

Thermochromic VO₂ nanorods and other vanadium oxides nanostructures

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Abstract

Thermochromic VO₂ nanorods were prepared via thermal conversion of the metastable VO₂-B phase synthesized by hydrothermal methods. We observe an increased thermochromic transition temperature to ~75–80 °C by variable-temperature infrared spectroscopy. Nano- and sub-micron structures of other vanadium oxides (V₃O₇, (NH₄)_{0.5}V₂O₅, and V₂O₅) were obtained simply by varying the starting materials in the hydrothermal synthesis. We also obtained nanostructures of the high temperature tetragonal rutile phase of VO₂ by thermolysis of single-source vanadium (IV) precursors.

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1. Introduction

The development of a wide range of nanomaterials has sparked tremendous interest on account of their novel physical properties and their potential applications in constructing electronic and optoelectronic devices at the nanoscale [1]. Much of the effort has been focused on nanoparticles and nanowires of semiconducting and metallic systems such as CdSe [2], GaN [3], ZnO [4], In₂O₃ [5], and metals [6]. Among such systems, thermochromic rutile-type vanadium dioxide (VO₂) is of considerable interest due to its applications in optical switching devices, smart windows, thermal sensors, and field-effect transistors. These applications are based on its ability to undergo a reversible structural distortion as a function of temperature that is accompanied by a semiconductor-to-metal transition [7]. Above the transition temperature ($T_c = 67$ °C), VO₂ is metallic and adopts the tetragonal rutile ($P4_2/mnm$) structure with chains of edge-shared VO₆ octahedral along the *c*-axis (the V–V distances along the chain are 2.851 Å). Below T_c , in the semiconducting monoclinic ($P2_1/c$) crystal structure, the vanadium atoms dimerized and have alternate V–V distances of 2.619 and 3.12 Å. The behavior causes large reversible changes of optical and magnetic properties, as well as a change of resistivity by several orders of magnitude.

Nanostructures of VO₂ have been prepared using various techniques. Thin films of thermochromic VO₂ have been obtained by pulsed laser deposition onto SiO₂/Si substrates [8], sol–gel deposition using vanadium alkoxides [9,10], and atmospheric pressure chemical vapor deposition with VOCl₃ [11]. VO₂ nanowires and nanorods have been prepared by hydrothermal methods using glycol reduction [12] or surfactants [13,14], and Liu et al. have recently

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showed that VO₂ nanobelts can be synthesized hydrothermally using formic acid as the reducing and acidifying agent [15]. However, these nanowire, nanorod and nanobelt materials adopt the metastable VO₂-B structure, which does not exhibit the metal to semiconductor transition. Nanoparticles of thermochromic VO₂, on the other hand, have been prepared by pulsed laser deposition followed by thermal oxidation [16,17], and stoichiometric vanadium and oxygen ion implantation [18,19].

VO₂ nanowires of the low temperature monoclinic phase have been prepared by vapor transport method from bulk VO₂ powders in flowing argon [20], but their thermochromic behavior was not reported. Here, we describe the synthesis and thermochromic behavior of VO₂ nanorods through phase conversion of the metastable form, VO₂-B, as reported in Ref. [15]. Other methods of preparing VO₂ nanorods have also been explored in the present work. For example, thermolysis of V (IV) precursors of acetates, glycolates, and tartrates under nitrogen atmosphere yielded tetragonal VO₂ nanorods and nanoparticles. We have also synthesized nanorods of other vanadium oxides by varying the starting materials and conditions in the reaction medium.

2. Experimental

Nanorods of metastable VO₂-B were synthesized hydrothermally, as reported in Ref. 15. NH₄VO₃ (Aldrich) was used as the source of vanadium. In a typical synthesis, formic acid was added to a 10 ml aqueous solution containing 0.1 mol of vanadium, while stirring, until the pH reached ~2.5. The mixture was then sealed in a Teflon-lined autoclave and heated at 180 °C for 2 days. After cooling to room temperature, the precipitate was separated by centrifugation (3000 rpm for 15 min) and the supernatant liquid was discarded. This separation procedure was repeated twice more after additional rinsing with ethanol. The product was then dried in a vacuum oven at 60 °C for 3 h. Conversion of the metastable phase VO₂ nanorods to the thermochromic phase was performed by heating up to 700 °C at 10 °C/min in an N₂ atmosphere. Variations on this synthetic procedure in which we used alternative sources of vanadium, such as VOSO₄ and V₂O₅, in combination with other carboxylic acids, including acetic, oxalic and propionic acids, yielded nanostructures of other vanadium oxides.

