Int. J. Electrochem. Sci., 10 **(2015)** 6014 - 6019

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Short Communication

Simple and Facile Synthesis W-doped VO_2 (M) Powder Based on Hydrothermal Pathway

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Received: 12 March 2015 / *Accepted:* 30 April 2015 / *Published:* 27 May 2015

The present study provides a simple and facile pathway to obtain undoped and W-doped VO_2 (M) powder by utilizing the inexpensive and low toxic NH_4VO_3 precursor with an economical and environmental friendly method. The XRD patterns exhibited that the W-doped VO_2 powder was monoclinic phase, and W atom doping almost had no influence on the crystal structure of VO_2 lattice. The grain size of W-doped VO_2 particles decreased as W atom concentration increasing. SEM images showed that particles with 1~2 microns diameter of W-doped VO_2 (B) were obtained by hydrothermal synthesis directly. VO_2 (B) transformed to VO_2 (M) after annealed at 750 $^{\circ}$C in nitrogen atmosphere.

Keywords: W-doped; VO_2 powder; hydrothermal method

1. INTRODUCTION

Vanadium dioxide (VO_2) has intrigued researchers for five decades since the first discovery of the existence of thermochromic properties [1, 2]. Monoclinic VO_2 (M) has a reversible metal-semiconductor phase transition (MST) property at about 68 $^{\circ}$C, and its unit cell distorts during the MST transition, accompanied by a reversible switch in optical transmittance and reflectance in the infrared range. Above the phase transition temperature, it has a tetragonal lattice with the $P4_2/mnm$ rutile space group (R phase), which is reflective to infrared light; however, it shows a monoclinic structure with the P21/*c* space group (M phase) below the phase transition temperature, which is transparent to infrared light. On its own, VO_2 is important for many applications of its phase transition,

including electrochemical devices as a cathode[3, 4], smart windows[5, 6],optical switching devices[7], optical storage devices[8], etc.

A number of strategies have been employed to produce undoped or doped VO_2 thin films, such as sputtering[9], sol-gel methods[10], chemical vapor deposition[11], pulsed laser deposition[12] and spray pyrolysis[13]. These methods are capable of producing VO_2 films with various thermochromic properties. Unfortunately, the low visible light transmittance, weak optical contrast in the IR region and high metal-insulator phase transition are three main issues must be addressed, if VO_2 is to be used in applications like smart windows. Compared with thin films, powder can overcome such shortcomings and work more effectively, and the cost is inexpensive. Furthermore, the powder can remarkably lessen the stress for the phase change; offer the possibility of obtaining a sharper and more reproducible transition. There were also several methods that have been reported on the preparation of VO_2 powder, such as spray pyrolysis [14] and hydrothermal synthesis[15, 16]. For the hydrothermal synthesis, most of the studies [17, 18] used V_2O_5 as a reactant, which exhibited a toxic property, thus limited the usage and development of this method.

In this work, we highlighted an available and facile way to synthesize high-quality W-doped monoclinic VO_2 (M) powder with inexpensive and low toxic NH_4VO_3 precursor. This reaction is not limited to just VO_2, but could be extended to other vanadium oxides to manipulate the composition of powder.

2. EXPERIMENTAL

2.1. Synthesis of undoped or W-doped VO_2 powder

Ammonium metavanadate (NH_4VO_3, ChengDu Kelong Chemical Co., Ltd.) and tungsten dichloride dioxide (WO_2Cl_2, Sinopharm Chemical Reagent Co. Ltd) were used as vanadium and tungstate source, respectively. Certain amount oxalic acid (ChengDu Kelong Chemical Co., Ltd.) was added to 10 ml NH_4VO_3 aqueous solution containing 0.10 mol vanadium with strong stirring. Then diluted H_2SO_4 was added dropwise to the above solution, until the pH reached ~2.5. The resulting solution was introduced into a Teflon-lined stainless steel autoclave and maintained at 180 °C for 48 hours. After air-cooling to room temperature, the dark blue precipitates were collected by centrifuging. The powder was washed with deionized water and alcohol for three times, and then dried in a vacuum oven at 70 $^{\circ}$C for 8 h. At last, VO_2 powder was annealed at 750 $^{\circ}$C in nitrogen atmosphere for 2 h.

