

A Simple and Direct Method for Synthesis of Vanadium Oxide Ribbon-Like Nanobelts

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A low-cost, a high-yielding of vanadium oxide nanobelts **2** was simply synthesized by hydrothermal treatment of our $(\text{NH}_4)_2\text{V}_3\text{O}_8$, **1**, with deionized water at 200 °C for 3 days. The SEM observations show that ribbon-like nanobelts are about 150-300 nm wide and thousands of nanometers long. The XRD pattern reveals a set of the paper form reflections, characteristic of (00l) reflections for layered phases. Based on FT-IR results and the EDX spectra, the chemical formula of the as-obtained ribbon-like nanobelts could be described as $\text{V}_x\text{O}_y \cdot n\text{H}_2\text{O}$ with a mixed valence V(V) and V(IV).

Keywords: Vanadium oxide ribbon-like nanobelts, Hydrothermal treatment, Mixed valences, Layered structure, A paper form

INTRODUCTION

In recent years, there has been and increased interest in synthesizing quasi one-dimensional (1D) nanostructures of vanadium oxides and their derivative compounds [1-9]. This is due to their potential applications such as catalysts [10], cathode materials for lithium batteries [11], high-energy density lithium batteries [12], chemical sensors [13], electric field-effect transistors [14], and electrochemical and optical devices [15-16].

Among one dimensional structures, nanobelts and nanoribbons 1D nanostructures are greatly expected to represent important building blocks for nanodevices [1,7-8,17-18]. The typical ribbon-like nanobelts are chemically pure and structurally uniform of a rectangular cross-section. With well intrinsic geometry and perfect crystal quality, vanadium oxide nanobelts and nanoribbons might be an ideal system for a

systematic experimental investigation of confined transport phenomena and show promising application in building nanodevices [17].

A great attention has recently been focused on vanadium oxides containing V(V) and V(IV) because of their layered structure and redox activity. The synthesis and characterization of vanadium oxide nanostructures have been developed extensively. Hydrothermal treatment of ammonium metavanadate with water gives self-assembling $(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5$ nanowires [3]. Some self-assembled nanobelts are observed with a thickness of 18 nm and width of 100-200 nm. Electrical transport measurements show that the nanovanadium oxides are semiconductors with a conductivity of about $10^{-3} \text{ s cm}^{-1}$ at room temperature [19]. The synthesis of multicomponent $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$ single-crystal nanobelts took place in the presence of F^- ions and, unfortunately, without F^- ions or in the presence of other anions such as Cl^- , Br^- , NO_3^- and SO_4^{2-} , nanobelts could not be obtained [19]. The large-scale single crystalline vanadium oxide nanobelts were synthesized by

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hydrothermal treatment of NH_4VO_3 in the presence of polymer polyethylene glycol 4000 (PEG-4000) [7]. These nanobelts are up to several hundreds micrometers in length, 100 nm in width, 20-30 nm in thickness, and grow along the [100] direction.

PEG plays a critical role for the formation of the vanadium oxide nanobelts in the present synthetic system. The preparation of single-crystal $\text{VO}_x \cdot n\text{H}_2\text{O}$ nanoribbons can be obtained from direct hydrothermal processing of the aqueous solution of NH_4VO_3 and polyethylene glycol 400 (PEG-400), but the values of x and n are uncontrolled. The $\text{VO}_x \cdot n\text{H}_2\text{O}$ nanoribbons are up to *ca.* 200 μm in length, 100-150 nm in width, 20-30 nm in thickness, and grow along the [010] direction. The PEG carries the roles of both transport and reducing agent. Coordination self-assembly mechanism was proposed to elucidate the formation of the $\text{VO}_x \cdot n\text{H}_2\text{O}$ nanoribbons [9]. In another work, the metastable vanadium dioxide single-crystal nanobelts have been synthesized by a direct hydrothermal reduction method using formic acid as a reducing agent [1a]. The morphology and electric properties of this metastable were investigated and the magnetic measurement showed VO_2 (B) was a paramagnetic material. This hydrothermal method should be applicable for large-scale production of low-dimensional nanostructured vanadium dioxides [1]. The synthesis using divanadium pentoxide as a precursor undergoes hydrothermal conditions gives the $\text{H}_2\text{V}_3\text{O}_8$ single-crystal nanobelts [8]. The nanobelts which revealed a thickness of less than 30 nm and a length up to several hundreds of micrometers have been synthesized using bulky divanadium pentoxide powders as a precursor. The belt-like $\text{H}_2\text{V}_3\text{O}_8$ with a high surface area may be beneficial to lithium insertion between the V_3O_8 layers for application in batteries [8].

