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A NEW ROUTE FOR THERMOCHROMIC VANADIUM DIOXIDE SYNTHESIS

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In a typical hydrothermal process it takes a long time to form the monoclinic phase of vanadium dioxide that has thermochromic properties. We propose and demonstrate a new route for the synthesis of vanadium dioxide with a short hydrothermal treatment followed by a heat treatment under nitrogen atmosphere at 700˚C for one hour. It was also found that the addition of oxalic acid affects the annealing process and transforms $NH_4V_4O_{10}$ or V_2O_5 and V_6O_{13} to the desired monoclinic VO_2-M phase. Only monoclinic vanadium dioxide was obtained from a 4 h hydrothermal process followed by the thermal annealing with a suitable dosage of oxalic acid dihydrate.

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1. Introduction

Monoclinic vanadium dioxide (VO_2-M) has been the subject of intensive research due to its reversible semiconductor-metal phase transition around Tc = 68˚C. This monoclinic phase is a semiconductor and infrared (IR) transparent below Tc, and changes to a tetragonal metallic phase that is highly IR reflecting above Tc [1]. The VO_2 has potential applications in energy-efficient window coatings [2] and in various advanced devices, such as thermal sensors [3] and switches [4]. Several processes have been used to synthesize VO_2-M, such as a solution-based process [5], chemical vapor deposition, a sol-gel process, sputtering, and pulsed laser deposition [6]. However, these approaches require specific instruments and tools.

Hydrothermal synthesis is an alternative with 2 subtypes. The first one is classical with a hydrothermal process at 170-260˚C that takes a few days. The second synthesizes an intermediate phase prior to forming VO_2 (M) at 500-700˚C [7, 8, 9]. This second hydrothermal technique requires also a long time (1-3 days) to complete, and the final product contains also metastable VO_2-B and $(NH_4)_{0.5}V_2O_5$. In this paper, a new method for the synthesis of VO_2-M from NH_4VO_3 is proposed and demonstrated. An intermediate phase (IM) is first synthesized hydrothermally at 180°C over 2-8 hours. Then a phase transformation is induced by annealing at 700°C under nitrogen atmosphere for one hour. The synthesized samples were characterized using several techniques, and their thermochromic properties were determined. In addition, the effects of oxalic acid dihydrate (OAD) on VO_2-M yield were investigated with very positive results.

2. Experimental

2.1 Intermediate Phase Synthesis

The vanadate solution was prepared by dissolving 0.60 grams ammonium metavanadate (NH_4VO_3) in 50 mL distilled water and stirring at 55°C for 10 minutes. After that, 0.60 mL formic acid (H_2CO_2) was added to the solution and stirred for 20 minutes. The solution was immediately transferred to a 100 mL Teflon-lined autoclave and kept in an oven at 180˚C for 2, 4 and 8 hours. When the autoclaves had naturally cooled down to room temperature, the precipitate was filtered with a filter paper and washed several times with distilled water and with ethanol. The product is here called an intermediate phase, and this IM was dried in an oven at 60˚C for 24 hours.

2.2 Phase Transformation

The IM product from the hydrothermal 4-hour process was calcined at 700 ˚C with the heating rate of 5˚C/min for 1 hour under nitrogen atmosphere. In addition, oxalic acid dihydrate (abbreviated OAD, $H_2C_2O_4{\cdot}2H_2O$) was also introduced to the calcination in order to investigate its effects on the VO_2-M synthesis. The weight ratio of OAD/IM was set at 0:1, 0.50:1, 1:1, 1.10:1, 1.25:1, 1.50:1, and 1.75:1 in these experiments.

2.3 Characterization

The phase composition of each synthesized sample was characterized with an x-ray diffractometer (XRD, Phillips Expert MPD, Cu-Kα), and the phase transition temperatures were determined with a differential scanning calorimeter (DSC, Perkin Elmer DSC7) as they relate to the thermochromic properties. The morphology of the synthesized powder was assessed using a scanning electron microscope (SEM, FEI Quanta 400) and a transmission electron microscopy (TEM, JEOL JEM-2010).

3. Results and discussion

3.1 Effects of Hydrothermal Reaction Time

XRD patterns were observed to determine the phase composition of the intermediate phase. As shown in Figure 1(a), $(NH_4)_2V_6O_{16}$ and $NH_4V_3O_7$ were found after a 2-hour treatment, and these components decreased when the treatment continued for 4 hours or 8 hours. Also $NH_4V_4O_{10}$ was found with the 4-hour treatment, and this component increased with treatment time. This indicates that $(NH_4)_2V_6O_{16}$ and $NH_4V_3O_7$ were transformed to $NH_4V_4O_{10}$ with sufficiently long hydrothermal treatments.

