

W-doped VO₂ (M) with tunable phase transition temperature

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Abstract: W-doped VO₂ (B) nanoneedles were successfully synthesized by sol-gel combing with hydrothermal treatment, in which the polyethylene glycol (PEG) was used as both surfactant and reducing. The metastable VO₂ (B) was completely transformed to thermochromic VO₂ (M) after annealing at high purity N₂ atmosphere. The DSC results exhibit a strong crystallographic transition, and the phase transition temperature of VO₂ (M) can be reduced to about 38 °C by W-doping. Field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HR-TEM) were used to characterize the morphology and crystalline structure of the samples. The variable-temperature infrared transmittance spectra of VO₂ (M) demonstrate their potential applications in energy saving field.

Introduction

Vanadium dioxide (VO₂) can adopt several kinds of polymorphic forms, such as, VO₂ (M),[1] VO₂ (R),[2] two metastable forms VO₂ (A)[3] and VO₂ (B),[4] VO₂ (C)[5] and orthorhombic VO₂, depending strongly on the arrangement of VO₆ octahedra. The diversity of phase structures result in the widely physical and chemical properties of VO₂. Among them, VO₂ (B) has great promising application as cathode materials in lithium battery owing to its proper electrode potential and layer structure, which is benefit for Li-ions intercalation and de-intercalation;[6] VO₂ (M) exhibits an insulator to metal structural phase transition (VO₂ (M) ↔ VO₂ (R)) at ~68 °C accompanied by an abrupt change in the optical and electrical properties,[1] and has extensive applications ranging from intelligent window coatings,[7, 8] optical and electrical nanodevices,[9, 10] strain sensor[11] to gas sensor.[12] In view of the practical applications, it is desirable to depress the phase transition temperature of VO₂ from 341K to near room temperature. It is widely accept that the doping is an effective mean to control the phase transition temperature, and tungsten has been shown to be the most affective dopant in manipulating the phase transition temperature of VO₂.

Solution-based methods were exploited to synthesize devious structure of VO₂, including nanorods,[13, 14] nanobelts,[15, 16] microcrystals[17] and spherical particles.[18] A general strategy for producing VO₂ with a facile and low-cost method, however, remains a great challenge, because, in some cases, special equipments or expensive raw materials are indispensable, which is far away from the level of practical application. Consequently, a proper synthesis strategy of VO₂ (M) is essential in achieving the applications in energy saving field.

Each of synthetic strategies occupies some advantages in its own right, but the current trends in the synthesis of nanomaterials definitely point to the combination of the synergistic effect of different approaches as innovative routes to prepare nanomaterials.[19] The combination of classical sol-gel process with hydrothermal approach is a promising method to prepare vanadium oxides. By means of this composite method, vanadium oxides nanotubes were synthesized by Nesper et al.;[20] Chen and Mai et al. fabricated vanadium oxides nanotubes, nanorods by inorganic sol-gel coupled with a hydrothermal approach.[21, 22] However, the stoichiometric of these vanadium oxides is uncertain.

Herein, we report the synthesis of defined W-doped VO₂ by a PEG assisted hydrothermal treatment of V₂O₅ sol, which is a simple and low cost method. The direct product of hydrothermal was metastable monoclinic phase VO₂ (B), which could be completely transformed to VO₂ (M) phase by subsequent thermal treatment under high purity N₂ atmosphere at 700°C. The DSC results displayed a first-order metal-semiconductor phase transition of VO₂ (M), and the phase transition temperature was successfully reduced from 68 °C to about 37.22 °C through tungsten doping. The variable-temperature infrared transmittance spectra demonstrate the potential applications of VO₂ (M) in energy saving field.