Various methods have been developed to synthesize vanadium oxide 1D nanostructures. Notably, vanadium oxide nanostructures have been synthesized *via* hydrothermal treatment with various solutions. However, the synthetic route is still challenge and more development.

In our work, we provided a low-cost, simple approach, a high-yielding and facile synthesis of vanadium oxide nanobelts by hydrothermal treatment of our $(\text{NH}_4)_2\text{V}_3\text{O}_8$, **1**, with deionized water. Various techniques such as SEM with EDX, XRD and FT-IR were used to characterize the

morphology, composition and structure of the as-obtained ribbon-like nanobelts.

EXPERIMENTAL

Preparation of **2**

A ribbon-like nanobelt, $\text{V}_x\text{O}_y \cdot n\text{H}_2\text{O}$, **2**, was synthesized using soft chemical *via* hydrothermal synthesis of H_2O into the layer of **1** in one step. In a typical preparation, a 0.126 g (4 mmol) of our ammonium trivanadate **1** [20] and distilled water (40 ml) were put into a Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained at 200 °C for 3 days and then allowed to cool to room temperature. After the completed reaction, the resulting dark green product was filtered and washed with distilled water and ethanol for several times to remove any other possible residues and then finally dried at 70 °C.

Field Emission Scanning Electron Microscope

The surface morphology was determined by field emission scanning electron microscope (FE-SEM) using a JEOL JSM-6700F microscope with an energy-dispersive X-ray (EDX) fluorescence analyzer. An accelerating voltage is 0.5 kV to 30 kV with vary magnification between X 4,000 to X 130,000.

Powder X-Ray Diffraction Analysis

The variation of lattice parameters upon the chemical component was examined by X-ray diffractometer (XRD) Rigaku (Japan) D/MAX RINT2200-Ultima Plus. The accelerating voltage 40 kV, applied current 30 mA and the scan rate 0.02 °/s were applied to record the pattern in the 2 θ rang of 2-70° which used to characterize the crystalline phase of the products.

Fourier Transform Infrared Spectroscopy

The Fourier transform infrared (FT-IR) pattern was recorded on a Jasco 660 Plus spectrometer by standard KBr disk method.

RESULTS AND DISCUSSION

Compound **2** is dark green thin “paper form”. It is noteworthy that it formed this shape only after suction filtration, confirming that as-synthesized ribbon-like nanobelts

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can be either prepared as stable colloidal solutions or self-assemble into the “paper form” [1]. It yielded about 78 percents. This is again to confirm that hydrothermal method would be enable method for preparation of nanovanadium oxide compound. Its melting point is more than 300 °C. The color changed from original bronze to dark green, indicating that V(V) is partially reduced partly to V(IV) [7,9,21]. This is due to water which also acts as a reducing agent during the hydrothermal treatment. It is well-known that pH of the solution plays an important role for the formation of vanadium oxide ribbon-like nanobelts during the hydrothermal treatment [22]. As reported in the literature, the chemistry of aqueous vanadates in range of pH 4-8 is complicated, a new polyvanadate may be formed in this range [23]; a pH range of 6-7 is suitable for preparation of nanobelts [7].

