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The additives W, Mo, Sn and Fe for promoting the formation of VO_2(M) and its optical switching properties

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ABSTRACT

Belt-like X-doped VO_2(M) (X=W, Mo, Sn or Fe) with rectangular cross sections were successfully synthesized by a facile one-pot hydrothermal approach. The as-obtained samples were characterized by XRD, XPS, SEM, DSC and variable-temperature IR. The results showed that the additives W, Mo, Sn and Fe could promote the formation of VO_2(M) under hydrothermal conditions. The additives had little influence on the morphology of doped VO_2(M), but they were the key factor for the synthesis of VO_2(M). The W and Mo atoms could effectively reduce the T_c of VO_2(M), while Sn and Fe atoms had little influence on T_c. Furthermore, it was found that the as-obtained doped VO_2(M) possessed prominent thermochromic properties and optical switching characters.

1. Introduction

Monoclinic vanadium dioxide VO_2(M) exhibits a fully reversible first-order metal-to-insulator transition (MIT) with the phase transition temperature (T_c) at about 68 °C, accompanied by a crystallographic transition between a low temperature monoclinic phase (M) and a high temperature tetragonal rutile phase (R) [1,2]. On warming through the transition, drastic changes occur in both optical and electrical properties. For example, the change in electrical resistivity in the order of 10^5 and its infrared transmission characteristics changing dramatically over the phase transition [1,3]. Moreover, the T_c of VO_2(M) can be tuned by doping with W, Mo, Nb, F atoms, etc. or their mixtures [4–11]. These features make VO_2 to be suitable for applications [5,9,10,12–17] in optical switches, storage medium, smart window coatings, temperature-sensing devices, laser protection, etc. Therefore, the large-scale and low-cost synthesis of VO_2(M) are meaningful and challenge for materials scientists.

In the past decades, a lot of methods [4–11,14–24], such as RF sputtering, pulsed laser, deposition vacuum evaporation, physical vapor deposition, thermolysis, chemical vapor deposition, sol–gel, hydrothermal synthesis and so on, have been developed to synthesize VO_2(M) or doped VO_2(M). All of above methods, the hydrothermal method [5–7,11] has been paid increasing attention to synthesize W-doped VO_2(M) because of its uncomplicated route and mass production recently. However, the idea of promoting the formation of VO_2(M) with additives under the hydrothermal conditions has not been noticed. In the previous report [23], only VO_2(A) can be prepared by the hydrothermal reaction of V_2O_5, $H_2C_2O_4$, and H_2O. However, in our later research, it was found that VO_2(M) could be obtained with adding some additives to the above system at the same synthetic conditions, which has not been reported. Herein, we report the above idea and select W, Mo, Sn and Fe atoms for promoting the formation of VO_2(M).

2. Experimental

All reagents used in the experiments were of analytical grade and used without any further purification. In a typical synthesis, 0.91 g of V_2O_5, 1.26 g of $H_2C_2O_4 \cdot 2H_2O$ and an appropriate amount of H_2WO_4 [$n(W)/n(V+W) \times 100\% = 1.0\%$] were dispersed into 40 mL of deionized water with magnetic stirring vigorously for about 10 min at room temperature. After the solution became suspension, the mixed solution was transferred into a 60 mL stainless steel autoclave, which was sealed and maintained at 280 °C for 24 h and then cooled to room temperature naturally. The products were filtered off, washed with distilled water and absolute ethanol several times to remove any possible residue, and dried in vacuum at 75 °C for 12 h. Other additives, such as

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H_2MoO_4, SnO_2 and Fe_2O_3, were also used to synthesize doped VO_2(M).

X-ray powder diffraction (XRD) was carried out on D8 X-ray diffractometer equipment with Cu Kα radiation, $\lambda = 1.54060$ Å. X-ray photoelectron spectroscopy (XPS, KRATOS, XSAM800 with MgKα 1253.6 eV 16 mA × 12 kV) was used to confirm the composition of the sample. The morphology of the products was observed by scanning electron microscopy (SEM, Quanta 200). The phase transition temperature of the samples was measured by differential scanning calorimetry (DSC, DSC822^e, METTLER TOLEDO) at a heating rate at 5 °C/min with a liquid nitrogen cooling system. Optical properties of the samples were tested by variable-temperature Fourier transform infrared spectroscopy (FT-IR, NICOLET 5700) with an adapted heating controlled cell.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-obtained samples without and with the additives, which reveals that the additives W, Mo, Sn and Fe atoms can promote the formation of VO_2(M) under the current conditions. Pure VO_2(A) (JCPDS, no. 42-0876) [25] is synthesized without the additive, as shown in Fig. 1(b). However, VO_2(M) (JCPDS, no. 43-1051) [26] can be obtained in the presence of the additives W, Mo, Sn or Fe atoms, as depicted in Fig. 1(d–g). When W (Fig. 1d) or Mo (Fig. 1e) is used as the additive, VO_2(M) with high purity is synthesized. VO_2(M) can be also obtained in the presence of Fe atom (Fig. 1f), however, the intensity of the diffraction peak at 27.88° is comparatively weak compared, Fig. 1(f), with Fig. 1(c–e). The mixture of VO_2(M) and VO_2(A) is formed when Sn atom is used as the dopant (Fig. 1g). Although the results of using Sn and Fe as the additives are not very good, they can indeed promote the formation of VO_2(M) under the hydrothermal conditions. Besides, the peaks related to additives are not observed, indicating that VO_2(M) solid solutions are synthesized.

