Hexagonal VO$_2$ particles: synthesis, mechanism and thermochromic properties†

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Monoclinic vanadium dioxide VO$_2$ (M) with hexagonal structure is synthesized by hydrothermal method, and the phase evolution is evidenced. Interestingly, the hexagonal morphology comes into being as a result of the low-energy coherent interfaces, (211)$_1$//(211)$_2$ and (211)$_1$//(020)$_2$. The size of hexagonal particles is well controlled by changing the concentration of precursor solutions. Hexagonal particles exhibit excellent thermochromic properties with a narrow hysteresis of 5.9 °C and high stability. In addition, the phase transition temperature can be substantially reduced down to 28 °C by simply W doping.

1. Introduction

Vanadium dioxide (VO$_2$) possesses several phases, M, R, B,$^7$ A,$^2$ and D,$^4$ and exhibits fantastic phase transition between them.$^{5,5}$ The distinguishing feature of each polymorph is the arrangement of edge- or corner-sharing VO$_6$ octahedra. Monoclinic VO$_2$ (M) shows a reversible first-order metal-insulator transition (MIT) at 68 °C.$^6$ When the insulating VO$_2$ (M) is converted into the metallic rutile phase (R), drastic changes occur in both electrical and optical properties.$^{7,8}$ As a result, VO$_2$ has been attracting much attention owing to the potential applications in high-tech fields, such as, sensors,$^{9,10}$ catalysts,$^{11}$ lithium-ion batteries,$^{12}$ storage medium,$^{13}$ smart windows$^{14-17}$ and so on. Since the size and morphology of nanostructures affect the physical and chemical properties greatly, it is very important to understand the formation and growth behavior of VO$_2$ and make it controllable.

A variety of physical and chemical strategies, such as, atomic layer deposition,$^{18}$ sol–gel,$^{19}$ ion implantation technique,$^{20}$ chemical vapor deposition,$^{21}$ pulsed laser deposition,$^{22}$ magnetron sputtering$^{23,24}$ and solution-based synthesis$^{25}$ have been developed to fabricate VO$_2$ nanostructures. Among them, the solution-based method gained increasing attention because of the simple preparation process and low cost. In the solution-based synthesis, VO$_2$ nanostructures of different phases and morphologies have been produced, dependent on the reaction temperature (Fig. S1†), reaction time, precursor concentration and autoclave filling ratio. Hexagonal VO$_2$ (M) was obtained by the hydrothermal synthesis and, VO$_2$ (B), VO$_2$ (A) and VO$_2$ (D) phases appeared as intermediates. To be confused, different intermediates were involved in the hydrothermal process. VO$_2$ (B) is firstly transformed into VO$_2$ (A) and then into VO$_2$ (R).$^{26}$ However, VO$_2$ (A) does not appear in some cases.$^{15}$ Here, it is demonstrated that the hydrothermal reaction process is closely related to the reaction speed that is easily controlled by changing the concentration of precursor solutions. Hexagonal structure has been evidenced extensively, but the formation mechanism is still ambiguous. Cao $^{27}$ proposed that it could be ascribed to the similar growth rate along the six low-energy (201) facets, while someone suggested that it was assembled from nanobelts. In this paper, the coherent relationship between each branches of hexagonal structure is characterized, which provides deep insights into the morphology evolution of VO$_2$ (M).

2. Experimental details

VO$_2$ nanostructures were synthesized by the hydrothermal method using V$_2$O$_5$ as the vanadium source and oxalic acid (H$_2$C$_2$O$_4$) as a reducing agent. The filling ratio of the vessel is about 70%. Firstly, oxalic acid (H$_2$C$_2$O$_4$) and V$_2$O$_5$ (1 : 1 – 1 : 3 in molar) are directly added into 35 ml deionized water at room temperature (RT), and then ammonium tungstate ((NH$_4$)$_2$O$_7$·W$_{12}$O$_{41}$·xH$_2$O) is dispersed into the above solution and stirred for 4 hours. 35 ml of the precursor solution is transferred into a 50 ml stainless autoclave with a Teflon liner and ultimately the autoclave is heated up to 260 °C for 1–24 h and then cooled in air to room temperature. The resulting black precipitate is collected and washed with distilled water and ethanol three times by centrifugation and then dried in vacuum at 60 °C for 12 h. The as-prepared VO$_2$ nanostructures are ultrasonically dispersed in deionized water for 30 min, and an appropriate quantity of silane coupling agent KH-570 is added with ultrasonic treatment for another 30 min. Then, polyurethane (PU,
DISPERCOLLU54, Bayer) is added with magnetic stirring for 10 min. Finally, the suspension is uniformly cast onto a polyethylene terephthalate (PET) substrate using an automatic coating machine and dried at 80 °C for 1 min.39