The compound $(\text{NH}_4)_2\text{V}_3\text{O}_8$ clearly confirmed the 2D layered structure containing the $(\text{V}_3\text{O}_8)^{2-}$ and $(\text{NH}_4)^+$. This type of layer is typical for V_3O_8 two-dimensional vanadate frameworks and is built up of zigzag chains of $[\text{VO}_5]$ edge sharing square pyramids that are linked into the layer by sharing corners with $[\text{VO}_4]$ tetrahedral [20].

Thus, the basic reactions for vanadium oxide nanostructures can be expressed as follows. First, ammonium vanadate in aqueous solution forms $(\text{NH}_4)^+$ and $(\text{V}_3\text{O}_8)^{2-}$. As the temperature increases, some H_2O enters the gas phase while vanadate groups start to agglutinate into $[\text{VO}_4]$ tetrahedra chains, in which the tetrahedra are connected by sharing corners. When the reaction proceeds to a certain extent, the tetrahedral chains coalesce to form $[\text{VO}_5]$ pyramid by H_2O bridge connection between vanadium ions, in which pyramids are connected at corners or edges. Then this complex would gradually condense into solid phase $\text{V}_x\text{O}_y \cdot n\text{H}_2\text{O}$, and seeds (nanoribbons) appeared in the heating solution through nucleations.

The SEM micrographs shown in Fig. 1 revealed a plate-like morphology and exclusively belt-like nanostructures. They generally exhibit rectangular cross-section, and the straight or twisted morphology, typical of the geometrical shape of ribbon-like nanobelts [7,17]. The long fibrillar morphologies can even be seen with the naked eye. The dimension is about 200 nm wide, 10 nm thick and thousands of nanometers long. Generally, the ribbon-like nanobelts exhibit uniform width and thickness throughout their lengths [8]. The ends of

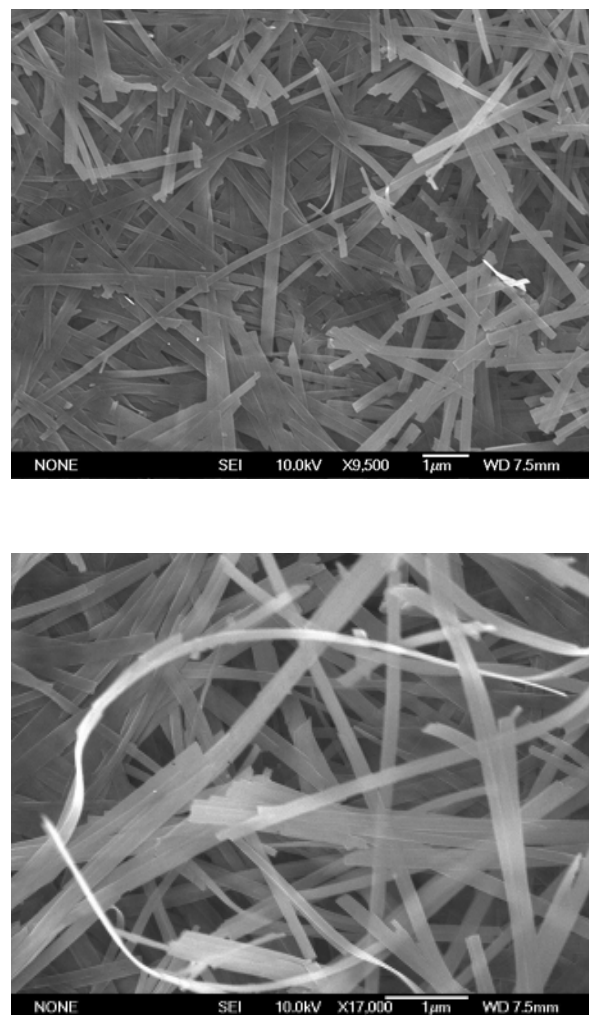


Fig. 1. SEM micrographs show photographs at magnification x 9500 (up) and at magnification x17000 (down).

these ribbon-like nanobelts are irregular. The cleaved layers are clearly visible, so it can be inferred that the belt-like materials derived from the cleavage of its starting material **1** layers in the reaction process. Moreover, some of ribbon-like nanobelts have terraces, indicating that some of the ribbon-like nanobelts stick together [7].

