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The character of W-doped one-dimensional VO_2 (M)

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ABSTRACT

The one-dimensional W-doped VO_2 (M) solid solutions with a various doped content were successfully synthesized under hydrothermal condition and subsequent calcination for the first time, and physical–chemical and phase transformation character were explored, subsequently. DSC analyses displayed that the phase-transition temperature of VO_2 (M) solid solution could be linearly tuned with the doped content. Promisingly, the one-dimensional W-doped VO_2 (M) had a good thermochromic property.

1. Introduction

Vanadium dioxide with monoclinic-type structure VO_2 (M) has attracted much interest because it has been observed to undergo a reversible phase transition at about 68 °C, accompanied by a structural transformation between a low temperature monoclinic phase and a high temperature tetragonal phase [1,2]. This is a fully reversible metal-semiconductor phase transition (MST) associated with drastic changes in electrical conductivity and optical properties in the IR region [3]. These features make VO_2 suitable for applications in various areas, such as intelligent energy conserving windows coating [4], electrical and infrared light switching device [5,6], storage medium [7], and so on. However, it is more practical to reduce its phase-transition temperature (T_c) closer to a comfortable room temperature value, especially for intelligent energy conserving windows coating [8]. Doping studies have shown that the transition temperature can be altered by the incorporation of ions into the VO_2 lattice, such as molybdenum, tin, niobium, aluminum, and gold. It was found that the most effective metal ion was tungsten, which can cause a reduction in the VO_2 thermochromic switching temperature of 19–25 °C per W at% [9,10].

So far, the study on W-doped VO_2 (M) mainly focuses on thin films and particles. W-doped VO_2 films have been prepared by a variety of methods including sol–gel [11], sputtering [12], and CVD [4,10] methodologies. However, it has been found that these methods are not suitable for coating the surface of substrates with a large surface area and/or complex morphology due to both technical and cost problems. Recently, Peng et al. [13] reported the synthesis of W-doped VO_2 (M) nanopowder by thermolysis, which can make the phase transition temperature decrease to near-ambient temperature. Yet, these prepared powders have irregular morphologies, which would change the transition behavior.

Recently, one-dimensional (1D) nanostructures of vanadium oxides, such as nanowires [14], nanobeams [15], nanorods [16,17], nanobelts [18], and nanotubes [19], are attracting much interest because of their high aspect ratio and easy diffusion path for carrier transport [20]. Taken the single-crystalline VO_2 nanobeams as an example, Gu et al. [15] observed a current-driven metal (M)–insulator (I) phase oscillation in two-terminal devices, and Wu et al. [21] investigated the effect of substrate-induced strain on the metal–insulator transition (MIT) in single-crystalline VO_2 nanobeams. In addition to that, VO_2 one-dimensional nanomaterials can provide an ideal model for the research of MIT property in nanoscale.

Usually, we can synthesize vanadium oxides and tungsten oxides nanomaterials with higher production under a low pH value through a hydrothermal process [18,22]. In addition, VO_2 crystal can grow along [010] direction and form one-dimensional nanostructrure under a hydrothermal condition when the pH value is about 2–3 [18]. Based on above analyses, we managed to make tungsten dope into vanadium dioxide and form one-dimensional nanostructure by a hydrothermal process.

In the present work, we synthesized one-dimensional W-doped VO_2 (B) nanostructure with various doped contents through co-precipitation under a hydrothermal condition. The

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one-dimensional W-doped VO_2 (M) solid solutions were subsequently obtained through thermal treatment. The one-dimensional doping can cause a decrease in phase transition temperature (T_c) of 20 °C per W at% without deterioration of the thermochromic property.

2. Experimental section

All of the chemical reagents were of analytical grade and used as received.