The morphology of VO₂ nanostructures were characterized by transmission electron microscopy (TEM) and field-emission scanning electron microscopy (FESEM, JSM-7000F). The crystal phases was determined by X-ray diffraction (GIXRD, Shimadzu XRD-7000) with Cu Kα radiation (λ = 0.154 nm) at a fixed incident angle of 0.5° and 2θ scanning rate of 8° min⁻¹. Differential scanning calorimetry (DSC, DSC204F1, NETZSCH, Germany) were measured at 50–100 °C with a heating rate of 5 °C min⁻¹ under a nitrogen flow. The elemental component and chemical valence states were determined by X-ray photoelectron spectroscopy (Thermo Scientific K-Alpha, XPS). The transmittance spectra were measured in the range of 300–2200 nm at normal incidence using a Hitachi U-4100 spectrometer.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples prepared at three molar ratios (r = 1, 2, 3) of H₂C₂O₄ to V₂O₅. Different phase evolutions, VO₂ (B) → VO₂ (A) → VO₂ (M), VO₂ (B) → VO₂ (M) and VO₂ (B) → VO₂ (D) → VO₂ (M) are evidenced. As shown in Fig. 1a, at the reaction condition of r = 1, only the diffraction peaks of VO₂ (B) are identified for 1 h hydrothermal reaction. The corresponding SEM image is shown in Fig. 2a, VO₂ (B) exists in the form of nanobelts with 2–4 μm long and 200–400 nm wide. The VO₂ (B) phase is confirmed by the TEM images in Fig. 3. The HRTEM image in Fig. 3b shows the lattice fringe spacing of 0.353 nm, corresponding to (110) lattice plane of monoclinic VO₂ (B). As illustrated by the selected area electron diffraction (SAED) pattern in the inset of Fig. 3a, the zone axis of the reciprocal lattice is [001]. If the hydrothermal reaction time is elongated to 6 h, new diffraction peaks corresponding to VO₂ (A) and VO₂ (M) phases appear on the XRD pattern, and a great number of nanobelts with rectangular ends emerge (Fig. 2b). If the reaction time is further elongated to 12 h, the peaks of VO₂ (B) vanish completely and the peak intensity of VO₂ (A) and VO₂ (M) increases greatly. As displayed in Fig. 2c, rectangular nanobelts and truncated nanorods coexist. Fig. 3d presents the HRTEM image of the rectangular nanobelts in Fig. 3c, the fringe spacing of 0.59 nm matches well with the (110) plane of tetragonal VO₂ (A). According to the SEM images in Fig. 2b–d and the XRD patterns in Fig. 1a, it can be concluded that the truncated nanorods should be VO₂ (M). If the reaction time is elongated to 24 h, the peaks of VO₂ (A) become weakened gradually, but those of VO₂ (M) are enhanced, that is, the growth of VO₂ (M) rather than VO₂ (A) dominates after the elimination of VO₂ (B). At the reaction condition of r = 2, no peak of VO₂ (A) appears on the XRD pattern in Fig. 1b, and the size of VO₂ (B) nanostructure (Fig. 2e) is reduced substantially as compared to that in Fig. 2a. Phase transition between VO₂ (B) and VO₂ (R) was studied in situ by electron microscopy,39 and it was found that VO₆ octahedra (Fig. S2†) in VO₂ (B) abruptly broke into nanocrystallites and half of VO₆ octahedra reorient into rutile structure. VO₂ (B) in spheroidal morphology appears (Fig. 2g) because of severe agglomeration. At the reaction condition of
that the growth is along [100] direction. As depicted in Fig. 4e, bud-like nanoparticles grow outwards from a nanorod, in which \((211)_{1}//(211)_{2}\) and \((211)_{1}//(020)_{2}\) coherent interface exist in the adjacent branches, thus small lattice distortions emerge if they are combined into a heterogeneous interface. It is demonstrated
that the angle (about 60°) between the adjacent branches is
decided by the coherent interfaces. The overlapped FFT patterns
in Fig. 4g confirm the coherent crystalline planes between the
adjacent branches, and Fig. 4h schematically shows the atomic
arrangement.