Vanadyl acetate and vanadyl glycolate precursors were prepared as reported by Weeks et al. [21]. Vanadyl D,L-tartrate precursor was synthesized in a closed vial containing 10 ml DI-H₂O and stoichiometric amounts of vanadyl acetate and D,L-tartaric acid at 100 °C for 2 days. Blue diamond-shaped crystallites were obtained after cooling to room temperature. The product obtained was rinsed with DI-H₂O and dried in air. All precursors were subjected to thermolysis in a N₂ atmosphere between 500 and 700 °C with a gas flow-rate of 50 ml/min.

X-ray diffraction (XRD) measurements were obtained with a Philips XPERT diffractometer (Cu K α radiation). Variable-temperature infrared spectroscopy (IR) was performed on a Nicolet Magna 850 IR spectrometer. Scanning electron microscopy (SEM) images were obtained using a FEI XL30 Sirion FEG microscope at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed with a FEI T20 microscope operating at 200 kV.

3. Results and discussion

The XRD patterns of the VO₂ nanorods are shown in Fig. 1. The pattern of the as-synthesized sample (Fig. 1a) can be indexed as the metastable VO₂-B phase [JCPDS 81-2392]. In Fig. 1b, the XRD pattern obtained after thermal treatment corresponds to the low temperature monoclinic VO₂ phase [JCPDS 44-0252]. No peaks of any other phases or impurities are observed, suggesting the conversion to thermochromic VO₂ nanorods is complete.

In Fig. 2a, we show the SEM image of the metastable VO₂-B nanorods with diameters ranging between 50 and 100 nm and with lengths extending up to several microns. After phase conversion of the VO₂ nanorods to the thermochromic phase, the overall rod-like morphology is maintained, with the majority of the nanorods having diameters between 50 and 250 nm (Fig. 2b). However, while the length of the nanorods remains nearly constant, we observe a decrease of the average aspect ratio due to agglomeration of neighboring nanorods, with their diameters increasing up to 500 nm; this is expected since grain growth of nanorods becomes more favorable with thermal treatment at high temperatures. A TEM image of the VO₂ nanorods after thermal treatment is shown in Fig. 3a. Selected area electron diffraction (SAED) patterns of individual nanorods reveal that they are single-crystalline (Fig. 3b). Careful analysis of the SAED pattern reveals that the nanorods grow along the [1 0 0] direction, as found in previous work [20].

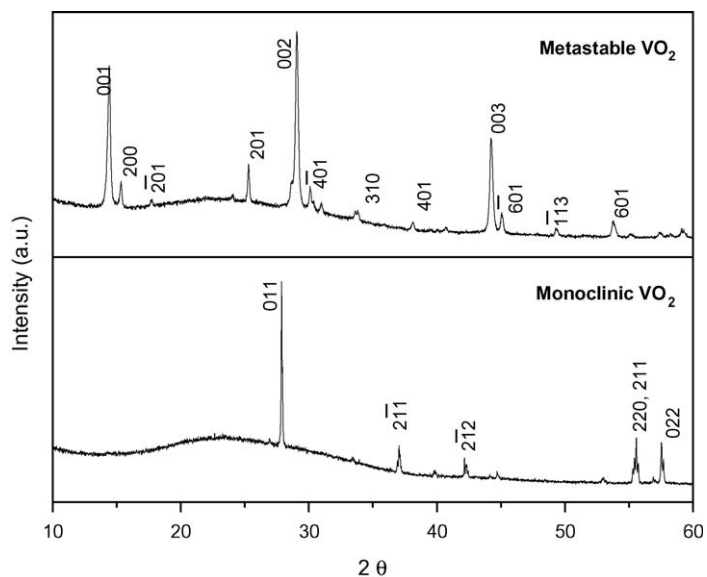


Fig. 1. X-ray diffraction pattern of VO₂ nanorods: (a) before and (b) after thermal treatment.

We have characterized the thermochromic properties of VO₂ nanorods by IR spectroscopy (Fig. 4). Changes in the vibrational modes are observed between 400 and 1000 cm⁻¹ as the thermochromic VO₂ nanorods pass through the monoclinic to tetragonal phase transition between 75 and 80 °C. The transition is also accompanied by a decrease in the transmittance due to the metallic nature of the high temperature phase. The IR response is reversible, changing