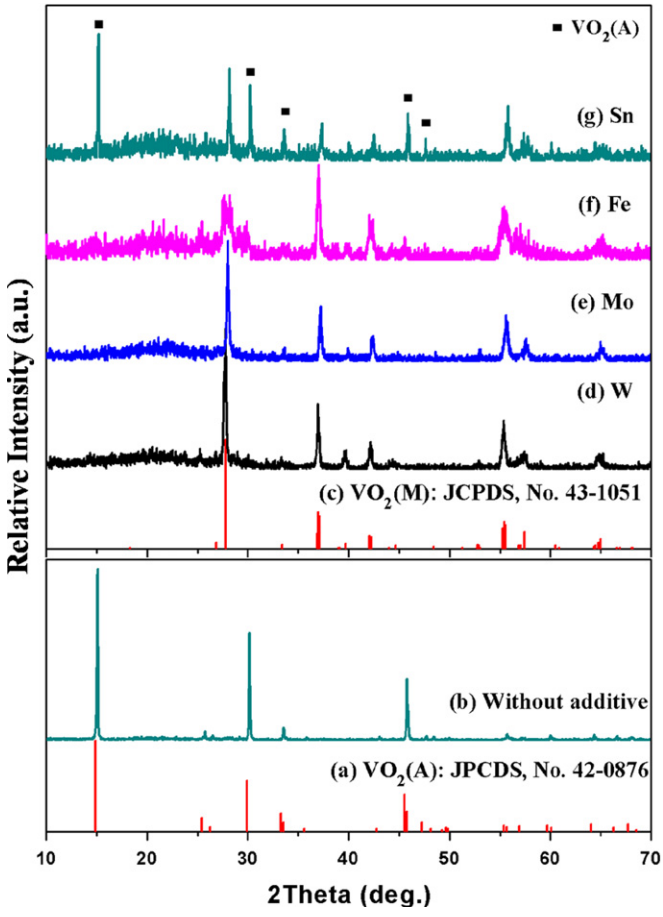

Fig. 1. XRD patterns of the as-obtained samples obtained with different additives: (a) the standard JPCDS plots of VO_2(A); (b) without any additives; (c) the standard JPCDS plots of VO_2(M); (d) W; (e) Mo; (f) Fe and (g) Sn.

Fig. S1 (Supplementary materials) represents the typical XPS spectra of Mo-doped VO_2(M), which indicates that there are only four elements: V, O, Mo and C, where the C peak is from surface contamination [14]. The peak at 233.6 eV (Fig. S1a) is attributed to Mo_{3d}, including $Mo_{3d3/2}$ (235.5 eV) and $Mo_{3d5/2}$ (232.3 eV), as shown in Fig. S2(b). According to the standard binding energy, the existing form of Mo ions in the sample is Mo^{6+} [27]. The above results indicate the successful synthesis of Mo-doped VO_2(M), in agreement with XRD observations.

Fig. 2 depicts the representative SEM images of VO_2(M) solid solutions using different additives. In all cases, it can be seen from Fig. 2 that the as-obtained VO_2(M) solid solutions predominantly consist of a large quantity of uniform micro- and nano-structures with well-defined facets. The VO_2(M) has the similar morphology with VO_2(A) which was obtained without any additives, as shown in Fig. S2 (Supplementary materials). It is noted that the formation of highly faceted micro and nanobelt structures with approximately rectangular cross sections wherein the widths exceed the thicknesses, as evidenced from the high-resolution SEM image (inset Fig. 2a), revealing the as-obtained VO_2(M) solid solutions have belt-like morphology. Obviously, the VO_2(M) solid solutions using W, Mo, Sn or Fe as the additives have the similar morphology, indicating that the above four additives have little influence on the morphology of doped VO_2(M). However, these additives are the key factors for the formation of VO_2(M). The belt-like VO_2(M) solid solutions basically consist of a large quantity of uniform micro- and nano-structures with typical lengths up to several tens of micrometers, widths ranging from several hundred nanometers to several micrometers, and thicknesses about 120–350 nm, which leads to the formation of belts with an ultrahigh-aspect-ratio.

When the phase transition of VO_2(M) occurs, it respectively exhibits a noticeable endothermal and exothermal profile in the heating and cooling DSC curves, which corresponds to the phase transition of VO_2(M). Fig. 3 shows the typical DSC curves of the doped VO_2(M) with different additives with heating and cooling cycles. There are endothermal and exothermal peaks in each of the DSC curves, which further confirm that the VO_2(M) solid solutions are successfully synthesized using the additives, in agreement with the XRD observations well. When W or Mo is used as the additive, there are two peaks in the heating curves. The explanation could be that two types of doped VO_2(M) are formed in the synthetic process, which should be confirmed in the following study. The T_c of W-doped VO_2(M) is about 53.3 °C in the heating cycle and about 43.3 °C in the cooling cycle, while the T_c of Mo-doped VO_2(M) is about 63.1 °C in the heating cycle and about 53.2 °C in the cooling cycle. The endothermal and exothermal peaks are asymmetric due to the hysteresis behavior in the sample. However, in the case of Sn and Fe, the T_c of doped VO_2(M) is approximately unchanged, compared with the undoped VO_2(M) [1]. The T_c of Sn-doped VO_2(M) is about 68.1 °C in the heating cycle and about 54.5 °C in the cooling cycle, while the T_c of Fe-doped VO_2(M) is about 66.2 °C in the heating cycle and about 47.8 °C in the cooling cycle. These results reveal that the Sn or Fe atoms have little influence on the T_c of VO_2(M), but they can promote the formation of VO_2(M) under the hydrothermal conditions.

So far, the research about the formation mechanism of VO_2(M) using additives is still processing. The possible