2.1. Preparation of one-dimensional W-doped VO_2 (B) nanostructure

The synthesis of one-dimensional W-doped VO_2 (B) nanostructure with different amounts of tungsten was based on the hydrothermal process reported by Li et al. [18]. In a typical synthesis, 2 mmol ammonium metavanadate (NH_4VO_3) and ammonium tungstate ($N_5H_{37}W_6O_{24}\cdot H_2O$) with different W/V molar ratios (W/V: 0%, 0.5%, 1.0%, 1.5%, 3.0%) were dissolved in 20 mL deionized water to form a light yellow clear solution. Formic acid was then added dropwise to the above solution under stirring until the final pH of the solution reached about 2–3. A clear orange solution was formed and the resultant solution was then transferred into a Teflon-lined autoclave with a stainless-steel shell. The autoclave was kept at 180 °C for two days and then allowed to cool to room temperature. The final product was washed with deionized water and pure alcohol for several times to remove any other possible residues and naturally dried in the air.

2.2. Preparation of one-dimensional W-doped VO_2 (M) solid solution

The hydrothermal product was heated in a tube furnace with 5 °C min^{-1} heating rate under a flow of nitrogen gas at 700 °C for 2 h, and cooled to room temperature in the nitrogen flow to prevent oxidation of vanadium dioxide. One-dimensional W-doped VO_2 (M) solid solutions were obtained through phase transition.

2.3. Characterization

The chemical composition of as-obtained samples was explored by ICP Optical Emission Spectrometer (Varian 710–ES). The morphologies and structures were obtained by a transmission electron microscope (TEM; JEOL JEM-200CX) and a scanning electron microscope (SEM; S-4300). The structure of the samples was determined by X-ray diffraction (XRD; Bruker D8 Focus and Cu$K\alpha$ radiation at 1.54056 Å). Differential scanning calorimetry (DSC) experiments were performed using a Dupont differential thermal analyzer under nitrogen flow in the range of 0–100 °C