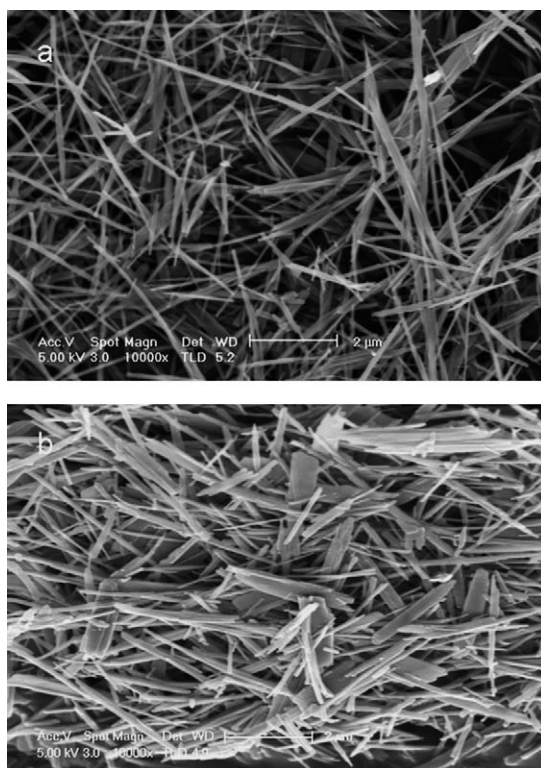


Fig. 2. SEM images of VO₂ nanorods: (a) before and (b) after thermal treatment.

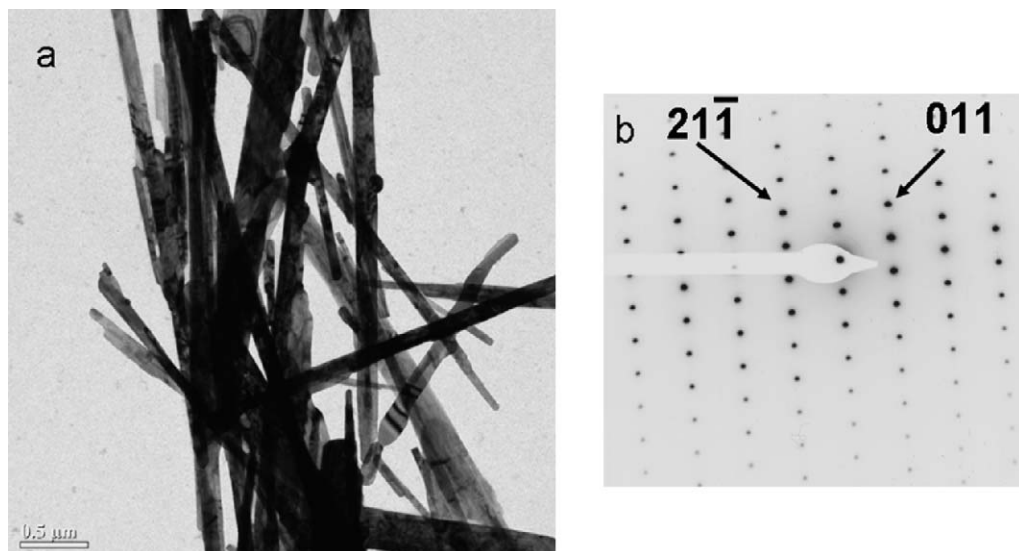


Fig. 3. (a) TEM image of the low temperature monoclinic VO_2 nanorods. (b) SAED pattern of an individual nanorod.

back to the original vibrational spectrum upon cooling. It is noteworthy to point out that the thermochromic transition temperature of the nanorods is slightly higher than that of bulk powders of VO_2 (67°C). Such behavior was reported for the VO_2 nanoparticles by Lopez et al. [17,19]. They concluded that the enhanced thermochromic transition temperature is due to size effects and surface defects. This is in agreement with our observation in the VO_2 nanorods, since their length scale is confined along the c -axis.

Other vanadium oxide nanostructures, including $(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5$, V_3O_7 , and V_2O_5 , were obtained as we explored the use of different vanadium and carboxylic acid starting materials during the hydrothermal synthesis (Fig. 5). Table 1 summarizes the products obtained under similar conditions of temperature, time, and pH to those used in the synthesis of metastable VO_2 nanorods. The nanorods and nanowires of $(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5$, V_3O_7 , and V_2O_5 were turquoise, green, and yellowish green color, respectively.

