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Short communication

Large scale hydrothermal synthesis and electrochemistry of ammonium vanadium bronze nanobelts

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Abstract

Single crystalline ammonium vanadium oxide bronze $NH_4V_4O_{10}$ nanobelts were synthesized by the hydrothermal treatment of $H_2C_2O_4 \cdot 2H_2O$ and NH_4VO_3 at 140 °C for 48 h. The $NH_4V_4O_{10}$ nanobelts were characterized using a combination of techniques including X-ray diffraction, transmission electron microscopy, selected area electronic diffraction, scanning electron microscopy and X-ray photoelectron spectroscopy techniques. The as-obtained nanobelts are several microns long, typically 30–40 nm wide, and 10–20 nm thick. The electrochemical properties of the nanobelts were tested in cells with metallic lithium as the negative electrode, the first discharge capacity of 171.8 mAh g^{-1} was achieved.

Keywords: Vanadium; Li-ion battery; Hydrothermal synthesis; Nanobelts

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1. Introduction

Vanadium oxides are among the best positive electrode materials for rechargeable lithium-ion batteries, due to their high intercalation voltage, large specific capacity and good cyclability [1]. The pure vanadium oxides that have made the largest advances are VO_2(B), V_6O_{13} and V_2O_5 [2,3]. 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 [4]. The interactions between these layers are rather weak, as indicated by the exceptionally long V–O distance of 0.279 nm [5]. This layer structural particularity permits the synthesis of the bronze phase $M_xV_2O_5$ (M: Li, Na, K, Cs, Ca, Ag, etc.) with various metal cation embedded between the layers without a far-reaching restructuring [6–9].

The discovery of carbon nanotubes in 1991 [10] has greatly initiated intense experimental and theoretical interest in one-dimensional (1D) nanostructured materials (nanotubes, nanobelts, nanowires and nanorods), due to their distinctive geometries, novel physical and chemical properties, and potential application in numerous areas such as nanoscale electronics and photonics [11]. So far, although many methods have been employed to prepared 1D nanomaterials such as electrochemistry [12], template-assisted growth [13], microemulsion-mediated systems [14], electric-arc [15], laser-assisted catalysis growth [16], solution [17], chemical vapor deposition [18] and solvothermal synthesis [19], they are usually related to high temperature, required pressure, complex equipment and special conditions. Moreover, these methods have mainly been focused on mono- and binary component structure, such as carbon [10], metals [20], oxides [21] and II–VI [22], III–V [23] compounds, and the synthesis of multicomponent 1D nanostructures is still a great challenge to material scientists [24]. Recently, much effort has been devoted to developing new approaches to fabricate nanobelt materials because of the promising building-block function for nanoelectronics and optoelectronics [21,25]. Herein, we report a facile method for the large scale synthesis of ammonium vanadium bronze $NH_4V_4O_{10}$ nanobelts, which was based on hydrothermal strategy with-

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out sophisticated techniques and catalysts. Although many methods have been developed to fabricate vanadium oxides electrode materials, to the best of our knowledge, it is the first time to report the synthesis of ammonium vanadium bronze nanomaterials.

2. Experimental

2.1. Hydrothermal synthesis and characterization of ammonium vanadium bronze nanobelts

The $NH_4V_4O_{10}$ nanobelts were synthesized under hydrothermal conditions. All of the chemical reagents used in this experiment were analytical grade without further purification. In a typical procedure, NH_4VO_3 (1.1699 g) was dissolved in 80 °C deionized water to form a light yellow solution. $H_2C_2O_4{\cdot}2H_2O$ (1.8912 g) solid powders were directly added to the solution under continuous stirring until the solid was completely dissolved. A clear black-green solution was formed and the resultant system was then transferred into a Teflon-lined autoclave with a stainless steel shell. The autoclave was kept at 140 °C for 48 h and then allowed to cool down to room temperature. The black-green precipitate was collected and washed several times with distilled water. The final product was dried at 110 °C for 5 h in the argon atmosphere.