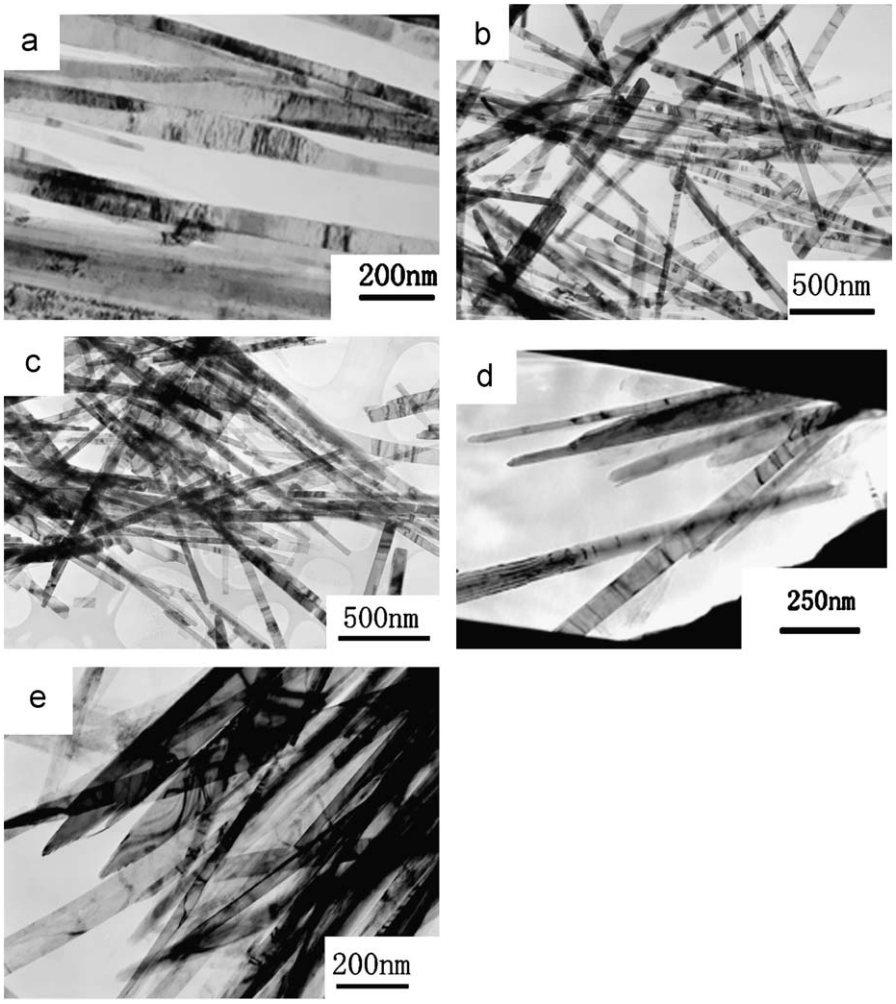

Fig. 1. TEM images of one-dimensional W-doped VO_2 nanobelts with different tungsten-doping contents: (a) 0%, (b) 0.5045%, (c) 0.9985%, (d) 1.4962%, and (e) 3.0008 at%.

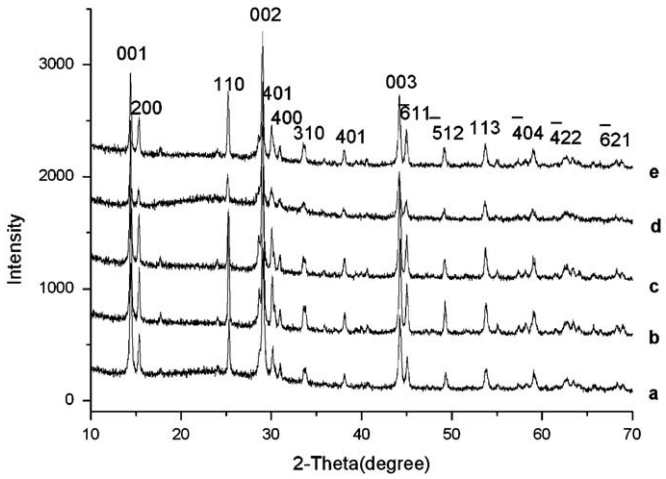

Fig. 2. XRD results of the as-prepared W-doped VO_2 one-dimensional nanobelt, the experimental condition is the same as that in Fig. 1.

with a heating rate of 2 K min^{-1}. The thermochromic performance was measured by a FT-IR Spectrometer (Excalibur 3100).

3. Results and discussion

3.1. One-dimensional W-doped VO_2 (B) nanostructure

As observed in Fig. 1, the average diameters and lengths of as-prepared one-dimensional nanobelts were 50–100 nm and several micrometers, respectively. And the W doping had no influence on the morphology of the products.

As Fig. 2 shows the XRD patterns of as-prepared VO_2 nanobelts were well crystallized and consistent with JCPDS 81-2392, indicating VO_2 (B) character. Compared with the XRD patterns of undoped nanobelts, W doping had little influence on the crystal structure of VO_2 (B) belts. And the peaks related to tungsten oxide were not observed.

