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. Thermochromic 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]2(VO)4(CO3)3(OH)·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].
However, these synthetic methods are not successful in fabricating of B phase VO$_2$ nanorods. To the best of our knowledge, the synthesis of B phase VO$_2$ nanorods has not been reported. Herein, we introduce the synthesis of VO$_2$ (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 nanostuctures, 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 V$_2$O$_5$ 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 $^\circ$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 $^\circ$C for 8 h.

X-ray powder diffraction (XRD) pattern was done on a D/MAX-III powder diffractometer with Cu K$_a$ radiation ($\lambda=0.15418$ nm) and graphite monochrometer. The diffraction data were recorded for $2\theta$ between 10 and 60$^\circ$, with a resolution of 0.02$^\circ$. 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 detail structure of VO$_2$ (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 VO$_2$ (B).

Fig. 5 shows that the obtained nanorods contain no organic component; all bands in the FT-IR spectrum of VO$_2$ 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 VO$_2$ (B) powder [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 VO$_2$ (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. 1. XRD pattern of the obtained VO$_2$ (B) nanorods.](image1)

![Fig. 2. SEM images of the obtained VO$_2$ (B) nanorods.](image2)
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$_{x}$V$_{2}$O$_{4}$–δ·H$_{2}$O started from V$_{2}$O$_{5}$ and tetramethyl ammonium, which forms [N(CH$_{3}$)$_{4}$]V$_{4}$O$_{10}$ phase [12], we assume that CTAB acts as a ligand which coordinates with central vanadium to form the possible [C$_{16}$H$_{33}$N(CH$_{3}$)$_{3}$]V$_{4}$O$_{10}$ complex. These complexes then reduced to form VO$_{2}$ particles under hydrothermal condition. Small amount of B phase VO$_{2}$ particles serve as seeds for further growth. The presence of CTAB facilitate the formation of rod-like micelle in solution, the VO$_{2}$ (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 VO$_{2}$ has been observed when other reaction conditions remained. More research will be done to testify our assumption.

In summary, novel B phase VO$_{2}$ 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 VO$_{2}$ (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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