The XRD patterns of samples after annealing at 700˚C for 1 hour are shown in Figure 1(b). The peak at 27.82˚ represents monoclinic VO_2(M) and was observed in the sample with 4-hour hydrothermal treatment. Further, this peak intensity increased with a longer hydrothermal treatment. With a 2-hour hydrothermal treatment this peak at 27.82° was not observed. This suggests that only $NH_4V_4O_{10}$ can transform to VO_2-M, while $(NH_4)_2V_6O_{16}$ and $NH_4V_3O_7$ cannot. However, the phases V_6O_{13} and V_2O_5 with excess oxygen were present in all samples.

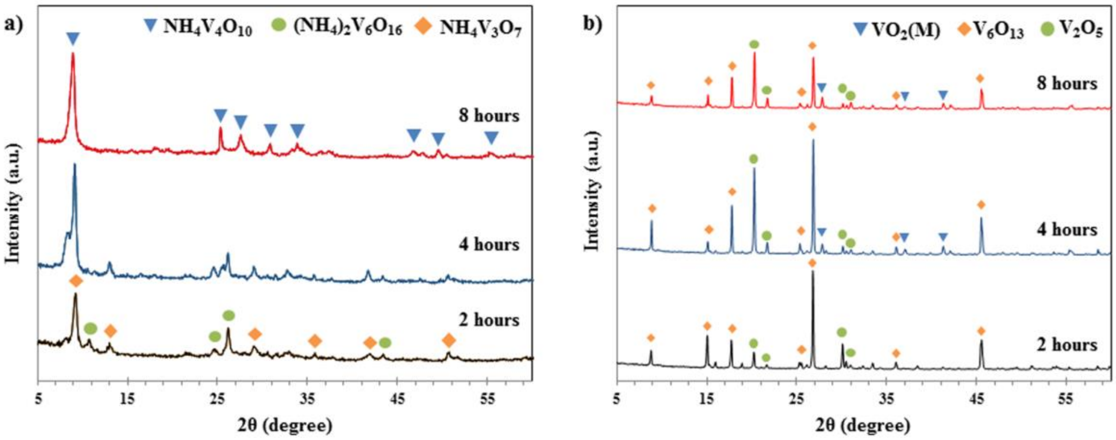

Fig.1 (a) XRD patterns of the intermediate phase (IM) from various hydrothermal treatment times: 2 hours, 4 hours and 8 hours; (b) XRD patterns of these IM samples after heating to 700 ˚C at 5˚C/min and holding for 1 hour, under nitrogen atmosphere.

3.2 Effects of Oxalic Acid Addition

As is well-known, oxalic acid decomposes at high temperatures producing carbon monoxide (CO) [10], which acts as a reducing agent that transforms V_6O_{13} and V_2O_5 to VO_2- M during a heat treatment [11]. Thus, we used oxalic acid to increase the VO_2-M yield. The ratio of OAD/IM was set at 0:1, 0.50:1, 1:1, 1.10:1, 1.25:1, 1.50:1, and 1.75:1.

As shown in Figure 2, the VO_2-M peak became strong as the OAD/IM ratio was increased up to 1.1:1. However, the yield again decreased at higher values of the ratio. This might be due to an excess of carbon monoxide that transforms the desired VO_2-M to V_3O_5 and V_2O_3. In addition, the lattice constant of VO_2-M was calculated and shown in Table 1. The results are in line with the standard values for VO_2-M (JCPDS 01-082).

During annealing in a nitrogen atmosphere, the mechanism of $NH_4V_4O_{10}$ transformation to VO_2-M may have been as shown in Eq. (1)-(3),

$$2NH_4V_4O_{10}\,(s) \rightarrow V_6O_{13}\,(s) + V_2O_5\,(s) + VO_2\,(s) + 2NH_3\,(g) + H_2\,(g) \tag{1}$$

$$H_2C_2O_4{\cdot}2H_2O\,(s) \rightarrow 3H_2O\,(g) + CO_2\,(g) + CO\,(g) \tag{2}$$

$$V_6O_{13}\,(s) + V_2O_5\,(s) + VO_2\,(s) + H_2C_2O_4{\cdot}2H_2O\,(s) \rightarrow 9VO_2\text{-}M(s) + 2CO_2(g) + 3H_2O\,(g) \tag{3}$$

In the beginning at 700˚C, the intermediate $NH_4V_4O_{10}$ phase is mainly transformed to V_6O_{13} and $V_2O_{5,}$ with a small amount of VO_2 and gasses, as illustrated in Eq.(1). Then, following Eq.(3), V_6O_{13} and V_2O_5 are converted to VO_2-M by the reducing CO gas, formed by the thermal decomposition of OAD shown in Eq. (2). However, VO_2-M can be converted to V_3O_5 and V_2O_3 in the presence of excess reducing agent. Therefore it is necessary to control the dosage of OAD.

