

A facile method for preparing VO₂ nanobelts

Xinghai Liu^a, Guangyong Xie^b, Chi Huang^{a,*}, Qian Xu^a, Yifu Zhang^a, Yunbai Luo^a

^a College of Chemical and Molecular Science, Wuhan University, Wuhan 430072, PR China

^b Key Laboratory of Catalysis and Materials Science of the State Ethnic Affairs Commission and Ministry of Education, College of Chemistry and Materials Science, South-Central University for Nationalities, Wuhan 430074, PR China

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Abstract

Metastable VO₂ nanobelts were synthesized via a facile hydrothermal approach. Then the as-obtained samples were characterized by X-ray diffraction (XRD), X-ray photoelectron spectra (XPS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Typical samples exhibited monoclinic phase VO₂ (B) indexed as XRD, and the XPS results demonstrated that the V (IV) existed only in vanadium oxides. According to the results of TEM and SEM, the VO₂ (B) nanobelts were 0.6–2.2 μm long, typically 70–180 nm wide and 20–30 nm thick. Some factors that affected the shape of One-dimensional (1-D) VO₂ nanomaterials were briefly discussed.

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1. Introduction

Nanobelts have been the subject of intensive research in recent years owing to their chemical and physical properties and potential applications in fabricating nanoscale electronic, optical, optoelectronic, electrochemical, and electromechanical devices [1–5].

Vanadium dioxide possessing unique electrical and optical properties, has led to a wide variety of potential application, such as the temperature sensing devices [6], optical or electrical modulators [7], rechargeable lithium batteries [8], intelligent thermochromic windows [9], and uncooled infrared detector [10].

Although several methods to synthesize one-dimensional (1-D) V (IV) oxides have been reported, the new methodology is still worthy to be developed. Using VO₂ powder as a starting material, VO₂ nanorods [11] and nanowires [12] were obtained at high temperature in an argon atmosphere. Rutile VO₂ nanorods were obtained by the hydrothermal reaction of KOH, V₂O₅ and N₂H₄·H₂O [13]. Needle-like VO₂·H₂O was prepared using NH₄VO₃ and hydrazine as reagents [14]. Nanotextured VO₂ (B) reported by Baudrin [15] was synthesized through heat treatment of

vanadium oxide aerogels under vacuum. VO₂ (B) nanobelts was obtained using H₂C₂O₄·2H₂O as reducing and structure-directing reagent [16]. For all of these systems, additional surfactants were introduced into the reaction system, or the conditions of reaction were complicated.

Herein, we report a convenient and controllable approach for synthesis of 1-D structure of VO₂ nanobelts starting from V₂O₅,

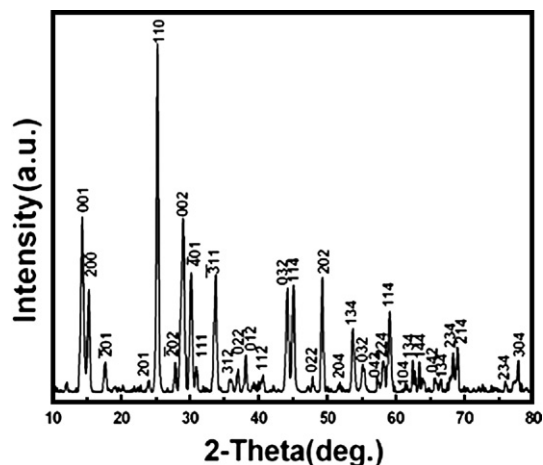


Fig. 1. XRD pattern of VO₂ (B) nanobelts.

* Corresponding author. Tel.: +86 27 62952899; fax: +86 27 68754067.

E-mail address: chihuang@whu.edu.cn (C. Huang).

