Mn_xV_2O_5$ and $V_2O_5{\cdot}xH_2O$ are detected from the XRD pattern, indicating that orthorhombic V_2O_5 nanowires with high purity were obtained under current synthetic conditions. The composition of the typical product

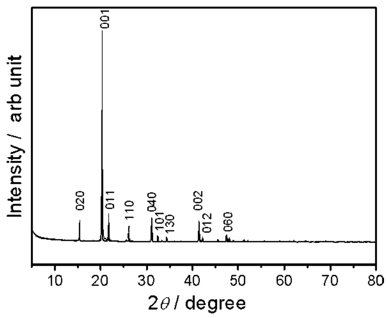

Figure 1. XRD pattern of the typical product.

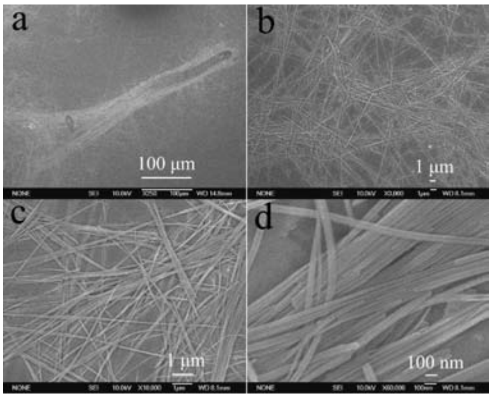

Figure 2. FESEM images of the typical product.

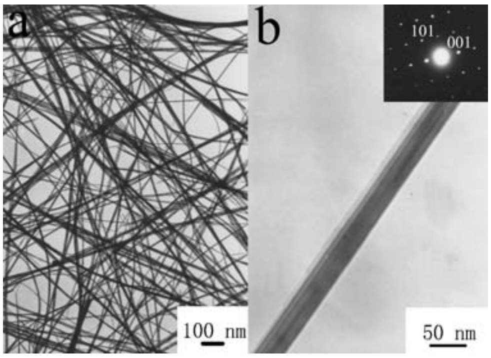

Figure 3. TEM images of the typical product.

was further determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The Mn/V atom ratio of the final product was only around 0.005/1, indicating that there was no manganese left in the crystal structure of the final product and that the product is a pure phase of orthorhombic V_2O_5.

The FE-SEM images of the typical product were shown in Figure 2. The microstructures of the product were long uniform nanowires, and the proportion of the nanowires in the sample was almost 100% (Figure 2a). The length of as-obtained orthorhombic V_2O_5 nanowires reached hundreds of micrometers as calculated from the panoramic image shown in Figure 2a, which was by far the longest length reported for the fabrication of 1-D vanadium oxide nanostructures, indicating the superiority of our synthetic method. The diameters of the nanowires ranged from 30 to 50 nm (Figures 2b–2d), and the as-obtained nanowires had a strong tendency to self-assemble into nanowire arrays. Figure 3 showed the TEM images of the typical product, indicating that nanowire arrays of orthorhombic V_2O_5 with diameters around 40 nm and length up to hundreds of micrometers were obtained by our synthetic method, which agreed well with the result of the XRD and SEM test. The inset SAED image in Figure 3b indicated that the as-obtained V_2O_5 nanowires are well single crystallined with the preferential growth along the [001] direction.

The oxidizing agent played an important role for the successful synthesis of orthorhombic V_2O_5 nanowires. Control experiments were made using other kinds of oxidizing agent such as $KClO_3$ and $K_2S_2O_8$ while keeping all other synthetic parameters the same. Under these conditions, only layered phase $V_2O_5 \cdot xH_2O$ was obtained as the final products, as shown by the XRD patterns in Figure 4. It is well known that V_2O_5 can be regarded as a layered structure in which VO_5 square pyramids are connected by sharing corners and edges.[17] The interactions between these layers are rather weak, as indicated by the exceptionally long V–O distance of 0.279 nm.[18] In particular, this structure permits H_2O molecules to be embedded between the layers without a far-reaching restructuring, which leads to the formation of the $V_2O_5 \cdot xH_2O$ phase. From the results of above experiments, it is believed that only $KMnO_4$ can be the suitable oxidizing agent that can supply the necessary driving force for the removal of H_2O molecules from the interplanar regions of the layered structures of $V_2O_5 \cdot xH_2O$, thus leading to the formation of orthorhombic V_2O_5 nanowires. The exact functional mechanism of $KMnO_4$ in our synthetic method is still under research in our laboratory and will be reported later.

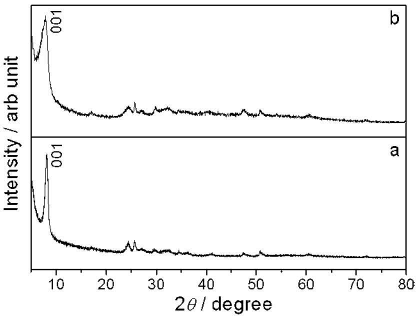

Figure 4. XRD pattern of the products using (a) $KClO_3$; (b) $K_2S_2O_8$ as oxidizing agents.

In conclusion, we have developed a novel facile hydrothermal method to synthesize uniform orthorhombic V_2O_5 nanowires with the lengths up to hundreds of micrometers, which was by far the longest reported 1-D nanostructure fabricated for vanadium oxides. The synthetic method was base on the mild and direct reaction between $VOSO_4 \cdot xH_2O$ and $KMnO_4$ and needed no templates or complex treatments, which was very economical and environmentally friendly. These ultralong V_2O_5 nanowires, which own large specific areas and short diffusion length, may be a superior cathode material for application in the lithium ion batteries. Further work is under way in our laboratory to study the electrochemical properties of these ultralong orthorhombic V_2O_5 nanowires, which will be reported later.

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Published on the web (Advance View) January 27, 2007; doi:10.1246/cl.2007.310