Experimental section

The W-doped V_2O_5 sol was obtained by melt quenching process. The powder mixture of V_2O_5 (99.9 %) and ammonium tungstate ($N_5H_{37}W_6O_{24}H_2O$) was heated up to $850\text{ }^\circ\text{C}$ in a alumina crucible until molten, then quickly poured into distilled water at room temperature. After vigorous stirring of one day, a red V_2O_5 sol was obtained. In a typical reaction, 25 % PEG-6000 solution was added into W-doped V_2O_5 sol (volume ratio: $V_{\text{sol}}:V_{\text{PEG}}=1:4$) to form a homogeneous precursor, and hydrothermal treatment at $200\text{ }^\circ\text{C}$ for two days. After cooling down to room temperature, the precipitates were collected and washed with copious amounts of deionized water and ethanol alternately, and then dried at $70\text{ }^\circ\text{C}$ in air. The precipitates were further heat-treated under high purity N_2 atmosphere at $700\text{ }^\circ\text{C}$ for 2 hrs. X-ray diffraction (XRD) using $\text{Cu K}\alpha_1$ line (Philips X'Pert), Field emission scanning electron microscopy (FESEM, Sirion 200) and transmission electron microscope (TEM, JEM-2010) were used to investigate the structure and morphology of the obtained materials. Differential scanning calorimetry (DSC) analysis was performed using a Dupont differential thermal analyzer under nitrogen flow with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. The Fourier transform infrared (FTIR) spectroscopy was performed by a Bruker Vector-22 FTIR spectrometer.

Results and Discussion

Fig. 1 shows the XRD pattern of the precipitates after hydrothermal treatment of the precursor at $200\text{ }^\circ\text{C}$ for two days, all the diffraction peaks can be indexed to metastable monoclinic crystalline phase of VO_2 (B) (JCPDS: 81-2392). No characteristic peaks of impurity phases or tungsten oxide are found, indicating VO_2 (B) is the only phase present.

Fig. 2a shows the typical SEM image of the VO_2 (B) nanorod, from which one can see that the nanorod is needle-like with length of about $1\text{-}2\text{ }\mu\text{m}$ and diameter of $80\text{-}150\text{ nm}$. The high magnification SEM image shown in Fig. 2b clearly displays that the tip-top parts of the nanorods which have the lateral dimension gradually shrunk from $60\text{-}90\text{ nm}$ to $15\text{-}25\text{ nm}$. The needle-like

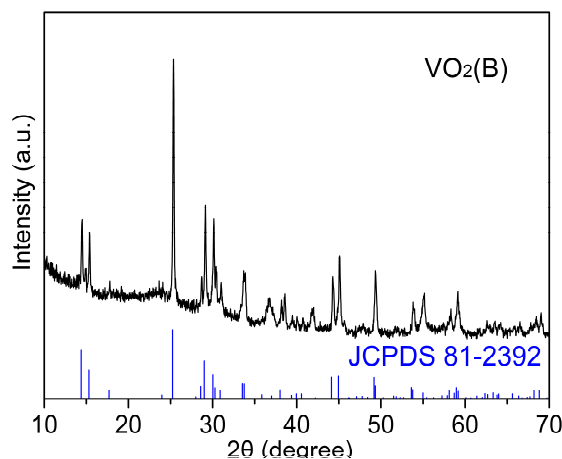


Fig. 1 XRD pattern of VO_2 after hydrothermal treatment of W-doped V_2O_5 sol at $200\text{ }^\circ\text{C}$ for 2 days together with that from JCPDS card No. 81-2392 of monoclinic phase VO_2 (B).