For the preparation of W-doped VO_2, the different stoichiometric volume of aqueous tungsten dichloride dioxide solution was added into the NH_4VO_3 solution before $H_2C_2O_4$ was added. The W content in VO_2 sample could be controlled by changing tungsten concentration in precursor; other processes were the same as synthesis of VO_2 powder.

2.2. Characterization

X-ray diffraction (XRD) analysis was conducted on XRD diffractometer (TD-3500, Dandong Tongda, Ltd) at 0.4º per second with 2θ ranging from 10^o to 70^o, using Cu Kα1 radiation (λ=0.154056

nm). Morphologies of prepared particles were observed by scanning electron microscopy (FEI Quanta 250, USA) at an acceleration voltage of 10 KV.

3. RESULTS AND DISCUSSION

3.1 Synthesis of VO_2 (M) powder

X-ray diffraction was used to check the powder structures. All peaks are indexed to VO_2 (B) (JCPDS no. 81-2392, C2/m, a = 1.209 nm, b = 0.370 nm ,c = 0.643 nm) from Fig. 1. While Fig.1b diffraction peaks are indexed to JCPDS 72-0514, indicating the formation of monoclinic VO_2 (M), after annealing at 750 $^{\circ}$C for 2h under nitrogen atmosphere, which is in accordance with other reports [19, 20]. No other phase or impurities are observed in VO_2 (M) powder, and the VO_2 phase transformation temperature in our sample was 69.9^{o}C.

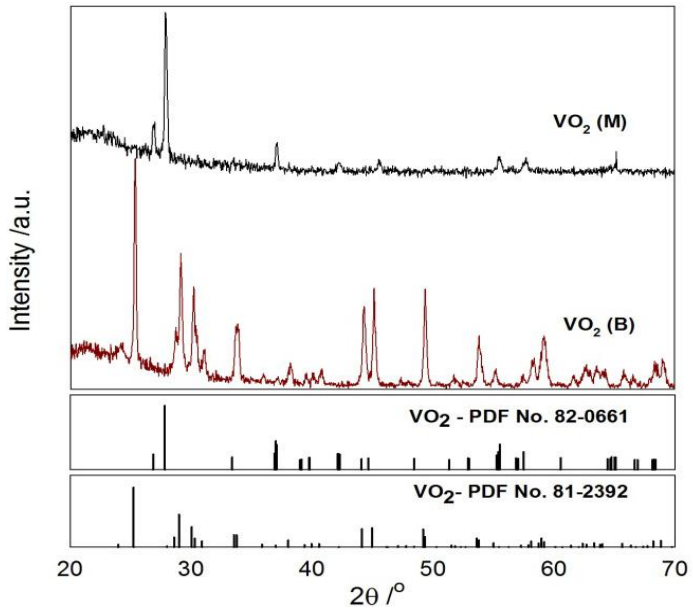

Figure 1. XRD patterns of prepared VO_2 samples: (a) VO_2 (B) powder (red line) and (b) VO_2 (M) powder (blue line).

SEM images of pure VO_2 (B) and VO_2 (M) are shown in Fig. 2a and Fig. 2b. The microstructure of VO_2 (B) phase presents needle-like structure; VO_2 (M) powder that was annealed at a relatively higher temperature (750°C) shows better crystallinity and conductivity. According to the SEM image, VO_2 (M) particles with a diameter about 1~2 microns, closed to the calculated grain size from X-ray diffraction results by using Debye-Scherrer formula[21]. Interestingly, the VO_2 (B) powder after being annealed presents granular shape. Such a result is in coincidence with the grain growth mechanism, and the powder experienced a series of morphological changes because of the subsequent annealing.