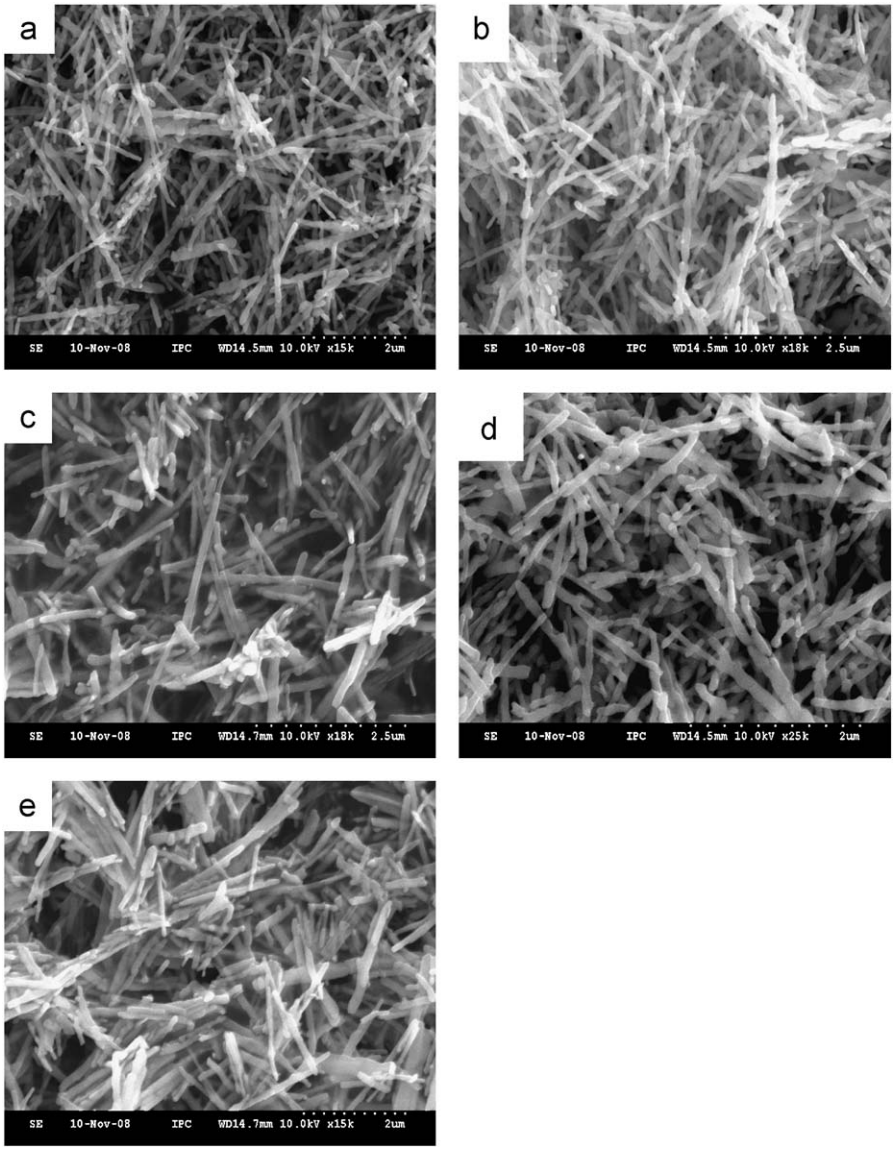

Fig. 3. SEM images of the one-dimensional W-doped VO_2 (M), and the tungsten doped content is the same as in Fig. 1.

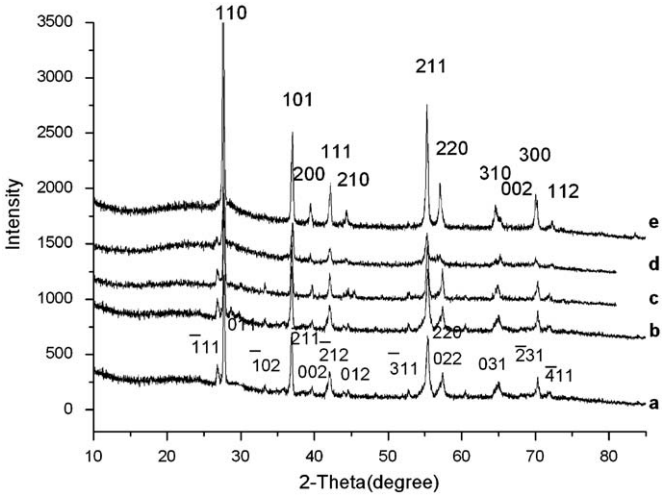

Fig. 4. XRD patterns of the one-dimensional W-doped VO_2 solid solution. The tungsten doped content is the same as in Fig. 1.

