Sol-Gel/Hydrothermal Method for the Synthesis of Ultralong (NH₄)₂V₆O₁₆·1.5H₂O Nanobelts

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Keywords: (NH₄)₂V₆O₁₆·1.5H₂O, Nanobelts, Sol-gel/hydrothermal method

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Abstract

Ultralong (NH₄)₂V₆O₁₆·1.5H₂O nanobelts have been synthesized by sol-gel method coupled with hydrothermal method using V₂O₅, H₂O₂ and (NH₄)₂SO₄ as raw materials. The synthesis conditions including temperature, reaction time and amount of ammonium sulfate have been optimized. The chemical phase, morphology and microstructure of the as-prepared products were characterized by XRD, FT-IR, FE-SEM/EDX and TEM, respectively. Typical (NH₄)₂V₆O₁₆·1.5H₂O nanobelts as-prepared are several hundreds of micrometers in length, 50–100nm in thickness and 200nm–1μm in width. Oriented Attachment mechanism was proved to be responsible for the formation of (NH₄)₂V₆O₁₆·1.5H₂O ultralong nanobelts. The proposed approach is a facile and cost-saving method, which particularly fits for synthesis of (NH₄)₂V₆O₁₆·1.5H₂O nanobelts on large scale.

Introduction

Vanadium oxide and their derivatives have attracted considerable attention due to their outstanding structural flexibility, low cost, novel electric and optical properties[1], which brings them wide applications in areas such as catalysts[2] and lithium batteries[3]. Among the vanadium-based materials, NH₄V₃O₈ has gained great attention, mainly because of its attractive electrochemical characteristics including high specific energy, good rate capacity, low cost and long cycle life, which is a promising electrode material for energy storage[4]. NH₄V₃O₈ consists of VO₅ square pyramids and VO₆ octahedrons with hydrated NH₄⁺ cations located between the vanadium-oxide layers[5], which is similar to the layered structure of Li₁+xV₃O₈ in hamburger form[5,6].

In recent years, there are increased interests in synthesizing one dimensional (1D) nanostructures of vanadium-based materials. As a representative of 1D nanostructure, nanobelts with rectangular cross-section, anisotropic shape and well-defined surfaces are believed to exhibit special properties[7] such as observe unique piezoelectricity[8] and provide efficient 1D electric transportation[9,10]. Therefore, NH₄V₂O₄ nanobelts are expected to exhibit good electrochemical performance and have promising applications in energy storage. Belt-like NH₄V₂O₄·0.5H₂O was prepared by the classical acidification of NH₄VO₃ solution with hydrochloric or sulfuric acid, adjusting pH to 1.5, and subsequent hydrothermal treatment[11]. Since V₂O₅ is quite abundant in China, it is cost-effective to synthesize NH₄V₂O₄ nanobelts with V₂O₅ as precursor. However, to our best knowledge, there is no report about synthesis of ultralong NH₄V₂O₄ nanobelts with V₂O₅ as precursor. The proposed method in combination of sol-gel and hydrothermal processes is facile, efficient, cost-saving and surfactant free. More importantly the products have good and uniform morphology in high purity with high yield. It’s believed that this approach could be extended to preparation of other nanomaterials.
Experiments

Synthesis route
All reagents used in the experiments are of analytical grade and used without any further purification. 4mmol \( V_2O_5 \) powder was dissolved in 32.64mL 10% \( H_2O_2 \) with vigorously magnetic stirring at 25°C for 1h. The obtained reddish orange solution was transferred to a petri dish and aged at room temperature for certain time. During aging, black precipitate formed progressively on the bottom and side walls of the petri dish. After centrifugation, 6mL of the supernatant liquor was then added into a 50mL Teflon container, followed by addition of 34mL de-ionized water and 3mmol \((NH_4)_3SO_4\) with stirring for 10min. Then the container was sealed in an autoclave and placed in an electrical oven at 180°C for 24h, which was then air cooled to room temperature. It was found that brown spongy precipitates existed in the solution. The precipitates were collected by centrifugation, followed by washed with distilled water and anhydrous alcohol for 3 times, respectively. The products were finally dried in vacuum at 80°C for 12h.

Characterization
The phase and chemical composition of the as-prepared products were characterized by X-ray powder diffraction (XRD, Rigaku D/max 2500PC, Cu Kα) and Fourier transform infrared spectroscopy (FT-IR, Nicolet 5DXC). The morphology and microstructure of the products were observed by scanning electron microscopy (SEM, FEI NOVA400 or ZEISS AURIGA SEM) and transmission electron microscopy (TEM, LIBRA 200 FE). Samples were coated with gold spray prior to SEM observation.

Results and Discussion
Chemical components of the products are characterized by XRD. Figure 1 shows the typical XRD patterns of the products which were synthesized at different experimental conditions. As shown in Figure 1a, when the synthesis was conducted at 180°C for 24h, all the diffraction peaks of the XRD pattern can be perfectly indexed to a monoclinic phase of \((NH_4)_2V_6O_{16}\cdot1.5H_2O\), indicating the high purity of the products. The calculated lattice constants \( a=12.3939\text{Å} \), \( b=3.587\text{Å} \) and \( c=16.3883\text{Å} \) are also consistent with the standard values (JCPDS card 51-0376, \( a=12.343\text{Å} \), \( b=3.5922\text{Å} \), \( c=16.41\text{Å} \)). When hydrothermal reaction time was decreased to 3h at 180°C, the diffraction peaks are readily indexed to \((NH_4)_2V_6O_{16}\cdot1.5H_2O\) with unknown impurity peaks (Figure 1b), but the crystallinity is obviously lower than that in Figure 1a. After decreasing hydrothermal temperature to 140°C for 24 h, not only \((NH_4)_2V_6O_{16}\cdot1.5H_2O\) phase but also \(NH_4V_3O_8\) (JCPDS card 51-0376) phase are present and the crystallinity becomes much lower, as shown in Figure 1c.