

Synthesis and characterization of novel vanadium dioxide nanorods

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Abstract

Novel vanadium dioxide nanorods were fabricated via a surfactant-assisted hydrothermal method at 180 °C for 48 h in the presence of cetyltrimethylammonium bromide (CTAB). The self-assembled samples were characterized by XRD, SEM, TEM, HRTEM and FT-IR. The results show that the products are nanorods, which are pure B phase vanadium dioxide with high crystallinity. The obtained nanorods have diameters of 40–60 nm with lengths up to 1–2 μm. The probable formation mechanism of vanadium dioxide is also discussed.

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1. Introduction

Over the past decade, one-dimensional (1D) nanostructured building blocks such as nanotubes, nanorods, nanowires and nanoribbons [1–4], have attracted worldwide interest because of their distinctive geometries, outstanding physical and chemical properties and their potential applications in electronics, optics, catalysis, ceramics and magnetic storage. To date, various 1D nanometer scale materials have been prepared with diverse techniques, including chemical vapor deposition (CVD), electrodeposition, template-based, hydrothermal and laser ablation methods [5–9], giving rise to the possibility of constituting a nanotoolbox for a ‘bottom-up’ approach in nanoscience and nanotechnology.

Among the numerous transition metal semiconductor oxides, vanadium dioxides with various phases are of

intense interest and have been extensively investigated for their distinctive optical and electrochemical properties. Thermochemical VO₂ has attracted much interest because it undergoes a phase transition at approximately 68 °C from a semiconductor to a metal and presents an optical switching behavior [10]. Moreover, B phase VO₂ was found to have good electrochemical performance [11,12]. Therefore, it is of interest to prepare low dimensional nanocrystals of B phase VO₂. Recently, considerable research efforts have been directed toward the preparation of vanadium dioxides with 1D nanostructures. Nanocrystal VO₂ (B) had been obtained by an ambient temperature reduction of aqueous vanadate ions with potassium borohydride and sodium dithionite followed by heating in vacuum at 230 °C [12]. Zheng et al. prepared VO₂ powders with size <30 nm by hydrolysis of [NH₄]₅[(VO)₆(CO₃)₄(OH)₉·10H₂O] [13]. Guo et al. prepared needle-like nanocrystalline VO₂·H₂O by hydrothermal reaction from NH₄VO₃ and hydrazine at 170 °C for 15 days, and single-crystal rutile VO₂ nanorods by thermal treatment of precursor hydrate, which was obtained via the hydrothermal reaction of KOH, V₂O₅ and hydrazine, at 340 °C for 1 day in flowing N₂ [14,15].

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However, these synthetic methods are not successful in fabricating of B phase VO₂ nanorods. To the best of our knowledge, the synthesis of B phase VO₂ nanorods has not been reported. Herein, we introduce the synthesis of VO₂ (B) nanorods using a convenient surfactant-assisted hydrothermal procedure. In addition, the aspect ratio of the final product could be controlled by changing the reactive conditions such as relative concentrations of precursors, pH value, hydrothermal time and temperature [16]. Due to their uniform nanostructures, distinguished electrochemical properties could be expected from these novel vanadium dioxide nanorods.

All chemical agents were analytical grade and used without further purification. In a typical procedure, 10 mmol V₂O₅ and 10 MMO CTAB was added into a Teflon-lined autoclave of 40 ml capacity and filled with distilled water to 90% capacity. The hydrothermal syntheses were conducted at 180 °C for 48 h. After the reactions, the autoclave was allowed to cool to room temperature naturally. The obtained black precipitate was collected and washed with absolute ethanol and distilled water several times to remove residual organic template in the final products and finally dried at 80 °C for 8 h.

X-ray powder diffraction (XRD) pattern was done on a D/MAX-III powder diffractometer with Cu K_α radiation ($\lambda=0.15418$ nm) and graphite monochromator. The diffraction data were recorded for 2θ between 10 and 60°, with a resolution of 0.02°. Scanning electron microscopy (SEM) images were taken in a JSM-5610LV microscope operated at 20 kV. High-resolution transmission electron microscopy was carried out in a JEOL 2010F high-resolution transmission electron microscope at an accelerating voltage of 200 kV. The Fourier transform infrared (FT-IR) instrument used was a Nicolet 60-SXB spectrometer from 400 to 3600 cm⁻¹ with a resolution of 4 cm⁻¹.

