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VO_2(A) nanorods: One-pot synthesis, formation mechanism and thermal transformation to VO_2(M)

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ABSTRACT

The monoclinic VO_2(M) has promising applications in intelligent devices but its preparation still requires improvement to permit cost-effective mass production. In this work, we report a 2-stage approach for producing VO_2(M) nanorods by (1) hydrothermal reduction of vanadium pentoxide by sodium bisulfate at 220 °C to form VO_2(A), and (2) subsequent thermal activated phase transformation of VO_2(A) to VO_2(M) at 350–450 °C in vacuum. The obtained VO_2(M) nanorods showed a reversible phase transition temperature at about 62.5 °C and a narrow thermal hysteresis width of 10 °C. The mechanism of the hydrothermal reduction was studied by combined *ex situ* microscopic and diffraction characterization of cooled samples as well as *in situ* PXRD experiments, in which the hydrothermal synthesis was monitored in real time by time-resolved diffraction datasets. It was found that the hydrothermal synthesis of VO_2(A) is a 4-step process: (1) reduction of V_2O_5 to form VO_2(B) nanoparticles, (2) oriented attachment of VO_2(B) nanoparticles along the [110] direction, (3) formation of VO_2(B) nanorods as a results of oriented attachments, and (4) hydrothermal transformation of the metastable intermediate VO_2(B) nanorods to VO_2(A) nanorods. This clear understanding of the mechanism will help the further optimization of synthesis temperature and time for preparing VO_2(A). This method provides a low temperature thermal treatment alternative and hence helps the reduction of cost for the production of VO_2(M), bring the mass application of VO_2(M) one step closer.

1. Introduction

The two vanadium dioxide polymorphs, monoclinic VO_2(M) and rutile VO_2(*R*), exhibit fast and reversible metal-insulator transition (MIT) at about 68 °C [1,2], hence they have been considered as promising materials for fabricating intelligent devices such as optoelectronic switches and energy-saving smart windows. Recently, intensive efforts have been made on the preparation of VO_2(M) focusing on controllable compositions and adjustable morphologies for improved thermochromic performance. A number of preparation protocols have been developed based on solution chemistry, including sol-gel processing [3], hydro/solvothermal treatment [4], co-precipitation [5], combustion [6], and hydrolysis [7]. Among the above approaches, research has shown that the hydrothermal method has been more efficient, controllable and environmental-friendly [8].

Besides the stable monoclinic and rutile phases, other vanadium dioxide polymorphic varieties include VO_2(A), VO_2(B), VO_2(C), VO_2(D), VO_2(T), and VO_2(P) [9]. They are metastable phases and usually present as an intermediate phase or co-precipitate with VO_2(M) and VO_2(*R*) during the hydrothermal synthesis. These metastable phases of vanadium dioxide may be further transformed to VO_2(M) by post heating under inert atmosphere or vacuum. For example, Popuri reported a two-step procedure to prepare thermochromic VO_2(M1), which involved the rapid synthesis of VO_2(B) nanoplates followed by thermal treatment at 600 °C [10]. Corr prepared rutile VO_2(*R*) by hydrothermal reduction of V_2O_5 to VO_2(A) using formaldehyde or isopropanol at first, and then post-annealing at 700 °C for 2 h under argon [11]. Huang reported the synthesis of VO_2(M) by the hydrothermal transformation of VO_2(B) to VO_2(A) followed by thermal treatment at 700 °C for 2 h under high purity Ar atmosphere [12]. We previously synthesized cucumber-shaped VO_2(D) nanoparticles and aggregates using ammonium metavanadate as the vanadium resource and oxalic acid dihydrate as the reducing agent. VO_2(M) with excellent thermochoromic performance was also produced by post-heating treatment [13]. However, the formation mechanism of the metastable phases under the hydrothermal reaction conditions and its subsequent phase

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transition to VO_2(M) are still remain unclear.

In this work, VO_2(A) nanorods (NRs) were successfully synthesized *via* the reduction of vanadium pentoxide with sodium bisulfate under hydrothermal conditions. To understand the formation mechanism, the effects of temperature and synthesis duration were investigated by structural and microscopic characterization on quenched products. Additionally, *in situ* powder X-ray diffraction (PXRD) experiments were conducted to fully reveal the mechanism of the hydrothermal phase transition process. The irreversible conversion from VO_2(A) NRs to VO_2(M) NRs was achieved by post thermal treatment, and the phase transition properties of the produced VO_2(M) NRs were investigated.

2. Experimental section

2.1. Preparation of VO_2(A) NRs and their transformation to VO_2(M) NRs

All reagents were analytical grade and used without any further purification. The VO_2(A) NRs were synthesized by a mild hydrothermal method. In a typical synthesis, 10 mmol sodium bisulfate ($NaHSO_3$) and 5 mmol vanadium pentoxide (V_2O_5) were added to 16 mL of distilled water, and the mixture was then stirred for 10 min. The resulting suspension was transferred into a 25 mL PTFE-lined stainless steel autoclave, which was sealed and heated at 160–220 °C in an oven for 1–24 h under autogenerous vapor pressure. After that, the autoclave was cooled down to room temperature and opened. The black precipitate VO_2(A) was washed first with distilled water and then with ethanol. Finally, the as-prepared product was dried at 60 °C for 12 h in a vacuum oven. To obtain VO_2(M), the dried VO_2(A) NRs were heat treated at 350–450 °C for 1 h under vacuum.

2.2. Characterization

The crystalline phases of the as-synthesized products were determined by PXRD (Rigaku D/Max-2550) with Cu-Kα radiation ($\lambda = 1.5418$ Å). The morphologies were examined by field-emission scanning electron microscopy (FESEM, JSM-6700F, JEOL) and transmission electron microscopy (TEM, JEOL Model 2010). The metal-insulator phase transition of VO_2(M) was measured using differential scanning calorimeter (DSC, NETZSCH 200) with a heating rate of 10 °C min^{-1}.

