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ARTICLE

Hydrothermal Synthesis and Phase Transition Properties of Uniform Free-standing Vanadium Dioxide Nanowires

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Abstract: Vanadium dioxide (VO_2) undergoes a Mott metal-insulator transition (MIT) close to room temperature, and has been suggested as a candidate for use in smart window and adaptive infrared camouflage. Here we report the synthesis of uniform free-standing VO_2 nanowires using a novel hydrothermal method. The synthetic nanowires have typical diameters of 150±30 nm and lengths of tens of micrometer. These VO_2 nanowires exhibit high crystallinity and a pure monoclinic phase, which were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, high resolution transmission electron microscopy and selected area electron diffraction. Moreover, reversible phase transition properties of VO_2 nanowires are monitored via differential scanning calorimetry, variable temperature X-ray diffraction and temperature-dependent Raman spectroscopy. The results show VO_2 nanowires obtained exhibit a reversible phase transition with an endothermic phase transition at 65.2 °C and a narrow hysteresis width of 6.5 °C. These VO_2 nanowires should be promising materials for fundamental investigations of nanoscale metal-insulator transitions.

Key words: vanadium dioxide; nanowires; hydrothermal; phase transition

Vanadium dioxide (VO_2) is one of the most interesting materials owing to its orders-of-magnitude first-order metal-insulator transition (MIT) at a temperature slightly above room temperature (T_c=68 °C)[1]. This fortunate circumstance has inspired considerable interest in device architectures that can take advantage of the abrupt switching of electrical and optical properties accompanying this phase transition [2]. Exploiting these switching behaviors across the MIT, a number of applications have been demonstrated or proposed in smart window[3-5], optical switches[6-8], Mott transistors[9,10], strain sensors [11-13], and adaptive thermal camouflage [14-17]. One-dimensional (1D) VO_2 nanowires have attracted a great interest as building blocks used for the fabrication of nanodevices, which triggers a wide range of subsequent research in searching for newer synthetic methods. There have been many existing preparative techniques for this material. Among them, a vapor transport and thermal evaporation are the two major vapor methods to fabricate one-dimensional VO_2 nanowires[18-23]. In addition to these techniques, it is well conceived that preparation of VO_2 nanowires via solution chemical routes provides a promising option for large-scale production of this material. Although they have long been used for VO_2 single-crystal nanowires growth[2,24-29], wet-chemical approaches still face the problems of polydispersity and complicated processes in post-synthesis heating treatment. Very recently, single crystalline VO_2(A) nanowires were synthesized by a hydrothermal method using oxalic acid as reducing agent and polyethylene glycol 6000 as surfactant[30]. Although high quality VO_2 (A) nanowires have been obtained, the reported method requires an additional surfactant as additive and cannot produce single-shaped and well-crystallized morphology. Therefore, it is still a

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meaningful challenge to develop a novel approach for producing uniform free-standing VO_2 nanowires in aqueous solution.

In the present work, we report a novel one-step hydrothermal method to synthesize uniform VO_2 nanowires with a significant advance in representing the first case for directly synthesizing VO_2 nanowires without additional surfactant as additive. Furthermore, the phase-transition properties of VO_2 nanowires were studied via variable temperature X-ray diffraction (XRD) and temperature dependent Raman spectroscopy.

1 Experiment

All reagents were purchased from Aladdin chemical reagent corporation and used without further purification. VO_2 nanowires were prepared by a novel one-step hydrothermal method using a vanadium source of V_2O_5 and a reducing agent of stearic acid without additional surfactant as additive. In a typical synthesis, 1.82 g Vanadium pentoxide (V_2O_5, analytically pure) and 8.54 g stearic acid ($C_{18}H_{36}O_2$, analytically pure) were dispersed in 60 mL deionized water. The mixture was stirred for 30 min and then transferred to a 100 mL Teflon-lined stainless-steel autoclave. The hydrothermal reaction was carried out at 260 °C for 24 h and then air-cooled to room temperature. The final products were collected via centrifugation, washed with acetone and ethanol three times and dried in a vacuum drying oven at 80 °C for 10 h.

