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VO_2(M) with narrow hysteresis width from a new metastable phase of crystallized VO_2(M)·0.25H_2O

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ABSTRACT

VO_2(M) nanomaterials with narrow hysteresis width of 3.4 °C has been prepared by dehydration of a novel phase of crystallized VO_2(M)·0.25H_2O. The structure and composition have been investigated, and the dehydration process has been analyzed combining the thermal analysis of TGA and DSC. It provides a new way to obtain efficient VO_2(M) that will be beneficial for high sensitive electrical/optical devices or other applications.

1. Introduction

Vanadium dioxide (VO_2) is a typical polycrystalline compound, including VO_2(A) [1], VO_2(B) [2], VO_2(C) [3], VO_2(D) [4], VO_2(M) [5], VO_2(R) [6], etc. Among which undergoes a fully reversible metal-semiconductor transition (MST) between VO_2(R) and VO_2(M) around 68 °C, accompanied by abrupt changes of optical and electrical properties. The MST gives rise to potential applications of VO_2 in smart optical and electrical switchers [7–9]. However, an obvious difference of phase transition temperature (about 5–20 °C) exists in the heating and cooling process during phase transition [10–13]. This phenomenon is called thermal hysteresis, and the corresponding width is defined as thermal hysteresis width (ΔT_c) [14]. The wider hysteresis is usually ascribed to the superheating and supercooling, which can accelerate the deterioration of the switching behavior and reduce the efficiency of the uncooled detectors operation [15,16]. Therefore, it is of great significance to reduce the ΔT_c for the development of sensitive electrical/optical devices, which is closely dependent on the synthesis method and growth control of VO_2(M). Among the methods to reduce the ΔT_c, including element doping [17,18], interfacial stress inducing [19] or effective defect generating [20], the element doping especially Ti-doped is considered to be the most effective method. For example, the ΔT_c of Ti-doped VO_2 film prepared by polymer-assisted deposition decreased from 38.2 °C to 3.5 °C [21]. However, element doping may change the phase-transition temperature and challenging to explore structural and mechanistic of dopants for phase transition behavior.

Herein, VO_2(M) nanomaterials with narrow hysteresis width of 3.4 °C is obtained by the dehydration of VO_2(M)·0.25H_2O, which is a new metastable phase of crystal. The intermedium VO_2(M)·0.25H_2O is formed during low temperature hydrothermal reaction in a VOC_2O_4-$H_2C_2O_4$·2H_2O system without any additive and template. This work will give new way to prepare VO_2(M) and be beneficial for applications in high sensitive electrical/optical devices.

2. Experimental

2.1. Preparation of star-like VO_2(M)·0.25H_2O

In a typical synthesis, 2.002 g V_2O_5 and 4.158 g $H_2C_2O_4$·2H_2O were dissolved in 100 mL of deionized water under vigorous stirring at 80 °C for 2 h until a blue clear solution is formed. 33 mL of the obtained solution (VOC_2O_4, 0.22 mol·L^{-1}) and 0.045 g $H_2C_2O_4$·2H_2O were added into a 50 mL stainless steel autoclave, which were sealed and maintained at 180 °C for 24 h and then cooled to room temperature naturally. The blue-black precipitate was filtered and washed with distilled water and anhydrous alcohol 3

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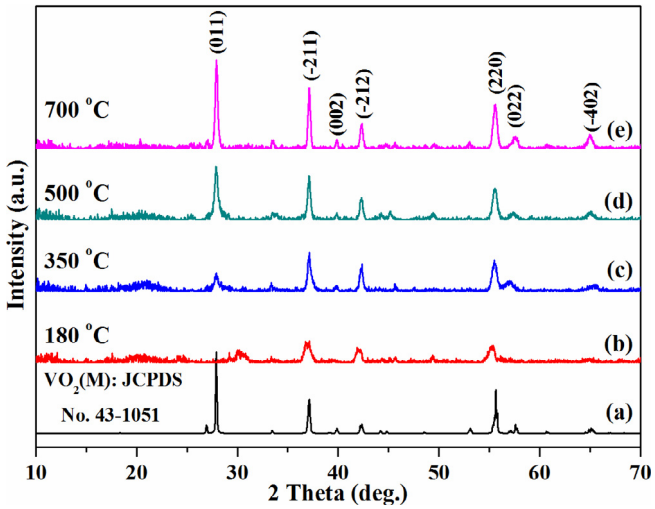

Fig. 1. XRD patterns of the obtained samples before and after heat treatment at different temperature.

times, respectively, and dried in air at 70 °C for 12 h to obtained $VO_2(M)\cdot 0.25H_2O$.

2.2. Preparation of star-like $VO_2(M)$

The as-prepared powders of $VO_2(M)\cdot 0.25H_2O$ were heated in a tube furnace with 5 °C/min heating rate under a flow of argon (99.999%) gas for 1 h at 350, 500, 700 °C, respectively, and cooled to room temperature in the argon flow to form $VO_2(M)$.

