Research Article

Synthesis of Thermochromic W-Doped VO$_2$ (M/R) Nanopowders by a Simple Solution-Based Process

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Thermochromic W-doped VO$_2$ nanopowders were prepared by a novel and simple solution-based method and characterized by a variety of techniques. We mainly investigated the effect of tungsten dopant on the structural properties and phase transition of V$_{1-x}$W$_x$O$_2$. The as-obtained nanopowders with tungsten content of ≤2.5 at% can be readily indexed as monoclinic VO$_2$ (M) while that of 3 at% assigned into the rutile VO$_2$ (R). The valence state of tungsten in the nanopowders is +6. TEM and XRD results show that the substitution of W atom for V in VO$_2$ results in a decrease of the $d$ space of the (011) plane. The phase transition temperature is determined by differential scanning calorimetry (DSC). It is found, for the first time, that the reduction of transition temperature reaches to 17 K per 1 at% of W doping with the tungsten extents of ≤1 at%, but only 9.5 K per 1 at% with the tungsten extents of >1 at%. The reason of this arises from the difficulty of the formation of V$^{3+}$-W$^{4+}$ and V$^{3+}$-W$^{6+}$ pairs by the increasing of W ions doping in the V$_{1-x}$W$_x$O$_2$ system.

1. Introduction

Vanadium oxides have nearly 15–20 stable phases, meanwhile metal-insulator transition (MIT) has been reported in at least 8 vanadium oxide compounds (V$_2$O$_3$, VO$_2$, V$_3$O$_5$, V$_4$O$_7$, V$_5$O$_9$, V$_6$O$_{11}$, V$_2$O$_5$, V$_6$O$_{13}$, etc.) at temperatures ranging from −147°C to 68°C [1–3], in which VO$_2$ materials show the fully reversible phase transition between monoclinic VO$_2$ (M) and tetragonal rutile phase VO$_2$ (R) fascinatingly around 68°C. As a result, the resistance has a sharp change of 4–5 orders of magnitude, and the optical transmission alters correspondingly. Below the critical temperature ($T_c$), VO$_2$ is in the semiconductive state, in which the energy gap is around 0.6 eV [4], permitting high infrared (IR) transmission. Above $T_c$, VO$_2$ is in the metallic state, in which overlap between the Fermi level and the V$^{3d}$ band eliminates the aforementioned band gap, causing vanadium dioxide to be highly reflecting or opaque in the near-infrared (NIR) region [5–8]. Furthermore, the phase transition temperature can be adjusted to near room temperature by doping, which is realized by the incorporation of metal ions into the VO$_2$ lattice [3]. Tungsten, molybdenum, chromium, titanium, fluorine, and niobium, and so forth are frequently used for this purpose because they produce relatively larger $T_c$ shifts with less dopant concentrations. It has been found that tungsten might be the most effective element [9–14]. Therefore, with such properties, VO$_2$ materials can be considered as a promising candidate for a variety of potential applications such as energy-efficient window coatings [8], thermal sensors [15], cathode materials for reversible lithium batteries [16], electrical and infrared light switching device [17, 18].

So far, as an intelligent window material, the study of W-doped VO$_2$ mainly focused on thin films and nanoparticles. It has been prepared by a variety of methods involving excimer-laser-assisted metal organic deposition (ELAMOD) [19], magnetron sputtering [20], chemical vapor deposition (CVD) [21], pulsed laser deposition (PLD) [22], and vacuum evaporation [23]. However, all of these methods are not suitable for putting into practice because of complex control parameters, unstable technology, and the necessity of special and expensive equipment [24]. Chemical solution deposition
Figure 1: SEM images of vanadium dioxide nanopowders with different W-doped concentration from 0 to 3 atom% (at the intervals of 0.5) (a–g). EDS pattern for 2 at% W-doped VO$_2$ (h).
seems to be an alternative solution to the above problems due to its low cost and the option of metal doping. But this method usually requires specific raw materials or pretreatments which limit their practical applications [6]. Up to now, other modified methods for synthesis of M- or R-phase vanadium dioxide have been presented such as hydrothermal processes [25] and reduction-hydrolysis methods [26]. Nevertheless, long reaction time (12 h to several days) is often needed, or virulent precursor such as V₂O₅ is always required. Thus, more simple method for preparing vanadium dioxide with MIT property needs to be developed to promote its practical applications.