Fig. 5 schematically shows the evolution of VO₂ (M) hexagonal
morphology. The reaction proceeds toward the lowest
energy, and promotes the oriented attachment. Firstly, VO₂
is reduced by H₂C₂O₄ and the interphase VO₂ (B) is produced. As
the reaction proceeds, oriented attachment or aggregation
occurs spontaneously in order to minimize energy, thus
a great number of belts (Fig. 2b) or urchin-like (Fig. 2i) structure
appear. Then metastable VO₂ (B) transforms into a more stable
phase gradually. As aforementioned, different growth processes
yield different interphases, which are dominated by nucleation
rate and growth rate. H₂C₂O₄ plays an important role in
reduction rate and further affects the supersaturation. The ratio
of growth rate to nucleation rate is high under low supersatura-
tion condition and vice versa. In another word, the competition
between nucleation rate and growth rate results in different morphologies, high nucleation rate results in aggregation and high growth rate leads to ultra-long nanobelts. VO₂ (A) is from the stack of VO₂ (B) nanobelts. At high nucleation rate, VO₂ (B) prefers to aggregation rather than stacking, and thus no VO₂ (A) appears. Hydrothermal reaction condition of

\[ r = 1 \] (Fig. 2d) yields large hexagonal structure with ultra-long
branches in the range of 4–8 µm and 600 nm in width. The
length decreases to 4–6 µm \((r = 2)\) and 2–4 µm \((r = 3)\) respectively
with increasing H₂C₂O₄. VO₆ octahedra of VO₂ (B) is
different from VO₂ (R), but similar to VO₂ (A) (Fig. S2†). Thus,
more energy is needed for the transformation from VO₂ (B) to
VO₂ (R) \((r = 2)\) than to VO₂ (A) \((r = 1)\). So an appropriate H₂C₂O₄
could promote the formation of VO₂ (R).

Fig. 6a shows the DSC curves of the as-synthesized VO₂ (M)
with \( r \) of 1, 2 and 3. The DSC curves of both \( r \) = 1 and 2 display
endothermic and exothermic profiles upon heating and cooling
in the temperature range of 0–100 °C, indicating a reversible
phase transition, but only an endothermic profile is observed
in the heating process for \( r \) of 3. So the temperature range from
70 to 100 °C was adopted for the DSC measurement for \( r \) of 3,
and the results are displayed in Fig. 6b. The phase transition
temperature and hysteresis width of the samples are summa-
rized in Fig. 6c. Apparently, the samples exhibit dramatically
different phase transition properties. The \( T_C \) is 68, 60.5 and
62.5 °C during heating process, and 61.1, 137 and −42 °C
during cooling process. The hysteresis width is about 6.9, 48.6
and 104.5 °C for the as-synthesized VO₂ (M) particles obtained
at \( r = 1, 2, 3 \), respectively, and the hysteresis width is not
dependent on the particle size of micrometers. As shown in
Fig. 7a, some residual VO₂ (A), VO₂ (B) and VO₂ (D) phases exist

**Fig. 4** (a) Low-magnification TEM images, (b) HRTEM image at the VO₂ rod end, (c) SAED pattern of the particle in (b) and (d) the calculated SAED pattern from [102] zone axis, (e) low-magnification TEM image, (f) HRTEM image of the overlap region between adjacent branches, (g) the FFT pattern of the overlap region from panel (f) and (h) the atomic arrangement in panel (f).

**Fig. 5** Schematic evolution of the polymorph morphology.
except the dominating VO$_2$ (M) phase at $r = 1, 2$ and 3, respectively. The residual VO$_2$ (A) has little effect on the phase transition of VO$_2$ (M) obtained under $r = 1$, as shown in Fig. 6c. On the contrary, the phase evolution of VO$_2$ (M) obtained under $r = 2, 3$ is indeed a recrystallization process, and thus there is a considerable interaction between VO$_2$ (B) and VO$_2$ (M) as well as between VO$_2$ (D) and VO$_2$ (M), so the residual VO$_2$ (B) and VO$_2$ (D) affect the phase transition of VO$_2$ (M) obtained under $r = 2$ and 3. The transformation from monoclinic (020)$_M$ plane at room temperature to (200)$_R$ plane at high temperature was accompanied by the peak shift from 39.88° to 39.67°. As shown in Fig. 7b, the peak of (020)$_M$ plane shifts toward the smaller angle at $r = 2$ and 3. In addition, a new peak appears at 39.5° for the sample prepared under $r = 3$, and it is lower than 39.67°, implying increased V–V bond length and stabilized VO$_2$ (R) at room temperature. Therefore, more energy is needed to induce the phase transition in the cooling cycle, resulting in the large hysteresis width. Fig. 9a and b show the optical transmittance of the as-synthesized and annealed samples, respectively. All the samples show a sharp optical contrast in near infrared at 20 and 90 °C. The $T_{\text{vis}}$ and $\Delta T_{2000}$ obtained from Fig. 9a and b are displayed in Fig. 9c and d, respectively. $T_{\text{vis}}$ changes a little but $\Delta T_{2000}$ increases significantly upon thermal annealing. It means that the residual phases affect the NIR modulation ability of VO$_2$ (M) considerably.