The results from EDX spectra showed that the nanobelts only contain V and O atoms. No other elements are found. However, the atom ratio of V and O cannot be determined because one peak for the V atom overlaps with the peak for

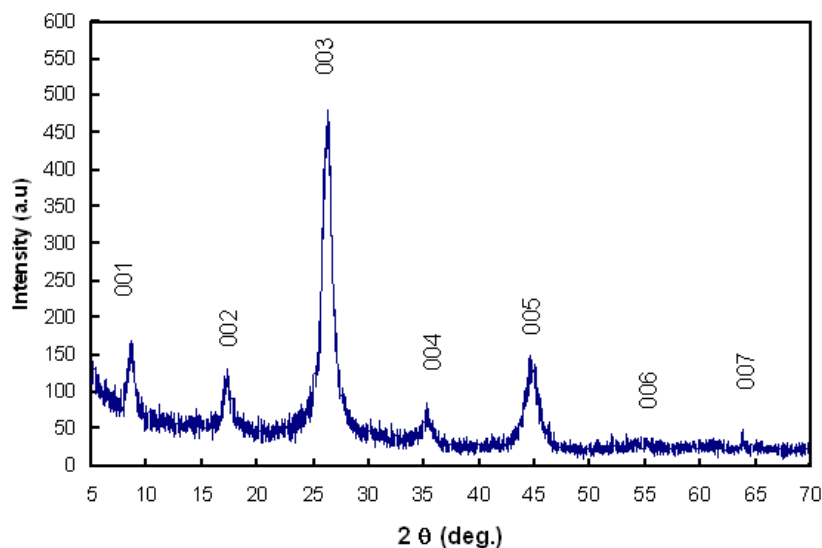


Fig. 2. XRD Pattern of ribbon like nanobelts **2**.

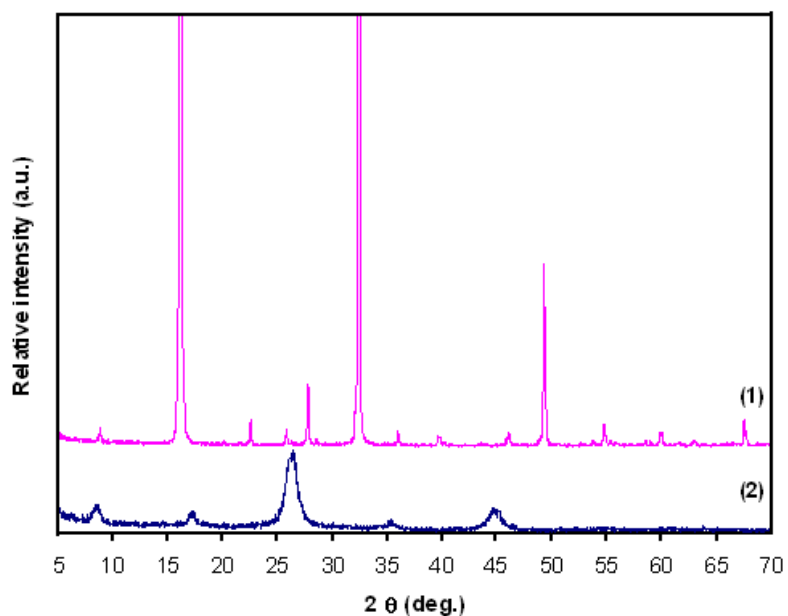


Fig. 3. XRD Pattern of starting Material **1** and ribbon like nanobelts **2**.

the O atom [1a].