Fig. 1 displays the XRD pattern of the obtained samples. All the peaks can be rapidly indexed to VO₂ (B) phase consisted with the standard value of JCPDS 31-1438 (*C2/m*, $a=1.203$ nm, $b=0.3693$ nm, $c=0.642$ nm, $\beta=106.6^\circ$).

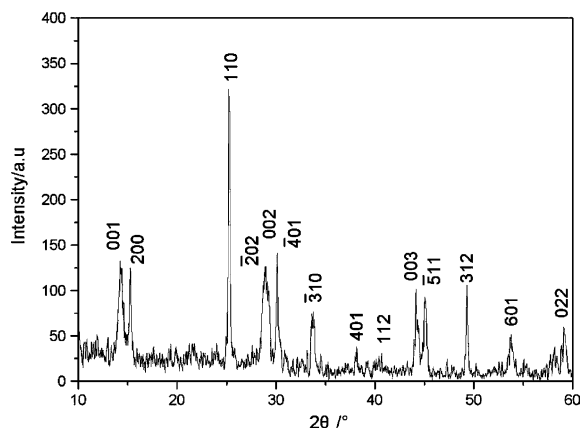


Fig. 1. XRD pattern of the obtained VO₂ (B) nanorods.

Compared with the standard data, the (110) peak is relatively strong which may be caused by the orientation growth of VO₂ (B). No impurity phase such as VO₂ (M), VO₂ (R) and V₆O₁₃ was found from the XRD pattern, indicating that VO₂ (B) nanorods with high purity could be obtained under the current synthetic procedure.

The final products consist mainly of vanadium dioxide nanorods. Rod-like morphology could be observed in the SEM image in Fig. 2. Typical TEM images (Fig. 3) show that samples display rod-like shape and that these nanorods are straight with uniform diameters in the range 40–60 nm and lengths ranging from 1 to 2 μm. The aspect ratio of the corresponding nanorods lies in the range of 25–40. The detail structure of VO₂ (B) nanorods is further examined by HRTEM. Representative HRTEM images of respective nanorods together with corresponding fast Fourier transformation (FFT) in Fig. 4 show clear lattice fringes without defects or dislocations, thus providing additional confirmation that these nanorods are of high crystallinity. The interplanar spacing is 0.35 nm, combined with the result of FFT analysis, it is found to agreement with the *d* spacing of (110) plane of monoclinic VO₂ (B).

Fig. 5 shows that the obtained nanorods contain no organic component; all bands in the FT-IR spectrum of VO₂ nanorods can be attributed to vibration models of inorganic clusters. Bands at 3400 and 1650 cm⁻¹ can be attributed to different vibration models of O–H group of adsorbed water molecules. The absorption band at 534 cm⁻¹ can be associated to V–O–V octahedral bending modes. Compared with FT-IR spectrum of crystalline VO₂ (B) power [17], bands at 1000 and 880 cm⁻¹ disappears, while a new broad and weak band at 917 cm⁻¹ appears. This band may be associated to some disordering in the initial VO₂ (B) octahedral arrangement. The stretching modes associated with the corner and edge sharing of octahedra are broadened, giving rise to intermediate vibration states, mixing 1000 and 880 cm⁻¹ modes. Meanwhile, due to the numerous boundaries of crystals and a huge specific surface

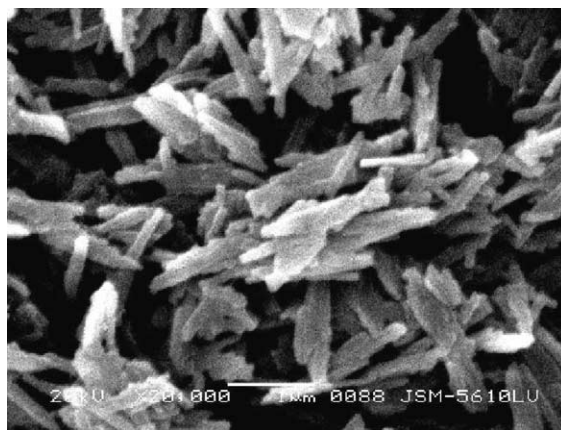


Fig. 2. SEM images of the obtained VO₂ (B) nanorods.