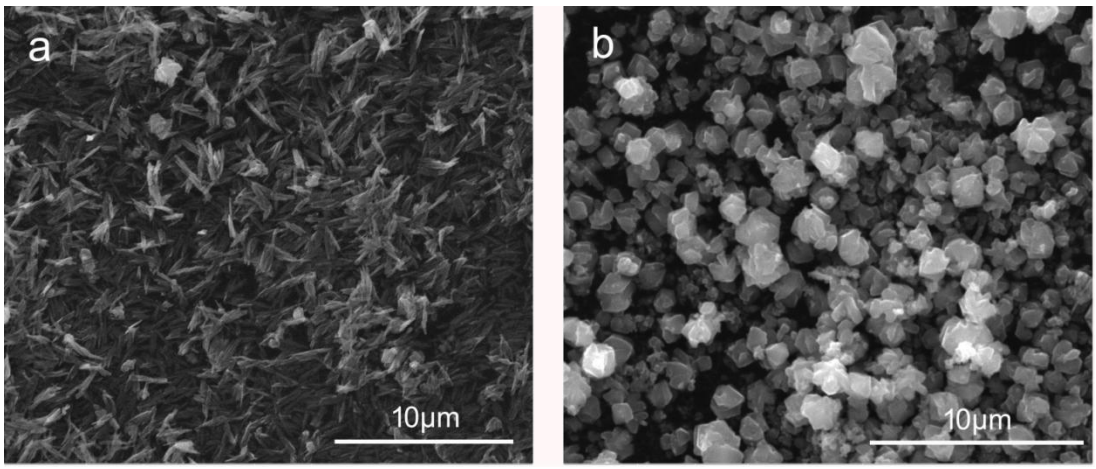

Figure 2. SEM images of the as-received VO_2 samples: (a) VO_2 (B) powder and (b) VO_2 (M) powder.

3.2. Synthesis of W-Doped VO_2 (M) powder

X-ray diffraction patterns displayed in Fig. 3 (a) exhibit two main characteristic diffraction peaks, (110) and (002), Which are assignable to the VO_2 (B) for all doped samples (JCPDS 81-2392). Booth et al.[22] suggested that doping element could induce a local structural distortion, which restrained the grain growth of VO_2. The magnified XRD pattern around (110) peak are displayed in Fig. 3b. We find that (110) peak shifts toward small reflection angle, from 25.5 ^{o} to 25.3^{o}, when W atomic concentration increases from 0.5% to 5%. So the interplanar distance (d-value) increases lightly according to Braggs law, which may be attributed to the larger tungsten atom size than vanadium atom[23].

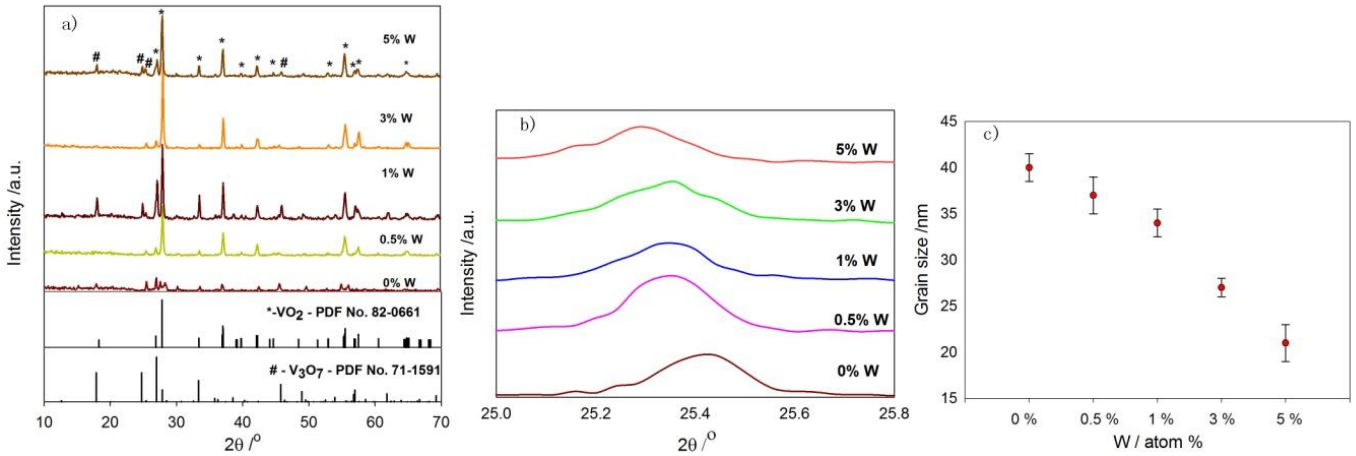

Figure 3. (a) The XRD patterns of obtained W-doped VO_2 (B) powder, (b) (110) peak of W-doped VO_2 (B) powder and (c) The plot of grain size as function of W concentration for W-doped VO_2 (B) powder.