It is difficult to obtain pure VO$_2$ (M) in a V$_2$O$_5$–H$_2$C$_2$O$_4$ reaction system if no thermal annealing or doping is done. As shown in Fig. 8a, pure VO$_2$ (M) is obtained after thermal annealing at 450 °C for 2 h. The $T_C$ is about 70.5, 69.3 and 68 °C during the heating process, and 61.5, 61.9 and 62.1 °C during cooling process (Fig. 8b), and the hysteresis width is about 9, 7.4 and 5.9 °C when $r$ is 1, 2 and 3, respectively. Apparently, the hysteresis widths of the samples prepared at $r = 2, 3$ are reduced dramatically upon thermal annealing. But the particle size and structure changes little [Fig. S5†], indicating high stability of the hexagonal VO$_2$ (M). As stated above, the intermediate phases indeed have a great influence on the hysteresis width. In addition, the hysteresis width of the pure VO$_2$ (M) obtained here is significantly smaller than what was reported. It can be due to the lattice distortions in coherent interface of adjacent branches. The defects act as nucleation site for metal-insulator transition and decrease the driving force. The number of branch grows as increasing $r$, as shown in Fig. 2, and the smallest hysteresis is obtained at $r = 3$.

Based on the preparation process in Fig. S6,† the composite films are prepared to measure the optical properties. The suspension composed of VO$_2$ (M) particles is uniformly cast on the PET substrate and the film exhibits a canary yellow color.
Fig. 9a and b show the optical transmittance of the samples before and after annealing, respectively. All the samples show a sharp optical contrast in near infrared at 20 and 90 °C, indicating that the phase transition occurs. In addition, \( \Delta T_{2000} \) is continuously improved from 28.3% to 41% as \( r \) increases from 1 to 3, due to the reduced sizes of the particles.

Tungsten (W) is the most effective dopant for reducing the phase transition temperature. Fig. 10a shows a wide-range survey X-ray photoelectron spectroscopy (XPS) of W-doped VO\(_2\) (M). C, V, W and O are detected, in which the signal of C is from the contamination on surface. From Fig. 10b, it can be seen that the \( V_{2p3/2} \) peak of the particles is centered at 516.3 eV. As shown in Fig. 10c, the W4f orbital has the binding energies at 35.36 and 37.38 eV corresponding to W4f7/2 and W4f5/2, respectively. Accordingly, W in the powders is in the form of W\(^{6+}\). It confirms that W atoms are actually doped into the VO\(_2\) nanoparticles. Fig. 10d shows the energy dispersive spectroscopy (EDS) of which V, O, W and C are involved. Fig. 11a shows the DSC curves of W\(_x\)V\(_{1-x}\)O\(_2\) samples with different W concentrations. Each DSC curve displays sharp endothermic and exothermic profiles upon heating and cooling cycles. In addition, the double endothermic/exothermic peaks appear during the heating/cooling process, probably due to the non-uniform doping or the polydispersity in the size distribution. As shown in Fig. 10b, \( T_C \) is reduced down to 28 °C and the hysteresis width is less than 10 °C when the doping level is 2.0 at%. The substantially lowered transition temperature and small hysteresis width can meet the requirement for the applications in smart window completely. The hysteresis width is sensitive to the doping concentration. However, the doped samples with hexagonal structure are more stable with a hysteresis width changing from 5 to 8 °C. In fact, the hexagonal porous morphology can provide a rigid framework and free volume simultaneously for the abrupt change between monoclinic and tetragonal phases.
4. Conclusion

In summary, VO₂ (M) has been successfully synthesized through one-step hydrothermal method. H₂C₂O₄ plays a role in adjusting the phases and dimension of VO₂. This can be understood from the competition between the nucleation and growth rates. The coherent [(211)/(020)] interfaces between adjacent branches promote the formation of hexagonal structure. Furthermore, it is demonstrated that the VO₂ (M) with hexagonal morphology improves the sensitivity and stability. The combination of hexagonal structure and W doping leads to substantially reduced phase transition temperature down to 28 °C.

Conflicts of interest

There are no conflicts to declare.

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