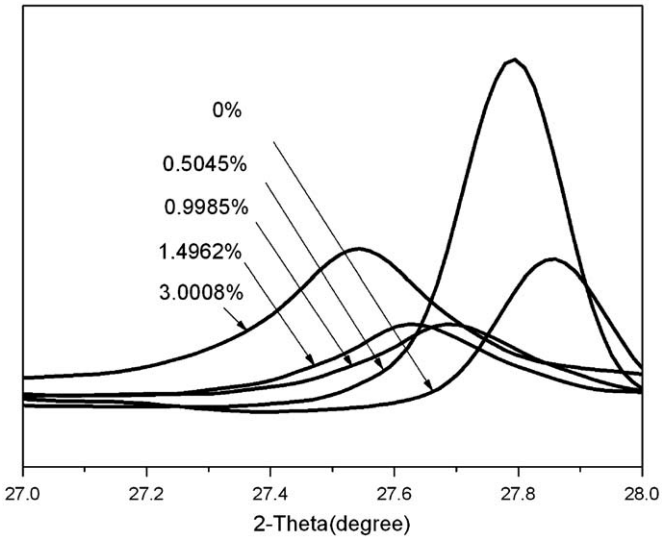

Fig. 5. The magnified XRD patterns of the one-dimensional W-doped VO_2 (M) solid solution in the range of 27° and 28°; and the number in the chart is the W doped content.

3.2. *One-dimensional W-doped VO_2 (M) solid solution*

A solid solution could be obtained after heating the as-prepared W-doped VO_2 (B) at 700 °C for 2 h. Fig. 3 shows the SEM images of one-dimensional W-doped VO_2 (B) after the heat treatment. Obviously, the thermal treatment had little influence on the one-dimensional structure, the width of the nanobelts, however, increased to 100–300 nm due to the growth or aggregation by surface and boundary diffusion during thermal treatment.

As Fig. 4 exhibites the one-dimensional W-doped VO_2 solid solution (0%, 0.5045%, 0.9985%, 1.4962%) were well crystallized and consistent with JCPDS 43-1051, showing VO_2 (M) character; and one-dimensional VO_2 (R) (JCPDS 71–421) structure could be got when W contents reached 3.0008%. Fig. 5 clearly shows that the (110) peak shifted toward small reflection angle with increasing W-doping fraction, meaning the adjacent interplanar distance (*d*-value) slightly increased. The slight increase in the *d*-value should be attributed to the larger size of tungsten atom than vanadium atom [11]. The (110) peak for the monoclinic phase disappeared when the W content reach 3.0008%, and a new peak due to the (110) tetragonal reflection was observed at slightly lower 2θ, demonstrating the phase transition from monoclinic phase to tetragonal phase. In addition, the peaks related to tungsten oxide were not observed.

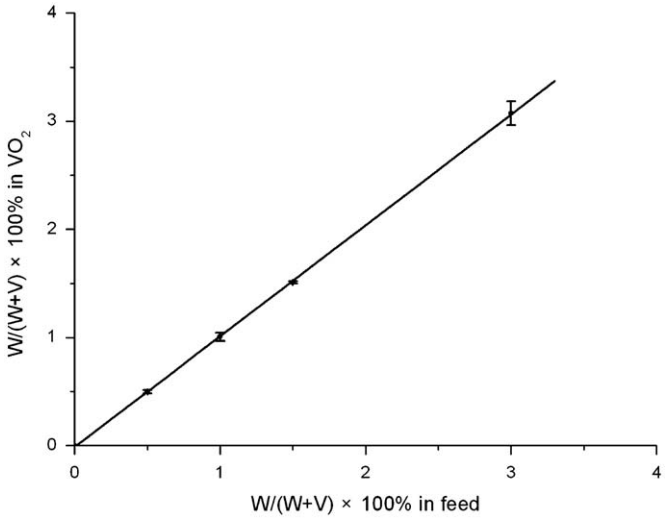

Fig. 6. Relationship of the W atomic percent in W-doped VO_2 (M) solid solution and W atomic percent fed.

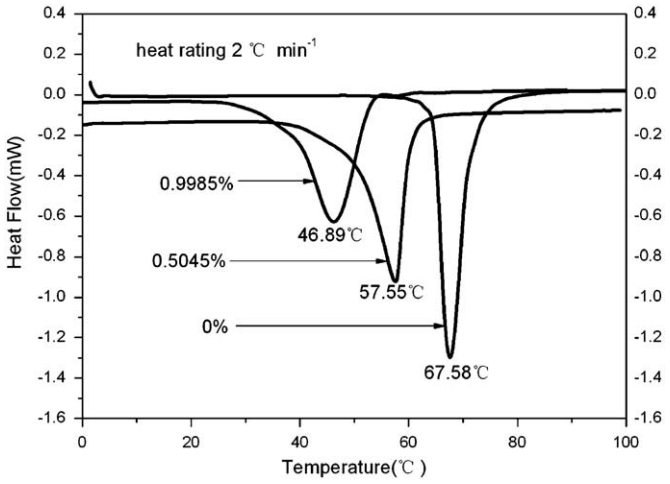

Fig. 7. DSC results of the W-doped VO_2 (M) solid solution and the number in the chart is the W doped content.