In this paper, we report a simple solution-based process to prepare pure VO₂ and W-doped VO₂ nanopowders with cheap and nontoxic vanadium (V) precursors and short reaction times. The characterization of the obtained nanopowders is studied through a variety of techniques. Furthermore, doping with tungsten could adjust the phase transition temperature remarkably, and thus put the thermochromic application into practice.

2. Experimental Section

2.1. Preparation of \( V_{1-x}W_xO_2 \) Nanopowders. First, a 0.5 g portion of ammonium metavanadate powders (NH₄VO₃, 99%, Tianjin Fuchen Chemical Reagents Factory) and appropriate amount of ammonium tungstate (N₅H₃₇W₆O₂₄·H₂O, 85–90%, Sinopharm Chemical Reagent Co, Ltd.) with different W/V atom ratios were dissolved in 50 mL deionized water, respectively. Then oxalic acid dihydrate (C₂H₂O₄·2H₂O, 99.5%, Guangzhou Chemical Reagent Factory) was added to the above solution, where the molar ratio of NH₄VO₃ and C₂H₂O₄·2H₂O was kept at 2 : 3. The mixture was stirred continuously for 30 min to form a sky blue clear solution, which indicated that the valence of vanadium in the solution was V⁴⁺. As is known, the solution of V⁵⁺ is yellow, V⁴⁺ is blue, and that of V³⁺ is green, respectively. Then the above solution was dried below 100°C. Finally, W-doped VO₂ products, denoting as \( V_{1-x}W_xO_2 \) (\( x \) was appointed a delegate to the atomic ratio of W/V in the reactive precursors, \( 0 \leq x \leq 0.03 \), at intervals of 0.005), were obtained after

Figure 2: XRD patterns of \( V_{1-x}W_xO_2 \) nanopowders annealing at 500°C for 8 h with molar ratio of 2 : 3 (a) adding different extents of tungsten doping. A magnified version of the XRD data depicted in (b) in the 26.5° ≤ 2θ ≤ 29° range and in (c) in the 64° ≤ 2θ ≤ 66° range.
annealing the collected powders at 500°C for 8 hours in nitrogen atmosphere. The possible reactions in the solution and the decomposition of the intermediate are listed as follows [27, 28]:

\[
2\text{NH}_4\text{VO}_3 + 4\text{C}_2\text{H}_2\text{O}_4 \rightarrow (\text{NH}_4)_2[(\text{VO})_2(\text{C}_2\text{O}_4)_3] + 2\text{CO}_2 + 4\text{H}_2\text{O} \tag{1}
\]

\[
(\text{NH}_4)_2[(\text{VO})_2(\text{C}_2\text{O}_4)_3] \rightarrow 2\text{VO}_2\text{C}_2\text{O}_4 + 2\text{NH}_3 + \text{CO} + \text{CO}_2 + \text{H}_2\text{O} \tag{2}
\]

\[
\text{VO}_2\text{C}_2\text{O}_4 \rightarrow \text{VO}_2 + \text{CO} + \text{CO}_2. \tag{3}
\]

2.2. Characterization. Powder X-ray diffraction (XRD, PANalytical B.V., X’Pert Pro MPS PW3040/60) patterns of the samples were recorded in the scanning range of 5–80° at room temperature of 25°C. The morphologies, dimensions, elemental composition, and crystallinity of the nanopowders were examined by scanning electron microscopy (SEM, Hitachi, S-4800), energy dispersive X-ray spectroscopy (EDS) attached to the SEM, transmission electron microscopy (TEM), and high-resolution TEM (JEOL, JEM-2010HR), respectively. Samples for TEM observation were prepared by dispersing in ethanol. Differential scanning calorimetry (DSC, Netzsch-Bruker, STA449F3 Jupiter-TENSOR27) experiments were performed using a DuPont differential thermal analyzer under atmosphere flow in the range of 25–120°C with a heating rate of 5 K min\(^{-1}\), and in the measure procedure heating process alternates with cooling process. The valance state of the as-obtained \(V_{1-x}W_x\text{O}_2\) nanopowders was characterized by means of X-ray photoelectron spectroscopy (XPS, Thermo-V-G Scientific, ESCALAB250).