X-ray powder diffractograms of **1** and **2** are presented in Figs. 2 and 3. The reflections at $2\theta < 15^\circ$ are $00l$ peaks, typical for layered structures [24]. The XRD shows a set of reflections at 8.7° , 17.4° , 26.4° , 35.5° , 44.7° , 54.2° and

63.9° that assembled into the paper form, characteristic of (001) reflections for layered phases. All the peaks in Fig. 2. can be perfectly indexed to the cubic crystalline phase of **2** with calculated lattice contents $a = 10.149 \text{ \AA}$. Interestingly, no peaks of any other phases or impurities were detected.

Considering these results with regard to the crystal structure of 2, it appears that most of the ribbon-like nanobelts packed along (001) in the paper-form sample, and the [010] direction was the growth axis of the belts. The XRD pattern was not similar to that of crystalline V_2O_5 [25], a paper form of $VO_2(B)$ [1]. However, the structure should be similar to that of $VO_x \cdot nH_2O$ [7], but its position and intensity of peak 001 are significantly different. The highest intensity of 003 peak appeared to be corresponding to the metastable phase of crystalline $V_2O_4 \cdot 0.25H_2O$ [26].

The FT-IR results of the band component analysis are reported in Table 1. The distinct bands are observed in infrared spectrum at 400-1000 cm^{-1} and 2900-3600 cm^{-1} . The spectrum of the as-obtained ribbon-like nanobelts indicates the presence of bound water and various V-O vibrations. An evidence for bound water is a broad and strong absorbance peak around 3440 cm^{-1} corresponding to the stretching vibration (H-O-H) and a medium peak at 1658 cm^{-1} corresponding to the bending vibrations (O-H) between oxygen and hydrogen atoms [27-28]. The very weak peak at 1434 cm^{-1} is ascribed as N-H bending, but there is no evidence for N-H stretching at between 2950 cm^{-1} and 3200 cm^{-1} , indicating that the NH_4^+ group was not completely removed during washing with deionized water and ethanol [27].

The terminal V=O bonds occur at 1007 cm^{-1} region which is slightly different from its starting materials at 997 cm^{-1} and slightly lower than that of the IR band of V(V)=O in crystalline V_2O_5 (1015-1020 cm^{-1}) [25]. The peak is attributed to the stretching vibration between vanadium and oxygen atoms and correspond to ribbon-like nanobelts $(NH_4)_{0.5}V_2O_5$ [7,28].

The weak absorption band at 927 cm^{-1} belonged to V(IV)=O stretching mode. This is confirmed that the molecule still has the mixed valence V(V) and V(IV) [20]. The FT-IR band found at 728 cm^{-1} is ascribed to V-O-V antisymmetric stretching mode [7]. The strong and broad signal at 547 is a V-O-V bending [17,28].

Based on FT-IR and the EDX results, it might be implied that a certain amount of water molecules is embedded between the vanadium oxide layers; thus, the chemical formula of the as-obtained ribbon-like nanobelts could be described as $V_xO_y \cdot nH_2O$ with a mixed valence V(V) and V(IV).

Table 1. FT-IR Spectrum Comparison of NH_4VO_3 , 1 and 2

NH_4VO_3	1	2	Type
		3440s	O-H stretching
3205b	3107b		N-H stretching
2964b,	3031b		N-H stretching
		1658m	O-H bending
1425s	1417s	1434w	N-H bending
1058w	997s	1007m	V(V)=O stretching
	935s	927w	V(IV)=O stretching
910b			V-O-V antisym. stretching
862b		860m	V-O-V antisym. stretching
	817s		V-O stretching
710b	739s	728w	V-O-V antisym. stretching
		547s	V-O-V bending
507w			
	430s		V-O bending

CONCLUSIONS

In conclusion, we provide a low-cost, a high-yielding and simple synthesis of vanadium oxide nanobelts by hydrothermal treatment. The SEM observations with EDX, the XRD pattern and the FT-IR results confirmed a plate-like morphology and exclusively belt-like nanostructures, and the chemical formula of the as-obtained ribbon-like nanobelts could be described as $V_xO_y \cdot nH_2O$ with a mixed valence V(V) and V(IV), respectively.

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