

Short communication

Large scale hydrothermal synthesis and electrochemistry of ammonium vanadium bronze nanobelts

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Abstract

Single crystalline ammonium vanadium oxide bronze $\text{NH}_4\text{V}_4\text{O}_{10}$ nanobelts were synthesized by the hydrothermal treatment of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and NH_4VO_3 at 140°C for 48 h. The $\text{NH}_4\text{V}_4\text{O}_{10}$ 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.

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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 $\text{VO}_2(\text{B})$, 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 $\text{M}_x\text{V}_2\text{O}_5$ (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 $\text{NH}_4\text{V}_4\text{O}_{10}$ 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 $\text{NH}_4\text{V}_4\text{O}_{10}$ 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. $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (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 diffractometer with Cu $\text{K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$), employing a scanning rate of $0.02^\circ \text{ S}^{-1}$ 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 $\text{K}\alpha$ source, a concentric hemispherical analyzer operating in fixed analyzer transmission mode and a multi-channel 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-

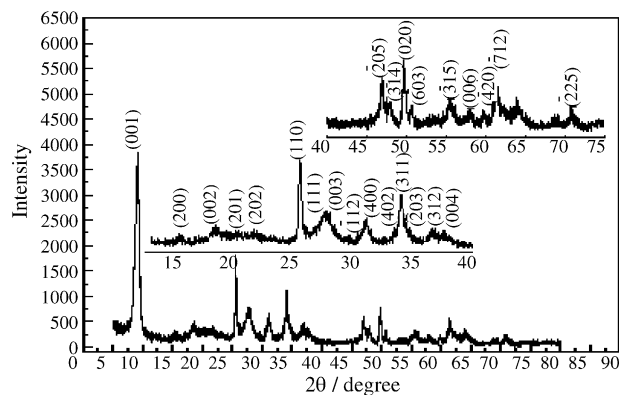


Fig. 1. XRD pattern of the as-obtained nanobelts.

2010 electron microscope, using an accelerating voltage of 200 kV.

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 $\text{NH}_4\text{V}_4\text{O}_{10}$ nanobelts. All of the peaks can be perfectly indexed to monoclinic crystalline phase. The lattice constants can be calculated as follows: $a = 11.66 \text{ \AA}$, $b = 3.61 \text{ \AA}$,

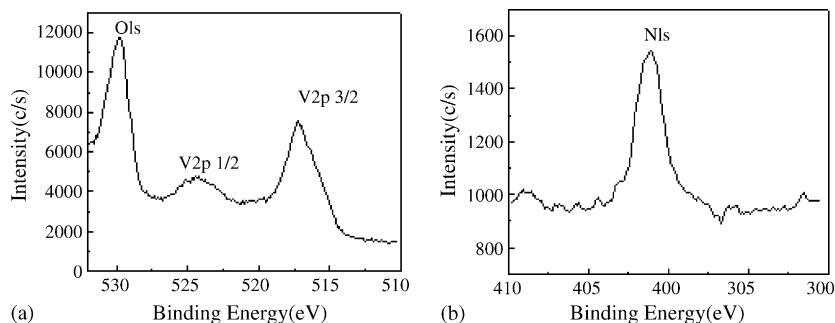


Fig. 2. (a) XPS spectra of V 2p and O 1s of the sample of $\text{NH}_4\text{V}_4\text{O}_{10}$ nanobelts; (b) XPS spectra of N 1s of the sample of $\text{NH}_4\text{V}_4\text{O}_{10}$ nanobelts.