3. Results and Discussion
The morphology of the undoped and W-doped VO\(_2\) nanopowders is characterized by SEM as shown in Figure 1. It is observed in Figures 1(a) to 1(g) that the tungsten dopant
concentration almost has no effect on the morphology of the nanoparticles, and the particle sizes are about 20–60 nm. The experimental results also indicate that particles will be congregated with the increase of annealing time. Especially, the particles with 2 at% W-doped are relatively uniform, and the size is about 25 nm, which is in favor of the practice application on thermochromic window coatings. As is known, small and uniform particles are relatively easy to disperse in solvent and obtain homogeneous coating. Therefore, the 2 at% W-doped sample is investigated in detail in the following experiments. EDS analysis results further confirm the existence of V, W, and O elements. The representative peaks of V and O elements appear in all of the obtained samples, and the representative peaks of W element also appear in each of W-doped products, which confirm a successful doping of W into VO₂. Here we just give the EDS pattern of 2 at% W-doped sample (Figure 1(h)) as a representative example.

The XRD patterns of W-doped VO₂ nanopowders with various tungsten contents are recorded in Figure 2(a). The magnified versions of the XRD data in the range of 26.5° ≤ 2θ ≤ 29° and 64° ≤ 2θ ≤ 66° are depicted in Figure 2(b) and Figure 2(c), respectively. It is found that the as-obtained samples with the tungsten extents of ≤2.5 at% can be readily indexed as monoclinic VO₂ (M) (JCPDS card number 79-1655), while that of 3 at% assigned into the rutile VO₂ (R) (JCPDS card number 43-1051). For the sample doped 3 at% tungsten, the peak in 26.5° ≤ 2θ ≤ 29° shifts left than the others figuring out the change of VO₂ (M) (011) to VO₂ (R) (110) in Figure 2(b), and meanwhile the VO₂ (M) (310) peak splits into the VO₂ (R) (013) and (002) in 64° ≤ 2θ ≤ 66° (Figure 2(c)). The above two phenomena together indicate the occurrence of the diagnostic feature for the structural phase transition from monoclinic to tetragonal VO₂ phase, which are in good agreement with previous reports [7, 29]. Therefore, the changes in peak positions of as-obtained samples indicate that an appropriate amount of tungsten doping can promote the phase transition [30].

In Figure 3, XPS analysis of the as-obtained nanopowders with 2 at% W-doped is performed to understand in detail the valance state. The spectra indicate that there are four elements: oxygen, vanadium, carbon, and tungsten with binding energy peaks corresponding to C1s, O1s, V2s, V2p, V3s, W4f, W4d, and W4p in W-doped VO₂ nanopowders.
(Figure 3(a)). The forms of carbon are possibly from surface contamination [5, 9, 30]. The data reveals that the peak at 530.3 eV is associated with O1s [26]. The peaks located at 516.6 eV (reported values: 515.7–516.6 eV [5, 6, 9, 26, 30, 31]) and 524.0 eV (reported values: 522.6–524.0 eV [5, 6, 9, 26, 29, 30]) correspond to V2p3/2 and V2p1/2 (Figure 3(b)), respectively, and the binding energy of V2p3/2 increases slightly after W doping [30]. The W4f peaks follow with binding energies of W4f7/2 and W4f5/2 at 35.28 eV and 37.45 eV, respectively. According to the standard binding energy, tungsten atoms in these nanopowders exist as W6+ (Figure 3(c)) [9]. N-type semiconductor could form as W6+ ions replace V4+ ions.

TEM images of the undoped VO2 and 2 at% W-doped VO2 nanopowders are shown in Figures 4(a) and 4(c). The morphologies and sizes of the as-obtained samples are consistent with those of SEM images in Figures 1(a) and 1(e). Figures 4(b) and 4(d) show the lattice-resolved HRTEM images. The fringe spacing is 0.321 nm for undoped VO2 (Figure 4(b)) sample, which is consistent with the d space of the (011) plane of monoclinic VO2 (M) phase [32, 33], and the fringe spacing reduces to 0.314 nm (Figure 4(d)) for the sample of 2 at% W-doped VO2. This decreased tendency of the fringe spacing with W doping is consistent with the calculated results by Scherrer formula. As the radius of W6+ ion (60 pm [34]) is smaller than that of the V4+ ion about 63 pm. The interstitial W6+ ions will cause the atoms to have larger interatomic spacings, and the interatomic spacings will be reduced in the case of substitutional defects with W6+ ions. The TEM results suggest that the substitution of W6+ ions for V4+ plays a dominant role in this work, which results in the reduction of d011 spacing. As the tungsten dopant concentration is 2 at%, the (011) peak of monoclinic VO2 (M) shifts from 27.74° (undoped VO2) to 27.79°, indicating the decrease of the crystal lattice spacing according to the Bragg equation ($2d\sin \theta = \lambda$; $\lambda_{Cu} = 0.154$ nm) [29, 35, 36].