2.3. Characterization

X-ray powder diffraction (XRD) was carried out on D8 X-ray diffractometer equipment with Cu Kα radiation, λ = 1.54060 Å. The morphology of the products was observed by scanning electron microscopy (SEM, Quanta 200) and transmission electron microscopy (TEM, JEM-2100). The phase transition temperature of the samples was measured by differential scanning calorimetry (DSC, DSC822^e, METTLER TOLEDO) in a heating rate at 5 °C/min with a liquid nitrogen cooling system. Thermal gravimetric analysis (TGA) was performed on TG 209 F1. Fourier transform infrared spectroscopy (FT-IR) patterns of the solid samples were measured using KBr pellet technique from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

3. Results and discussion

XRD patterns of the as-obtained samples before and after heat treatment are depicted in Fig. 1. From current hydrothermal process(Fig. 1b), the obtained sample shows low crystallinity with most of diffraction peaks are seem indexed to the metastable $VO_2(M)$ polymorph (Fig. 1a, Joint Committee on Powder Diffraction Standards JCPDS, No. 43-1051) [22]. Except a week peak at 30.5°, which is an unknown phase did not match any vanadium oxide or hydrated vanadium oxide phase in the ICDD PDF database. It seems an attribution for $VO_2(D)$ or others, indicating that the product maybe a new metastable phase [23]. After annealing at 350 °C for 1 h, every diffraction peak is indexed to the metastable $VO_2(M)$ polymorph without any other parasitic phases are detected. And all diffraction peaks become sharper and higher intensity after thermal treatment at 500 and 700 °C, indicating that monoclinic crystalline $VO_2(M)$ phase has been formed.

To confirm the phase and structure of the as-obtained products and understand the evolution of phases upon heating, the products were subjected to thermal analysis of DSC and TGA in a flowing N_2 atmosphere, as shown in Fig. 2a. An obvious broad endothermic peak in the heating circle of DSC curve around 200–400 °C, and a sharp exothermic peak occurs at 62.0 °C, indicating that $VO_2(M)$ has been obtained after heat treatment. In addition, the TGA plot exhibits a weight loss of ~5.06% at the range of 250–400 °C, which is believed to exclude the phase transformation between $VO_2(D)$ and $VO_2(M)$ during the heat treatment. Furthermore, FTIR results (Fig. 2b) show that the bands in the (3464, 3521 and 1641) cm^{-1} region which attributed to the H_2O molecules disappear after heat treatment, confirming the release of water [24]. And the peak at 1023 cm^{-1} which attributed to the stretching vibration υ(V-O) shifts to 1095 cm^{-1}, while the peak at 576 cm^{-1} which attributed to υ(V-O-V) are split into 2 peaks (605 and 507 cm^{-1}), indicating an effect of the O—H stretching from lattice water [25,26]. Therefore, the phase of the products synthesized from the hydrothermal process is suggested to be $VO_2(M)\cdot 0.25H_2O$ according to the weight loss of ~5.06% from the TGA result.

The size and morphologies of the as-obtained materials were examined by scanning SEM and TEM, and the results of which were displayed in Fig. 3. Both $VO_2(M)\cdot 0.25H_2O$ (Fig. 3a) and $VO_2(M)$ (Fig. 3b) exhibited similar star-like structure with six arms, indicating that the morphology of $VO_2(M)$ is depending on the $VO_2(M)\cdot 0.25H_2O$. Furthermore, the analyses of HRTEM image and the SAED pattern results show that there are two sets of lattice parameters and obvious distortion indicating that crystal water may affect the VO_2 structure, as shown in Fig. 3c. As expected, these novel

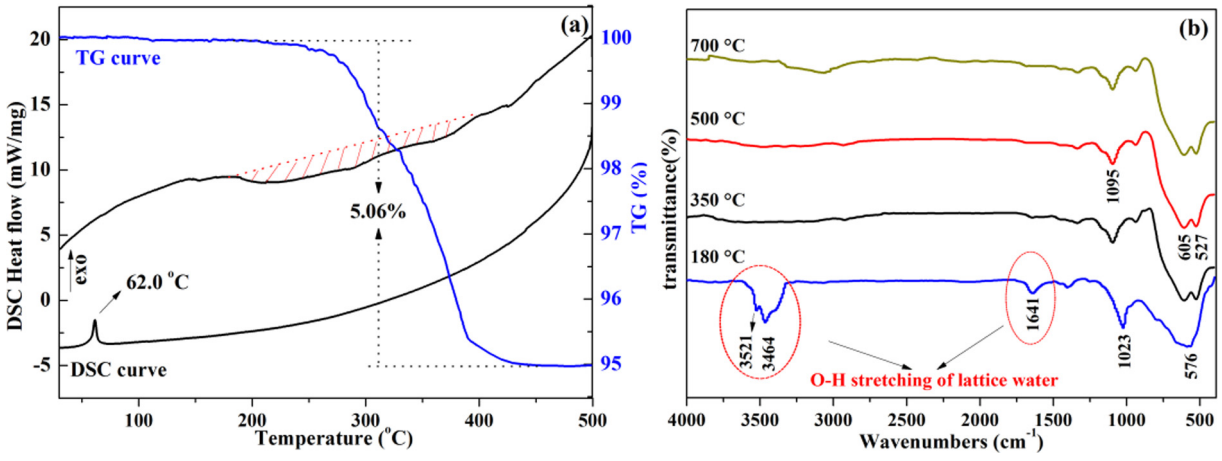

Fig. 2. Thermal analysis graph (a) and FTIR spectrum (b) of the obtained samples.