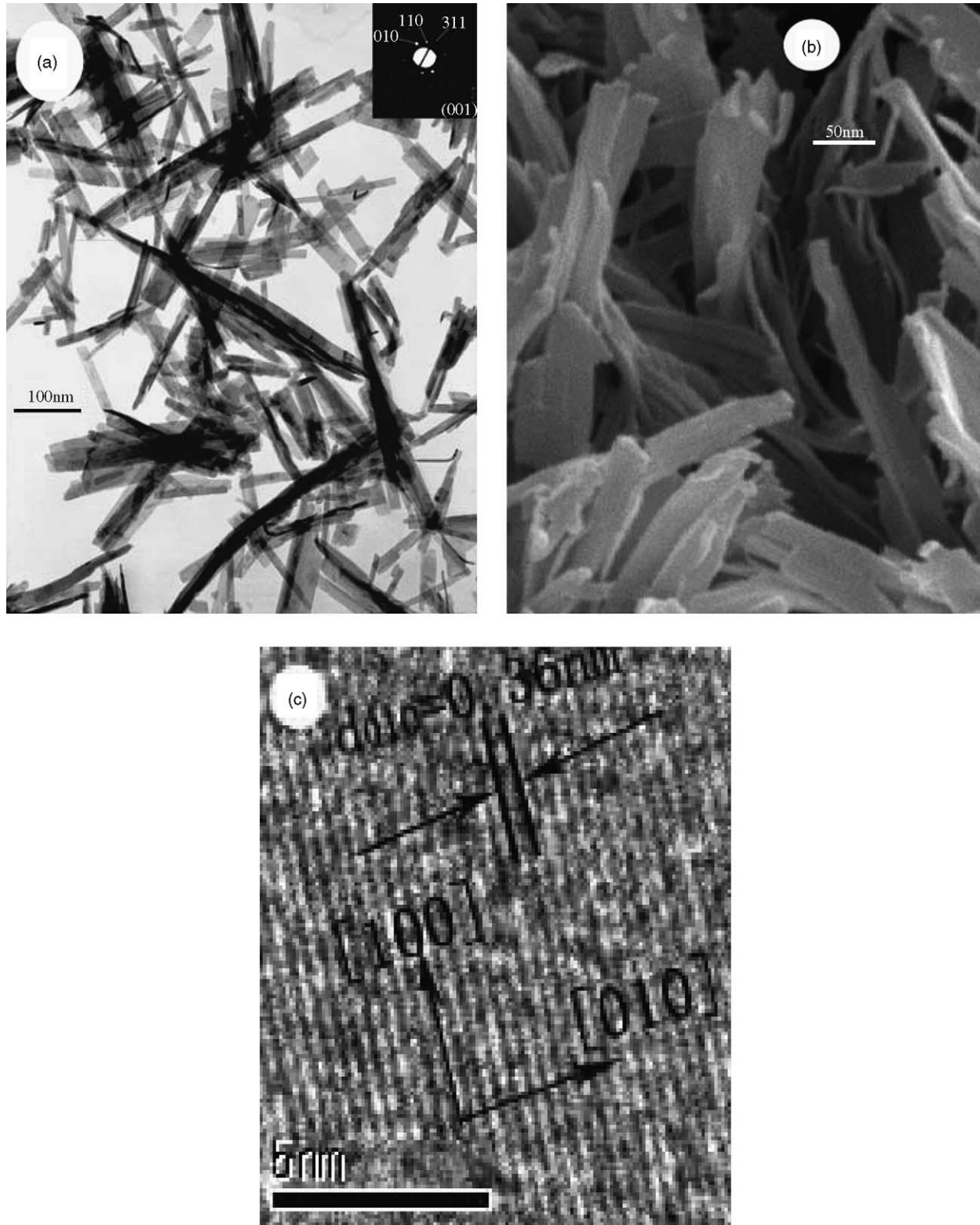


Fig. 3. (a) TEM images of the $\text{NH}_4\text{V}_4\text{O}_{10}$ nanobelts; (b) SEM images of the $\text{NH}_4\text{V}_4\text{O}_{10}$ nanobelts; (c) HRTEM images of the individual $\text{NH}_4\text{V}_4\text{O}_{10}$ nanobelts.

$c = 9.71 \text{ \AA}$, $\beta = 100.6^\circ$, which are in good agreement with the literature values (JCPDS, No. 31-0075). Compared with the bulk $\text{NH}_4\text{N}_4\text{O}_{10}$, the strongest peak (001) is given in XRD pattern of the as-obtained sample, and the other peaks are rela-

tively weak. It indicates the nanobelts may grow along [001] direction. Fig. 2 shows X-ray photoelectron spectroscopy (XPS), which indicates that N, O and V are present without any impurity elements in the as-obtained samples. There

is no free electron outside of the nuclear of H^+ , so we did not observe the presence of H element. 401.3, 529.7 eV are characteristic binding energy of N and O. It is obvious that the binding energy of V 2p for the as-synthesized sample is lower than that for V^{5+} in the starting materials. And the binding energy of V 2p_{3/2} for the product (517.2 eV) is between those of NH_4VO_3 (517.6 eV) and VO_2 (516.3 eV) [26]. The valence of V in the as-prepared sample can be therefore speculated as mixed-valence. Additionally, the nanobelts consist of N, V, and O in a ratio of 1:3.99:10.85 according to the calculus area, which is in agreement with our speculation.