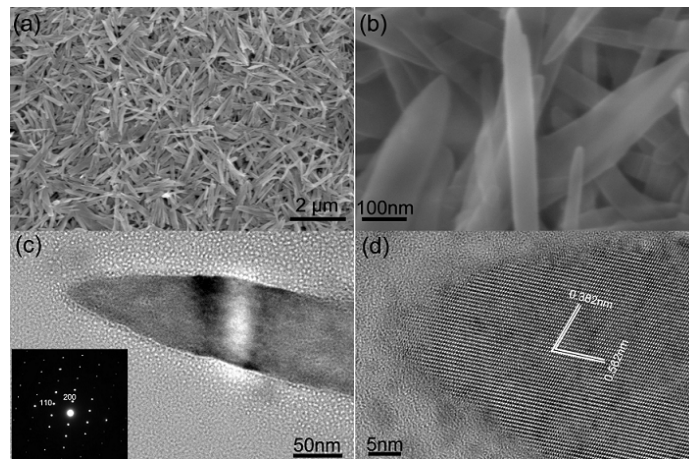


Fig. 2 (a) and (b) SEM images of $\text{VO}_2(\text{B})$ nanoneedles; (c) TEM of a single $\text{VO}_2(\text{B})$ nanoneedle and the inset is the SAED pattern; (d) HRTEM images corresponding to the top part of the nanoneedle in Fig. 2c.

feature can be clearly observed from TEM image shown in Fig. 2c. The corresponding SAED can be indexed as (110) and (200) reflections according to monoclinic metastable phase $\text{VO}_2(\text{B})$, as shown in the inset of Fig. 2c. Significantly, the diffraction pattern did not change as the electron beam moved along the nanoneedle, indicating that the nanoneedle is a single crystal. The detail structure of $\text{VO}_2(\text{B})$ nanoneedles is further examined by HRTEM, as shown in Fig. 2d, the interplanar distances of 0.382 nm and 0.562 nm match with the d_{110} and d_{200} spacings of $\text{VO}_2(\text{B})$, respectively.

The oriented attachment (OA) model is considered responsible for the formation of $\text{VO}_2(\text{B})$ nanoneedles in inorganic V_2O_5 sol under hydrothermal environment, as reported in our previous papers.[23-25] Shortly, the V_2O_5 nanofibers in the sol oriented attach with each other firstly, and then, the subsequent coalescence and further assemble leads to the formation of nanostructure of vanadium oxides. In addition, it is worth to note that W-doping does have profound effect on the morphology of VO_2 . It is well known that different crystal faces have different atomic arrangements,

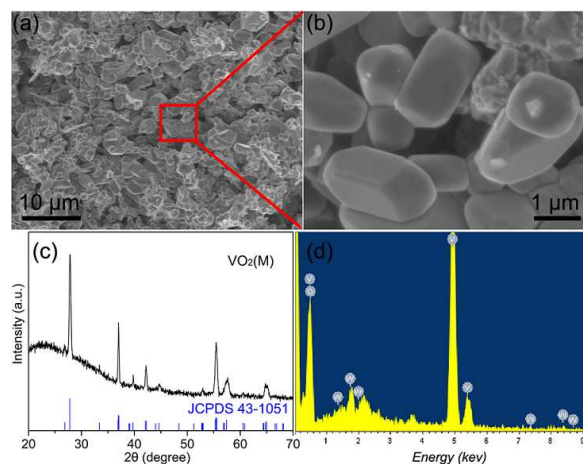


Fig. 3 (a) and (b) SEM images of $\text{VO}_2(\text{M})$, prepared by heating the metastable $\text{VO}_2(\text{B})$ in high purity N_2 at 700°C for 2hrs, (c) XRD pattern of $\text{VO}_2(\text{M})$ together with that from JCPDS card no.43-1051 and (d) EDX of W-doped $\text{VO}_2(\text{M})$.

which results in different surface energies and the disparity in growth rate, and these differences finally determine the shape of the crystal as it grows. Owing to the low solubility of V_2O_5 in the original sol, during the initial growth, the nucleation and growth along the preferential orientation of $\text{VO}_2(\text{B})$ would be accelerated until the dissolved V_2O_5 is exhausted, which result in the formation of $\text{VO}_2(\text{B})$ nanoneedles.