The W atomic percent doped in one-dimensional W-doped VO_2 (M) solid solution as a function of fed atomic percent was presented in Fig. 6. The W atomic percent in W-doped VO_2 (M) solid solution was almost the same as the W atomic percent fed, indicating that the W content in VO_2 (M) solid solution could be easily controlled by the change of tungstate concentration in the precursor solution in our process.

When the phase transition of VO_2 (M) occurred, it exhibits a noticeable endothermal profile in the DSC curve. The temperature of this endothermal profile corresponds to the VO_2 (M) phase change [13]. The typical DSC curves of the W-doped VO_2 (M) solid solution with various W fractions were manifested in Fig. 7. It can be seen that there was an endothermic phase transition in each of the DSC curves, where the phase transition temperature of un-doped VO_2 (M) solid solution was 67.58 °C. The T_c of one-

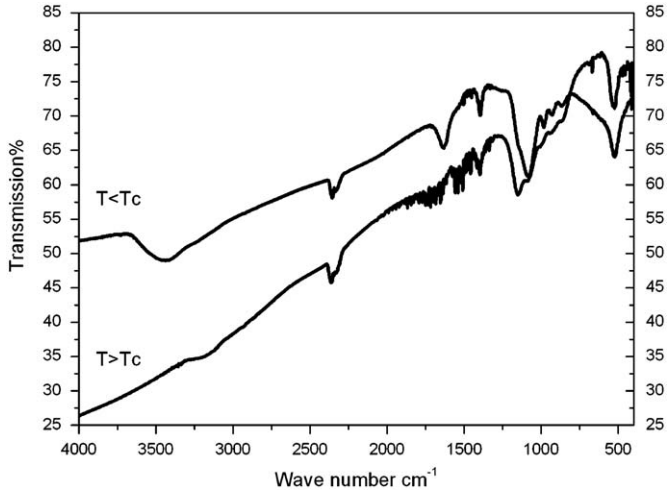

Fig. 8. The FT-IR spectrum for the 0.5045 at% tungsten doped one-dimensional VO_2 (M), above and below the transition temperature.

dimensional W-doped VO_2 (M) solid solution could be linearly tuned via W doping, with an average reduction of 20 °C per W at%.

According to the model of Tang et al. [23], the incorporation of W atoms would lead to the loss of V^{4+}–V^{4+} pairs, and destabilize the semiconductor phase and consequently lower the semiconductor-metal transition temperature. Because of the enhancement of the electron concentration from the presence of W donors, the Fermi level shifts toward the conduction band, resulting in the decrease of activation energy E_a, hence, temperature coefficient of resistance.

FT-IR spectra were used to test the mid-infrared properties of the 0.5045 at% tungsten doped one-dimensional VO_2 (M) at room temperature and 100 °C (above the transition temperature). A significant change in optical properties on switching was observed. A change of up to 25% was observed at 4000 cm^{-1} in the transmission spectrum (Fig. 8), suggesting that the one-dimensional W-doped VO_2 (M) had good thermochromic property.

Additionally, changes in the vibration bands from 400 to 1000 cm^{-1} were also observed while the one-dimensional structures of the VO_2 (M) turned from the monoclinic to tetragonal phase during heating.

4. Conclusions

The one-dimensional W-doped VO_2 (M) solid solutions with different tungsten-doped contents were successfully synthesized by co-precipitation under a hydrothermal condition and subsequent calcination.

The doped W content could be exactly controlled by the change concentration of the W precursor. The T_c of the VO_2 (M) solid solution could be linearly tuned by the doped W content. The one-dimensional W-doped VO_2 (M) had good thermochromic property with a change up to 25% at 4000 cm^{-1}.

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