Nanostructures of tetragonal rutile VO_2 were obtained after thermolysis of V (IV) precursors (Fig. 6). In Fig. 6a and b, we show TEM images of VO_2 nanostructures obtained after thermolysis of vanadyl acetate and glycolate,

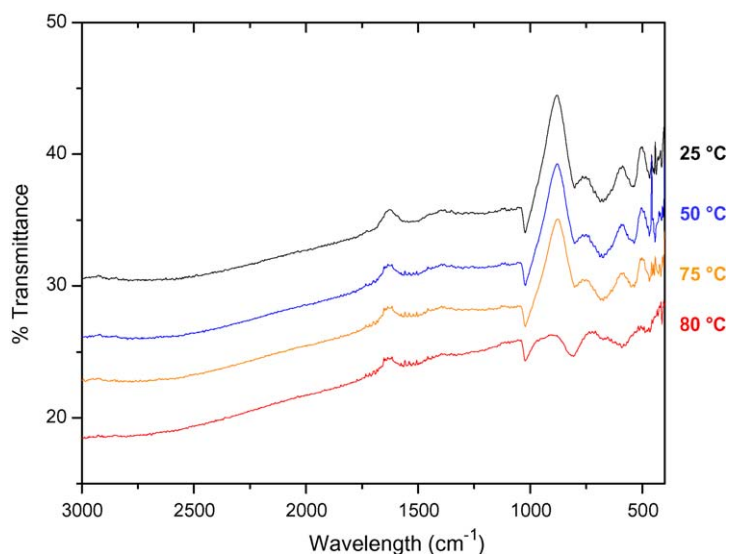


Fig. 4. Evolution of the infrared spectra as a function of temperature showing thermochromic behavior of VO_2 nanorods.

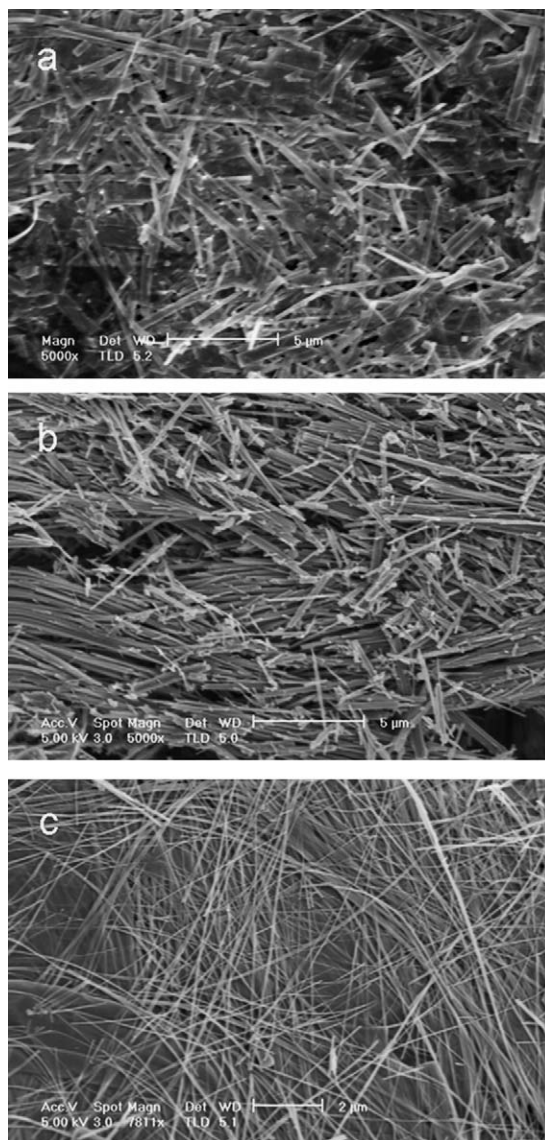


Fig. 5. SEM images of vanadium oxides nanostructures obtained: (a) $(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5$, (b) $\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$, and (c) V_2O_5 .

Table 1

Nano- and sub-micron structures of vanadium oxides synthesized hydrothermally at 180 °C for 2 days

	Reagents of vanadium NH_4VO_3	$\text{VOSO}_4\cdot\text{H}_2\text{O}$	V_2O_5
Formic acid	VO_2 , 1D nanowires 50–100 nm	VO_2 , 1D nanowires 150 nm	$\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}^a$, 1D nanowires 75–175 nm
Acetic acid	$(\text{NH}_4)_{0.5}\text{V}_2\text{O}_5^a$, 1D nanowires 100–200 nm	$\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$, 1D nanowires 100–150 nm	V_2O_5 , 1D nanowires 100–150 nm
Propionic acid	VO_2 , 1D nanowires 100–400 nm	$\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$, 1D nanowires 100–250 nm	V_2O_5^a , 1D nanowires 50–100 nm
Oxalic acid	VO_2 , square platelets 200–400 nm	$\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$, 1D nanowires 75–150 nm	$\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$, 1D nanowires 150–250 nm
Malonic acid	V_2O_5 , no nanowires obtained	$\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$, 1D nanowires 150–200 nm	V_2O_5 , 1D rods $\sim 0.5 \mu\text{m}$
Succinic acid	V_3O_7 , 1D nanowires 40–80 nm	$\text{V}_3\text{O}_7\cdot\text{H}_2\text{O}$, 1D nanowires 100–200 nm	V_2O_5 , 1D rods 100 nm–1 μm

The pH was adjusted to 2.5–3 using the carboxylic acids indicated. Diameters and morphology of the respective oxide are indicated.