Powder XRD characterization of the prepared materials was performed using monochromatic Cu Kα radiation with a D8ADVANCE diffractometer (Bruker, Germany). Infrared absorption spectra were recorded with a Bruker Vertex 70 FTIR instrument using KBr pellet method. The morphology was obtained using a field-emission scanning electron microscope (FESEM, NOVA NanoSEM 230). The microstructure of the samples was further analyzed using a transmission electron microscopy (TEM, JEOL2010) with a LaB6 source operating at an acceleration voltage of 200 kV. Selected area electron diffraction experiments were carried out in vacuum in a JEOL 2100 transmission electron microscope working at 200 kV. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The phase transition behaviors of the resulting products were measured by differential scanning calorimetry (DSC1, METTLER TOLEDO) over the temperature range from 0 to 100 °C using a liquid nitrogen cooling unit. The heating and cooling rates were set at 10 °C /min.

Variable temperature XRD data were obtained using a diffractometer (Rigaku TTR-III) equipped with a with a Cu Kα radiation (λ=0.15418 nm). Under steady N_2 flow, the sample was heated (from 30 °C to 70 °C) and cooled (from 70 °C to 30 °C) inside a Rigaku Reactor-X chamber fitted with a Beryllium window. Temperature dependent Raman spectroscopy was recorded using a Horiba JY HR Evolution Spectroscopy System. The excitation wavelength is 532 nm, with laser power kept at 1 mW to ensure that thermal heating due to the laser focusing does not trigger the MIT. External sample temperature was controlled via a programmable heating- cooling stage.

2 Materials and Methods

2.1 Characterization

The XRD pattern of a sample obtained at 260 °C for 24 h is shown in Fig.1a as a representative. All peaks can be indexed as a single monoclinic phase VO_2 (M) (JCPDS. Card. No. 43-1051). It can also be seen that all of the peaks are sharp and strong with relatively narrow peak widths, indicating the good crystallinity of VO_2 (M). The results indicate that phase-pure and well-crystallized VO_2 (M) nanowires can be synthesized by such a novel one-step hydrothermal method.

To investigate the chemical bonding between vanadium and oxygen ions and to confirm the phase purity, we performed FTIR spectrum measurement. Fig.1b shows the FTIR spectrum of VO_2 (M) sample prepared. The main vibrational bands observed from the FTIR spectrum are at 995, 735, 524, 433 cm^{-1} and can be considered as intrinsic to vanadium dioxide, which matches well with earlier reports: the initial broad vibrational band at 524 cm^{-1} and 433 cm^{-1} are assigned to the V-O-V octahedral bending modes; the band at 995 cm^{-1} and 735 cm^{-1} is attributed to the coupled vibration of V═O [31-34]. These FTIR observations confirm that the nanowires correspond to the VO_2 phase.

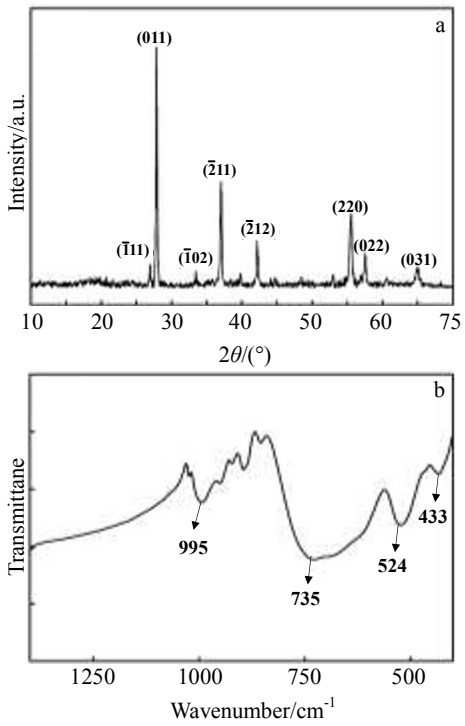

Fig.1 XRD patterns acquired for as-synthesized VO_2 nanowires (a) and FTIR spectrum of VO_2 sample prepared (b)