2.3. In situ PXRD investigation on the hydrothermal synthesis of VO_2(A) NRs

The *in situ* PXRD experiments were carried out at the Australian Synchrotron powder diffraction beamline using a monochromatic X-ray wavelength of 0.6889 Å (or 18 keV). A mixture of 30 μmol $NaHSO_3$,15 μmol V_2O_5, and 16 μL H_2O was injected into a quartz glass capillary microreactor (1 mm in outer diameter × 0.1 mm in wall thickness × 40 mm in length). Then, the microreactor was fixed at the X-ray beam center and pressurized to 3.0 MPa using N_2 gas. After that, it was heated to 220 °C with a heating rate of 5 °C min^{-1} by a hot air blower. The temperature was monitored by a K-type thermocouple placed 3.5 mm underneath the capillary and was calibrated according to the phase transition temperature (128.0 °C) and melting temperature (333.6 °C) of KNO_3. PXRD datasets were collected sequentially over the entire course of the hydrothermal synthesis with an acquisition time of 2 min per dataset, as shown in Fig. S1. More details of the experimental setup are described previously [13–17].

3. Results and discussion

3.1. Phase and morphology

The phase composition and purity of the as-synthesized products were examined by PXRD. As shown in Fig. 1a, all the diffraction peaks are sharp, suggesting that the products are well crystallized. Meanwhile, the intense diffraction peaks in the PXRD pattern are in agreement with the powder diffraction file (JCPDS No.: 70–2716) reported previously [18]. Apart from VO_2(A), no additional peaks were found, indicating the high purity of the as-synthesized VO_2(A) phase.

The morphology and size of the VO_2(A) products are characterized by SEM. The low-magnification SEM image shows that the sample is composed of a large quantity of regular nanorods of typically 0.5–3 µm long (shown in Fig. 1b, c). TEM and HRTEM images of a representative VO_2(A) NR are shown in Fig. 1d and e, respectively. An ordered and well-defined lattice fringe can be clearly resolved with interplanar distance of 0.598 nm, which is consistent with the (110) plane of VO_2(A) [15]. Moreover, the corresponding SAED pattern presented in Fig. 1f indicates a good crystallinity of the as-synthesized VO_2(A) NRs.

3.2. Growth mechanism

Time- and temperature-dependent experiments were performed to investigate the evolution of phase and morphology. The morphologies and phases of the nanorods obtained at different reaction stages were characterized by FESEM and PXRD. At the highest temperature 220 °C, when reaction time increased from 1 to 6, 12 and 24 h, homogeneously aligned nanorods with diameter of 20 nm and length of 0.1–1 µm were obtained (Fig. 2). It was observed that nanorods with sharp ends were mostly converted to cylindrical shape. The PXRD results suggest that the formation of VO_2(A) is a 2-step process, first forming VO_2(B) (JCPDS No. 81–2392) [10] at the early stage when hydrothermal treatment was less than 12 h (Fig. 3), and then with prolonged treatment for 24 h, VO_2(B) was further transformed to VO_2(A) (Fig. 1a).

The phase and morphology are also dependent on temperature. VO_2(A) was only produced at the highest temperature of 220 °C and longest hydrothermal treatment of 24 h. In other cases, when temperature was lower (160 °C, 180 °C, and 200 °C) or reaction time was shorter (up to 12 h), only VO_2(B) was produced (Fig. 4). The interplanar distances of 0.205 or 0.207 nm (shown in Fig. S2e, S3e and S4e) and 0.350 nm (shown in Fig. S4e) match well with the (003) and (110) plane spacing of monoclinic VO_2(B), respectively. The SEM images shown in Fig. 5 further illustrate the morphology changes by varying the reaction temperatures from 160 °C, 180 °C, 200 °C to 220 °C as the reaction time was fixed at 24 h. When the hydrothermal temperatures (160 °C or 180 °C) were lower, irregular agglomerations assembled from nanoparticles were formed (Fig. 5a, b). However, at a higher temperature of 200 °C, nanoparticles were assembled into stacked nanorods (Fig. 5c). At the highest temperature of 220 °C, relatively uniform nanorods with cylindrical morphology were produced (Fig. 5d).

The formation mechanism of VO_2(A) was further investigated by *in situ* PXRD, which is a powerful tool to obtain the direct and unambiguous information about the phase transformation, intermediate phases, and crystallite growth in real time [19]. Fig. 6 combines all the PXRD patterns along the time axis. The peak positions and intensities are clearly shown by color contrast and brightness (see color scale bar in Fig. 6). The results show that during the first 32 min, which corresponds to temperature increase from room temperature to 160 °C, only V_2O_5 precursor was observed. As soon as the temperature reached 160 °C, V_2O_5 disappeared rapidly and VO_2(B) formed immediately afterwards and the intensities of the diffraction peaks increased rapidly after VO_2(B) was first detected. The formation of VO_2(B) was accompanied by the formation and then disappearing of a small angle X-ray scattering (SAXS) tail at low angles below 1.0°. As stated in our previous work [15], this SAXS tail was most likely due to the nucleation and crystal growth of VO_2(B). However, when temperature reached 220 °C, VO_2(A) started to form at the expense of VO_2(B), which is clearly indicated by the change of peak intensities of the 2 phases that the peak intensities of VO_2(B) decreased continuously and at the same time those of VO_2(A) increased gradually and became constant after prolonged reaction for up to 84 min. This result revealed direct reduction of V_2O_5