X-ray diffraction (XRD) pattern was obtained on a Rigaku (Japan) D/max-2400 X-ray diffractormeter with Cu Kα radiation ($\lambda = 1.54178$ Å), employing a scanning rate of 0.02 ° S^{-1} in the 2θ range of 5–80°. TEM images and SAED patterns were taken with Hitachi H-800 transmission electron microscopy, using an accelerating voltage of 100 kV. X-ray photoelectron spectroscopy (XPS) data were obtained by a V.G.ESCALab. 2201-XL photoelectron spectrometer with an Al Kα source, a concentric hemispherical analyzer operating in fixed analyzer transmission mode and a multichannel detector. The spectra were acquired with a 30 eV pass energy and a binding energy was calibrated with reference to the C 1s level of carbon. Scanning electron microscopic (SEM) images were recorded with JSM-5600 LV microscope. HRTEM images were obtained on a JEOL-2010 electron microscope, using an accelerating voltage of 200 kV.

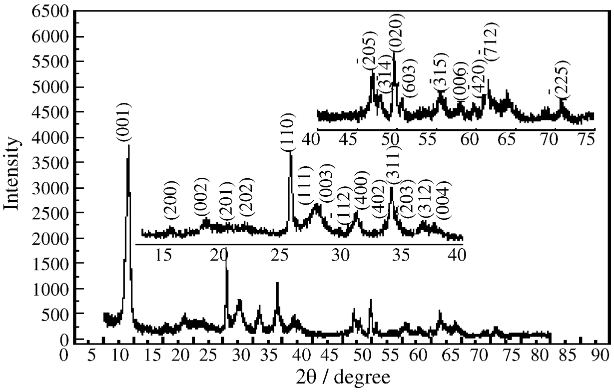


Fig. 1. XRD pattern of the as-obtained nanobelts.

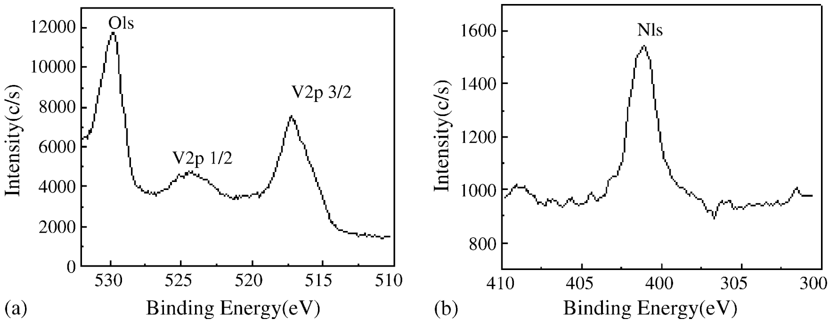
2.2. Primary test of electrochemistry

The electrochemical properties of the nanobelt cathodes were tested in cells with metallic lithium as the negative electrode. The electrolyte was 1 M $LiPF_6$ in the ethylene carbonate (EC) and dimethyl carbonate (DMC) (50:50). The positive electrode composites were made by mixing the active material, acetylene black and poly-vinylidene fluoride (PVDF) (75:15:10). All cells were assembled in an argon-filled glove box. Charge/discharge cycles were performed using a LAND BT-10 cycle life tester (China) with current density of 12.5 mA g^{-1} in the voltage range between 2.0 and 3.4 V versus Li/Li^+. All the tests were performed at room temperature.

3. Results and discussion

3.1. XRD and XPS results

Fig. 1 shows an X-ray diffraction (XRD) pattern of the $NH_4V_4O_{10}$ nanobelts. All of the peaks can be perfectly indexed to monoclinic crystalline phase. The lattice constants can be calculated as follows: $a = 11.66$ Å, $b = 3.61$ Å,



(a) (b)

Fig. 2. (a) XPS spectra of V 2p and O 1s of the sample of $NH_4V_4O_{10}$ nanobelts; (b) XPS spectra of N 1s of the sample of $NH_4V_4O_{10}$ nanobelts.