Figure 5: DSC curves of undoped VO2 and 2 atom% W-doped VO2 nanopowders during the heating and cooling cycles (a). The curves of as-obtained samples ($V_{1-x}W_xO_2$, $x = 0–0.03$, at intervals of 0.005) upon heating process (b). Effect of tungsten-doped vanadium dioxide concentration on the phase transition temperature upon heating process (c).
As regards the rule of substitution or interstitial of W\(^{6+}\) ions for V\(^{4+}\) is unknown, and it needs further research.

When the phase transition of VO\(_2\) occurs, it exhibits a noticeable endothermal or exothermal profile in the DSC curve. Figure 5(a) shows the typical DSC curves of undoped and 2 at\% W-doped VO\(_2\) nanopolymers. With 2 at\% W-doped sample, Mott phase transition arises at around 44°C and 34.5°C for the heating and cooling cycles, compared to 71°C and 58°C for the undoped VO\(_2\), respectively. The phase transition can be modified under the different factors such as defect density or lattice change [3, 29]. The appearance of endothermal and exothermal peaks during the heating and cooling process confirms the first-order transition between monoclinic VO\(_2\) (M) and tetragonal rutile VO\(_2\) (R) [7]. To be vital for the practical thermochromic effect applications, the phase transition temperature of W-doped must be approaching to room temperature. In this case, the phase transition temperature could be reduced to 35°C with 3 at\% W-doped in Figure 5(b).

A nonlinear decrease of the phase transition temperature with increasing percent of tungsten atom incorporation is observed upon heating process (Figure 5(c)). And the nonlinear decrease can be described by two linear fits. The reduction of transition temperature is estimated to be about 17 K per 1 at\% of W doping with the tungsten extents of ≤1 at\%, but only 9.5 K per 1 at\% with the tungsten extents of >1 at\%. With tungsten ion doping into VO\(_2\), the reaction takes place as follows: \(2V^{4+} + W^{4+}_2 \rightarrow 2V^{3+} + W^{6+}\), which results in the formation of V\(^{3+}\)-V\(^{4+}\) and V\(^{3+}\)-W\(^{6+}\) pairs [35]. Then the transition temperature will be reduced due to the loss of direct bonding between V ions, which is resulted from the forming of the pairs. We can now assume that the change of transition temperature is determined by the difficulty of initial formation of V\(^{3+}\)-V\(^{4+}\) and V\(^{3+}\)-W\(^{6+}\) pairs.

At the beginning, the pairs form easily with lower tungsten dopant concentration, so the transition temperature could remarkably change. By following the increase of W ions, it becomes relatively difficult to form the V\(^{3+}\)-V\(^{4+}\) and V\(^{3+}\)-W\(^{6+}\) pairs right away, resulting in a more gradual change in the transition temperature.

4. Conclusions

Well-crystallized nanopowders of W-doped VO\(_2\) (M/R) were successfully synthesized by a simple solution-based process through the reaction of ammonium metavandate (NH\(_4\)VO\(_3\)) and oxalic acid dihydrate (C\(_2\)H\(_2\)O\(_4\)·2H\(_2\)O) followed by adding to appropriate ammonium tungstate (N\(_2\)H\(_5\)W\(_6\)O\(_{24}\)·H\(_2\)O). It is shown that tungsten dopant concentration almost has no effect on the morphology of the nanoparticles and the granular particles are about 20–60 nm. As-obtained nanopowders with the tungsten extents of ≤2.5 at\% can be readily indexed as monoclinic VO\(_2\) (M), while that of 3 at\% assigned into the rutile VO\(_2\) (R). Substitutional W\(^{6+}\) ions could reduce the interatomic spacings, which results in the decrease of the d space of the (011) plane in monoclinic VO\(_2\) (M) phase. Moreover, we found that the difficulty level in initial formation of V\(^{3+}\)-V\(^{4+}\) and V\(^{3+}\)-W\(^{6+}\) pairs determines the rate of change of the critical temperature. The reduction of transition temperature is estimated to be about 17 K per 1 at\% of W doping with the tungsten extents of ≤1 at\%, only about 9.5 K per 1 at\% with the tungsten extents of >1 at\%. With 3 at% W-doped VO\(_2\), the phase transition temperature can be reduced to 35°C. In short, this paper provides a simple solution-based method to prepare W-doped VO\(_2\) nanopowders with good thermochromic properties showing the transition temperature required to building glazing, which is in favor of promoting the practical applications of smart window.

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References