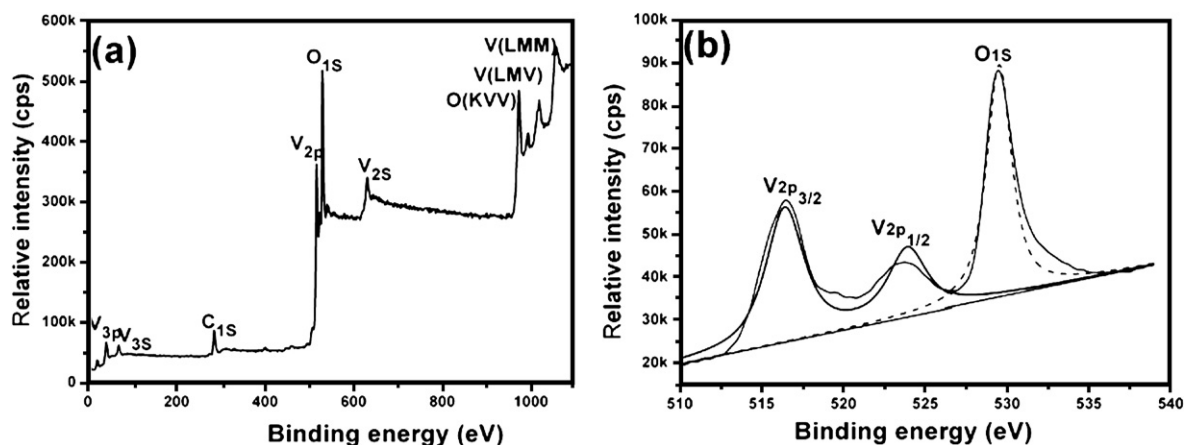


Fig. 2. XPS of VO_2 nanobelts: (a) survey spectrum; (b) core-level spectra of V_{2p} and O_{1s} .

EtOH and water, which required neither sophisticated techniques nor templates. The reaction involved in redox reaction and hydrothermal process were investigated, and some factors that affected the shape of 1-D VO_2 nanomaterials were briefly discussed.

2. Experimental section

All the reagents used in experiments were of analytical grade and used without further purification. In a typical procedure, commercial V_2O_5 powder (0.90 g), absolute alcohol (30 mL) and water (10 mL) were transferred into a 50 mL stainless steel autoclave. The autoclave was sealed and heated at 180°C for 24 h, and then cooled to room temperature on standing. The

product was collected and washed by distilled water and absolute ethanol for several times. The final product was dried in vacuum at 80°C for 10 h. TEM (JEM-100CX and JEM 2010, 100 KV and 200 KV accelerating voltage, respectively) and SEM (X-650) were used to characterize the morphology of samples, while XPS (VG Multilab 2000, Mg $\text{K}\alpha$ (1253.6 eV)) and XRD (Shimadzu XRD-6000, Cu $\text{K}\alpha_1$ ($\lambda = 1.54060 \text{ \AA}$)) were used to investigate the purity and crystalline structure of samples.

3. Results and discussion

The purity and crystallinity of the as-prepared product were determined using powder XRD. A typical XRD pattern of as-synthesized product is shown in Fig. 1. The peaks from the sample can be indexed as monoclinic VO_2 (space group $C2/m$) with lattice parameters $a = 12.093$,

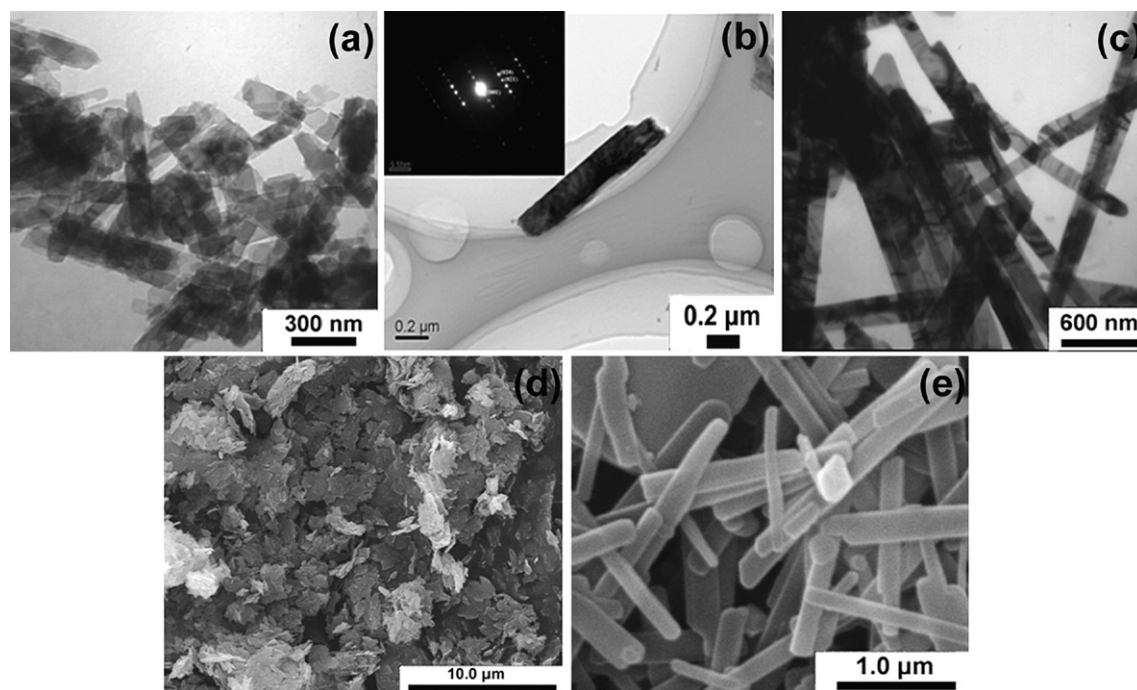


Fig. 3. TEM images: (a) 160°C for 12 h, (b) 180°C for 24 h (inset, SAED); (c) 200°C for 168 h; SEM images: (d) 160°C for 12 h, (e) 200°C for 168 h.