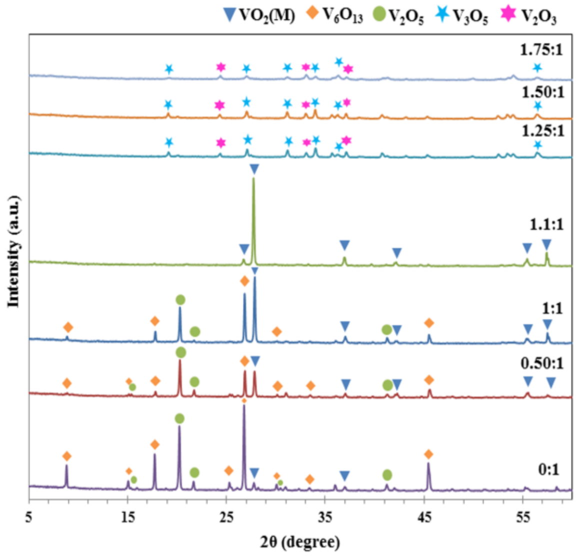

Fig.2 XRD patterns of the samples after heat treatment at 700˚C for 1 hour for various OAD/IM ratios shown as labels.

Table 1 The lattice parameters of VO_2-M based on XRD.

Materials	**Lattice Parameters**		
	a **(Å)**	***b*** **(Å)**	***c*** **(Å)**
VO_2-M 0:1	5.76036	4.54331	5.36844
VO_2-M 0.50:1	5.76353	4.52879	5.37914
VO_2-M 1:1	5.76157	4.55370	5.33971
VO_2-M 1.1:1	5.77420	4.53447	5.40973
VO_2-M (JCPDS 01-082)	5.75290	4.52630	5.38250

3.3 Morphology and Thermochromic Properties

To assess the thermochromic phase transition, a sample prepared with OAD/IM ratio of 1.1 was investigated by DSC. The sample was heated from 20˚C to 80˚C at the rate of 5 ˚C/min and then back to 20˚C. As shown in Figure 3(d), an endothermic peak was observed at 67.9˚C and an exothermic peak at 60.4˚C. This matches the VO_2-M $\rightarrow$$VO_2$-R semiconductor-metallic phase transition at 67.9˚C, of monoclinic end product.

Moreover, the morphologies of the intermediate phase and the VO_2-M were assessed. SEM images of the IM phase showed rod-like particles, while spherical particles were observed the images of VO_2-M. The TEM images were used to determine the particle sizes of VO_2-M, which were about 50-200 nm. These particle sizes from our proposed process are smaller than previously reported for other methods of synthesis [11,12].

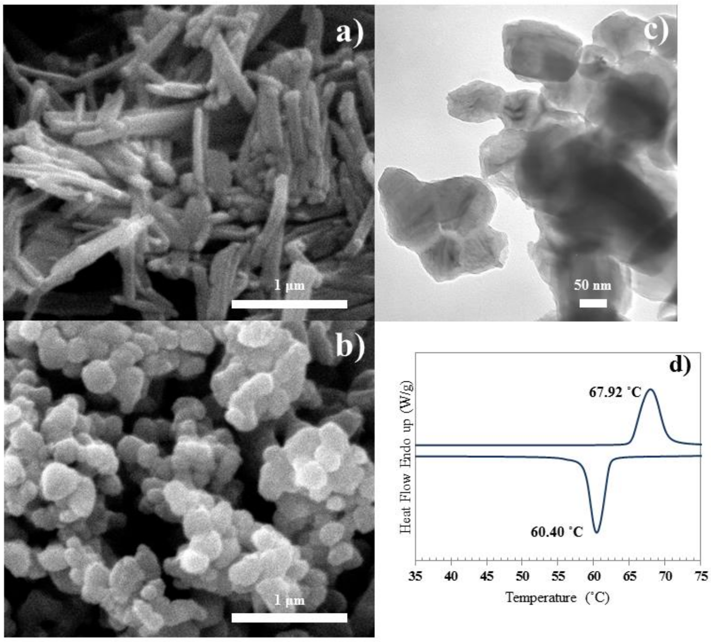

Fig.3 (a) SEM image of IM prepared by 4-hour hydrothermal treatment; (b), (c) SEM and TEM images of VO_2-M powder prepared from the IM by thermal annealing, using OAD/IM ratio of 1.1; (d) DSC curves of this VO_2-M powder.

4. Conclusions

Thermochromic VO_2-M has been successfully synthesized with a high yield by a new comparatively rapid method that includes a short 4-hour hydrothermal process followed by thermal annealing under nitrogen atmosphere at 700˚C for one hour. An oxalic acid addition gave complete control of the phase transformation of intermediate phase during annealing to the desired monoclinic VO_2-M. In addition, the particle sizes from this new process were smaller than those from prior reported hydrothermal synthesis that require several days to complete.

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