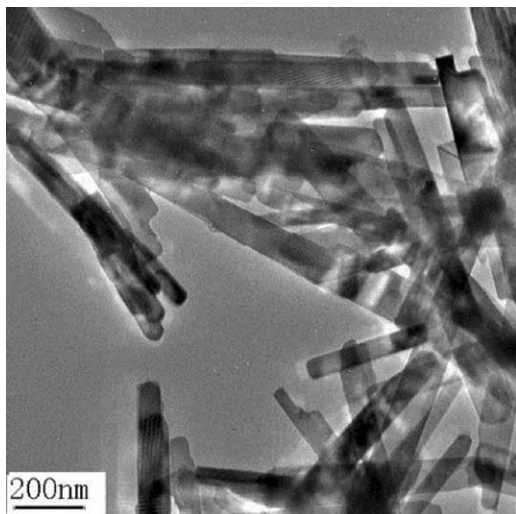


Fig. 3. TEM images of the obtained VO₂ (B) nanorods.

area, IR spectra of nanocrystals are quite different from that of microcrystals.

It is found that CTAB plays a key role in the synthesis of VO₂ (B) nanorods. CTAB is generally used as structure-directing template in the synthesis of 1D nanostructured materials [18–20]. Some literatures have reported that CTAB could reduce some inorganic materials with high redox activity, such as KMnO₄ and PbO₂ [21,22]. Similar to the synthetic procedure of Li_xV_{2-δ}O_{4-δ}·H₂O started from V₂O₅ and tetramethyl ammonium, which forms [N(CH₃)₄]V₄O₁₀ phase [12], we assume that CTAB acts as a ligand which coordinates with central vanadium to form the possible [C₁₆H₃₃N(CH₃)₃]V₄O₁₀ complex. These complexes then reduced to form VO₂ particles under

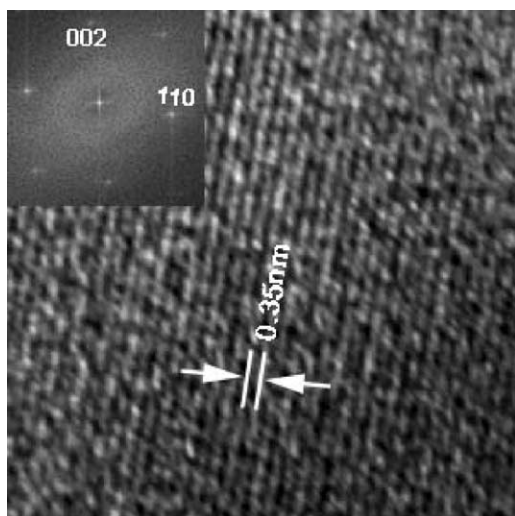


Fig. 4. HRTEM image of the VO₂ (B) nanorods, showing the lattice fingers of VO₂. The inserted image is the corresponding FFT pattern.

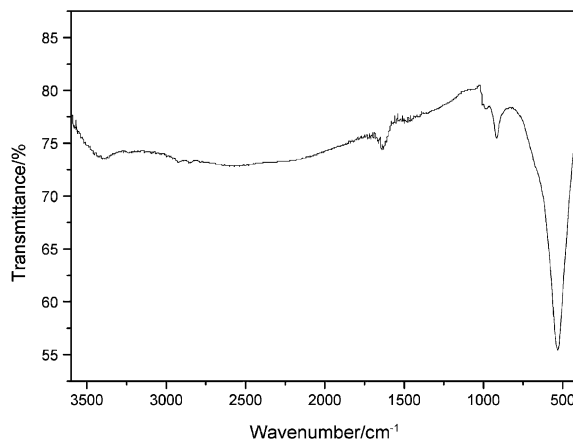


Fig. 5. FT-IR spectrum of the obtained VO₂ (B) nanorods.

hydrothermal condition. Small amount of B phase VO₂ particles serve as seeds for further growth. The presence of CTAB facilitate the formation of rod-like micelle in solution, the VO₂ (B) phase slowly grow along the surface of CTAB micelle through a solid–solution–solid transformation progress and finally nanorods are formed. In order to testify the crucial effect of CTAB, some other surfactant or reductants have been used such as hexadecylamine, ethylenediamine and hydrazine monohydrate, but no B phase VO₂ has been observed when other reaction conditions remained. More research will be done to testify our assumption.

In summary, novel B phase VO₂ nanorods with high crystallinity were successfully synthesized via a hydrothermal method at 180 °C with the assistance of CTAB. The high-yielding cost-saving synthetic procedure is expected to be applied in large-scale fabrication of VO₂ (B) nanorods. It is our hope that this simple aqueous solution synthetic route could be applied as a general method for the preparation of 1D nanostructured materials.

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