^a SEM images illustrated in Fig. 5.

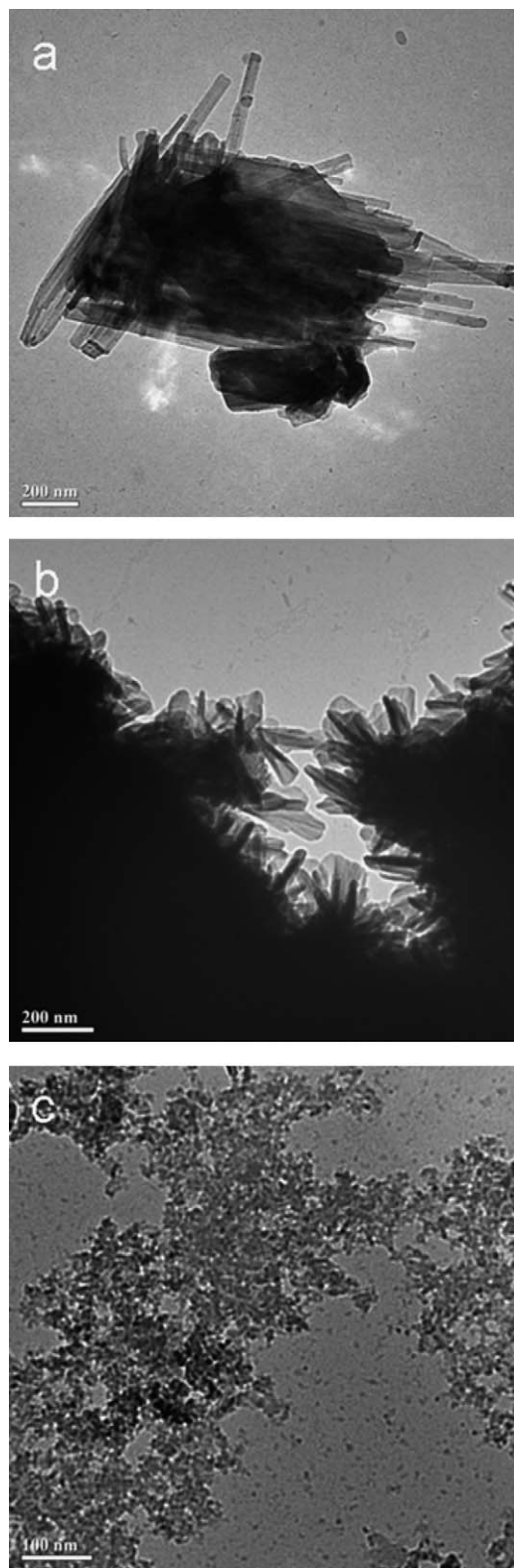


Fig. 6. TEM images of VO_2 obtained from (a) vanadyl acetate, (b) vanadyl glycolate, and (c) vanadyl D,L-tartrate.

respectively. It appears that the rod-like morphology with diameters between 30 and 60 nm may be driven by the precursors' 1D chain crystal structures. Additionally, the choice of precursor seems to play a role in the formation of VO₂, as the aspect ratio resulting from the glycolate is smaller than that from the acetate precursor. Fig. 6c shows tetragonal VO₂ nanoparticles that were obtained from thermolysis of vanadyl D,L-tartrate; these have an average particle size between 15 and 25 nm, as estimated from the TEM image. Though we were able to obtain nanowires and nanoparticles by the precursor route, we did not observe any thermochromic behavior upon heating or cooling these samples.

4. Conclusion

In summary, we have explored various synthetic routes for the formation of VO₂ nanostructures with thermochromic properties. We were able to obtain low temperature monoclinic VO₂ nanorods by conversion of the metastable VO₂-B obtained by hydrothermal synthesis. Interestingly, we found that the thermochromic transition temperature of VO₂ nanorods is ~10 °C higher compared to bulk VO₂. We have also obtained nanowires and nanostructures of other vanadium oxides by varying the reaction medium. In addition, thermolysis of V (IV) precursors provides nanostructures of tetragonal rutile VO₂ nanorods and nanoparticles, though no thermochromic properties were exhibited.

Acknowledgements

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