$b=3.7021$, $c=6.433$ Å. It correspond to the VO₂ (B) (JCPDS Card No. 81-2392, $a=12.09$, $b=3.702$, $c=6.433$ Å) [17].

Furthermore, XPS analyses provided additional insight into the composition and vanadium valence state of the surface of the as-obtained products. The peaks for O could be the O₂, CO₂, H₂O adsorbed on the surfaces of the samples, or VO₂ (Fig. 2a), which was revealed that the dark blue material consists of vanadium and oxygen by the XPS survey spectrum. It was reported that [18–21] the V_{2p3/2}³⁺ peak was located at 515.2–515.9 eV and V_{2p1/2}³⁺ peak was located at about 523 eV; the V_{2p3/2}⁵⁺ peak was located at 516.9–517.7 eV and the V_{2p1/2}⁵⁺ peak was located at 524.3 eV; and the V_{2p3/2}⁴⁺ peak was located at 515.7–516.2 eV and the V_{2p1/2}⁴⁺ peak was located at 523.4 eV. As can be seen from Fig. 2b, the binding energies of V_{2p3/2} and V_{2p1/2} centered at 516.10 and 523.40 eV was well consistent with the above-mentioned results. Therefore, the high resolution XPS region spectrum (Fig. 2b) further confirmed that vanadium oxide consists of V (IV).

The size and morphology of the products were examined by TEM and SEM. The TEM image (Fig. 3c) revealed that the VO₂ nanobelts were 0.6–2.2 μm long, typically 70–180 nm wide and 20–30 nm thick. Flexible nanobelts with uniform diameter were also observed in typical SEM image (Fig. 3e), which was in agreement with the TEM results. In addition, the selected area electron (SAED) pattern of an individual nanobelt was shown that the nanobelt was single crystal. The typical SAED pattern is presented in inset of Fig. 3b.

The synthesis parameters, such as temperature, reaction time, and the volume of EtOH played an important role in controlling the purity and morphology. A series of experiments showed that using a lower temperature (<160 °C) resulted in a V₂O₅ gel owing to inefficient reduction within 24 h, and shorter reaction times led to poor crystallization (Fig. 3a and d). Other vanadium oxide containing V⁵⁺ was generated due to insufficient amount of EtOH at 160–200 °C within 24 h. Only when the volume of EtOH was higher than 10 mL (summary volume was fixed) and the reaction time was longer than 24 h, uniform large amounts of VO₂ (B) nanobelts were obtained (Fig. 3c and e). Moreover, it was found that the longer the reaction time was, the more uniform the shapes of as-obtained products were according to our experiments (Fig. 3a, c, d, and e). The ethanol served both as the reducing agent and the solvent. A portion of it was oxidized to aldehyde. This was experimentally confirmed through chemical analysis (silver mirror reaction and GC analysis) of the final solution mixture. Thus, the reaction equation of VO₂ through the reaction of V₂O₅ and excess ethanol under the solvothermal condition could be expressed as follows: V₂O₅ + CH₃CH₂OH = 2VO₂ + H₂O + CH₃CHO.

Although the exact mechanism for the formation of these uniform nanobelts is still unclear, we believe that the growth axis of nanobelt is related to its crystallographic characteristics. VO₂ (B) is constructed from two different layers of VO₆ octahedra. These layers are linked to each other at the producing corners of each pair of octahedral to produce a three-dimensional framework [22]. Moreover, it is well known that many 1-D nanostructures (nanotubes or nanorods) have been synthesized from the layered structures [23]. The relative work is being proceeded by our research team.

4. Conclusion

In this method, no additional template materials are needed to obtain nanobelts. The content of EtOH, temperature, and

reaction time, played an important role in controlling the purity and morphology. When the volume of EtOH was higher than 10 mL (summary volume was fixed) and the reaction time was longer than 24 h, large amounts of pure and uniform VO₂ (B) nanobelts were obtained. The as-prepared VO₂ (B) nanobelts were 0.6–2.2 μm long, typically 70–180 nm wide and 20–30 nm thick. Additionally, The VO₂ (B) nanobelts prepared this way may be useful in many application fields.

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