Fig. 3a shows the SEM image of W-doped VO₂ (M) after thermal treating of VO₂ (B) in high purity nitrogen environment at 700 °C for 2 hrs, from which one can see that the size of VO₂ (M) increases substantially after annealing treatment. The higher magnification SEM observations indicate that the dimension of VO₂ (M) is in the micrometer range (Fig. 3b). Fig. 3c shows XRD pattern of W-doped VO₂ (M). One can see that the VO₂ (B) phase has completely transformed to VO₂ (M) (JCPDS card no. 43-1051), no other peaks were detected, indicating VO₂ (M) is the only present phase. Fig. 4d shows energy dispersive X-ray spectroscopy (EDX) analysis results, which show only W, V and O, the Cu signal is attributed to the copper mesh used for HRTEM. No evidence of other impurities is detected, which agrees well with the XRD analysis result.

When the phase transition occurs, VO₂ (M) exhibits a noticeable thermal flow in the DSC curve. The typical DSC curves of W-doped VO₂ (M) are shown in Fig. 4. It can be seen that the endothermic and exothermal peaks are sharp and symmetrical. The un-doped VO₂ (M) shows a phase transi-

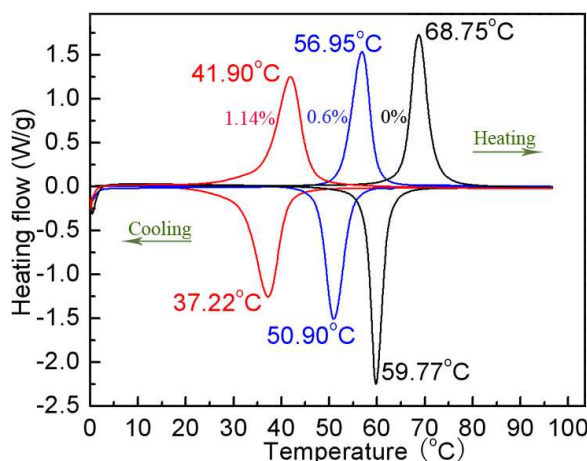


Fig. 4 DSC curves of W-doped VO₂ (M) with different W doping concentrations.

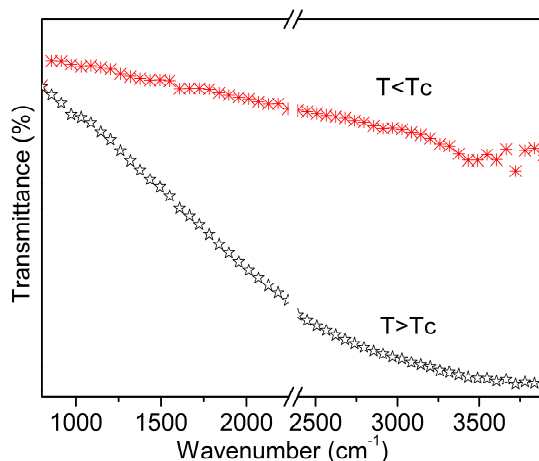


Fig. 5 Infrared transmittance spectra of W-doped VO₂ (M) phase, above and below the phase transition critical temperature (T_c).

tion critical temperature of about 68.75°C and 59.77°C in heating and cooling cycles, respectively. While, upon 0.6 and 1.14 at% W-doping, the phase transition temperature decreases respectively to 56.95 °C and 41.90 °C in heating process, and to 50.9 °C and 37.22 °C during cooling.

Fig. 5 shows infrared transmittance spectra of W-doped VO₂ (M), and an abrupt change in transmittance can be clearly seen at above and below the phase transition temperature. This result indicates that the phase transition temperature can be effectively depressed via W-doping, and the hysteresis loop is narrow enough for the application of VO₂ in the field of energy saving, take smart windows for instance.

Summary and Outlook

In summary, the present work suggests a method to synthesize W-doped VO₂ (M) with tunable phase transition temperature. The phase transition temperature has been depressed to as low as 37.22 °C from the 59.77 °C through W doping. Our method may be extended the preparation of other materials based on nanoscale building blocks via hydrothermal treatment sol.

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