Thermal treatment of VO_2 (B) powder leads to the formation of monoclinic phase (M-phase) VO_2 with a preferred orientation of $(011)_M$. The recorded diffraction peaks could be assigned to M-

phase VO_2 (JCPDS card no. 82-0661, P21/c, a=0.575nm, b= 0.453nm, c=0.538nm). However, V_3O_7 impurity peaks (JCPDS card no.71-1591) are detected. The (110) peak intensity first increase with W content increasing from 0 % to 3 %, while when W content increases to 5 %, the (110) intensity decreases. The plot of grain size as function of W concentration in fig. 4(b) also shows an obvious decrease trend, indicating the gradual expansion of VO_2 crystal lattice after W doped, thus inhibiting VO_2 grain growth.

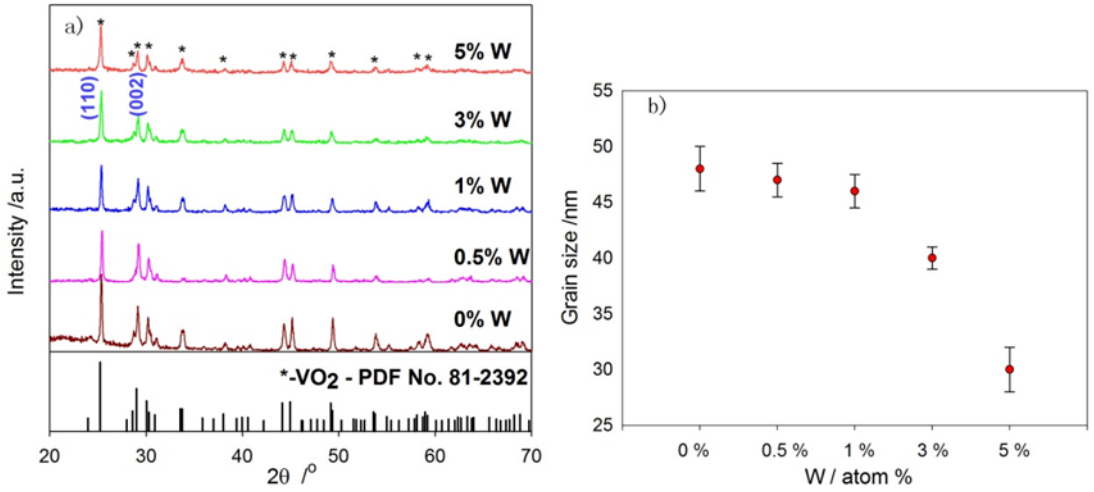

Figure 4. Fig. 4 XRD patterns and grain size analysis of annealed W-doped VO_2 powder: (a) The XRD patterns of obtained W-doped VO_2 (M) powder and (b) The plot of grain size as function of W concentration for W-doped VO_2 (M) powder.

4. CONCLUSION

In this paper, both W-doped and undoped monoclinic VO_2 (B) powder were synthesized by hydrothermal process. The pure VO_2(M) powder was obtained by heating dark blue VO_2(B) at 750^oC in nitrogen atmosphere for 2 h with granular VO_2(M) with diameter around 1~2 microns. Wide W-doped concentrations VO_2 powders were also synthesized. The (110) peak of W–doped VO_2 (B) presented a tendency of shifting toward small reflection angle. V_3O_7 phase was detected in W–doped VO_2 (M) samples, which suggested that subsequent annealing process and appropriate amount of WO_2Cl_2 promoted the phase transition. Additionally, it was found that the diameter of W-doped VO_2 (M) particles was about micron level, larger than undoped VO_2 sample slightly. For W–doped VO_2 (M) samples, the grain size showed a steady decrease trend, as W-doped concentration increasing. In summary, a facile and available pathway was used to obtain VO_2 (M) powder, and there was potential use for VO_2 (M) production.

ACKNOWLEDGMENTS
This work is supported by the college natural sciencefoundation (2013CJ29;R2013CJ08;M2014ME05). We appreciate Prof. Hongtao Zhang for theoretical instructions, Mr.Pu and Mrs.Teng for the XRD and SEM characterizations.

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