3.2. TEM and SEM analysis

The morphology and size of the resulting sample are shown in Fig. 3. As estimated from TEM and SEM images, the $NH_4V_4O_{10}$ nanobelts are several microns long, typically 30–40 nm wide, and 10–20 nm thick. Especially, the yield of the nanobelts is statistically counted to be higher than 98%. The selected area electron diffraction (SAED) pattern (inset in Fig. 3a) taken from a single nanobelt is single crystal with a preferential growth direction along the [0 0 1], which is consistent with the conclusion from XRD pattern. A high-resolution (HRTEM) image provides an insight into the prepared structure. As shown in Fig. 3c, the interplanar distance can be calculated to be about 0.36 nm, corresponding to the spacing of the [0 1 0] plane of the monoclinic $NH_4V_4O_{10}$ species, which further confirms the nanobelts grow along the [0 0 1] direction.

3.3. Mechanism of synthesis

We found that the formation of $NH_4V_4O_{10}$ nanobelts strongly depends on the chemical reaction conditions, especially the temperature and the molar ratio of the raw materials ($H_2C_2O_4 \cdot 2H_2O : NH_4VO_3$). When the reaction temperature is higher than 150 °C or the molar ratio is more than 1.5:1, other vanadium oxides are found in the product. The optimum condition for preparing $NH_4V_4O_{10}$ nanobelts should be at 140 °C with the molar ratio of the starting material of 1.5:1. Also, we have prepared VO_2 nanobelts using $H_2C_2O_4 \cdot 2H_2O$ as the reducing and morphology control reagent. So far, there are still no general mechanism for the formation of the nanobelts in hydrothermal system, however, we suggest that the bidentate coordination of $H_2C_2O_4 \cdot 2H_2O$ may play a crucial role in the control of one-dimensional belt-like morphology.

3.4. Initial electrochemistry results

The electrochemical properties of the as-obtained nanobelts as the cathode of the lithium-ion battery were investigated using a two-electrode cell in the voltage range 2.0–3.4 V versus Li^+/Li at constant current density of 12.5 mA g^{-1} . Fig. 4 shows the variations of voltage vs. charge/discharge capacity curves at 1st–17th cycle for

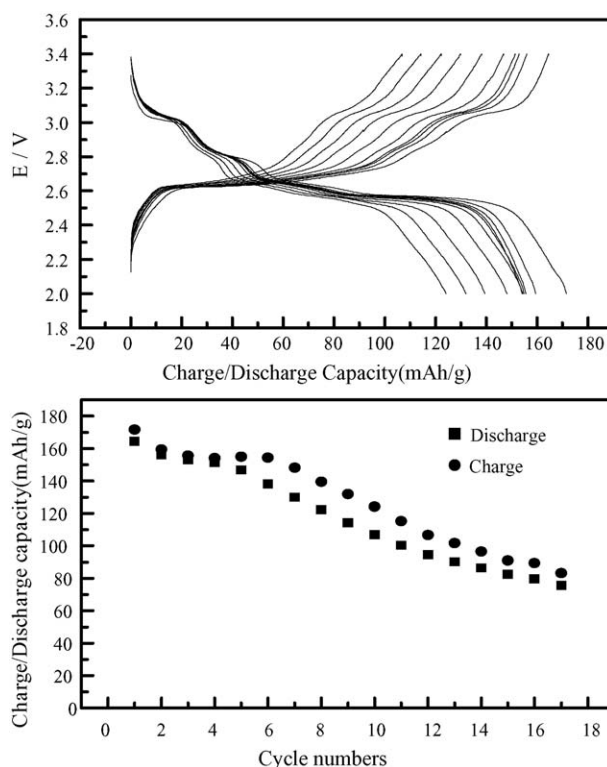


Fig. 4. Several typical charge/discharge curves (top) and cycling performance (bottom) of cells using nanobelts as cathode and lithium metal as anode in the voltage range of 2.0–3.4 V at a current density of 12.5 mA g^{-1} .

$NH_4V_4O_{10}$ nanobelts, in which the first discharge capacity of 171.8 mA $h g^{-1}$ was achieved. It also can be seen that there are three distinctive voltage plateaus in the discharge curves and two voltage plateaus in the charge curves. The detail discussion of discharge capacity attenuation and mechanism of charge/discharge will be published elsewhere.

4. Conclusions

In conclusion, we have developed a new and facile hydrothermal route to synthesize multicomponent vanadium oxide bronze $NH_4V_4O_{10}$ single crystalline nanobelts on a large scale. It has apparent advantages over the traditional approaches for the large-scale preparation of 1D multicomponent nanomaterials. And the belt-like $NH_4V_4O_{10}$ with a high surface area may be applied in rechargeable lithium-ion batteries. This synthetic strategy may be potentially extendable to prepare other multicomponent 1D nanostructured materials such as alkali-metal, alkali-earth metal and transition metal vanadium oxide bronzes.

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