Hydrothermal synthesis of VO$_2$(A) nanobelts and their phase transition and optical switching properties

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VO$_2$(A) nanobelts are successfully synthesised through a facile hydrothermal approach using peroxovanadium (V) complexes and green solvent (ethanol) as the reducing agent without using any surfactants or templates. The as-obtained products were characterised by X-ray photoelectron spectroscopy, X-ray powder diffraction, scanning electron microscopy and transmission electron microscopy. The as-obtained VO$_2$(A) nanobelts are with typical lengths up to several tens of micrometres, widths about 180 nm and thicknesses about 45 nm on average. The phase transition properties of VO$_2$(A) was investigated by differential scanning calorimetry, indicating that it exhibits a strong phase transition at around 160.9°C. Furthermore, the optical switching properties of VO$_2$(A) were first studied by the variable-temperature infrared spectra to the best of author’s knowledge, and it was found that VO$_2$(A) nanobelts could be used as the optical switch at different vibratory absorption bands.

1. Introduction: Recently, nanobelts have attracted increasing attention because of their structural, novel chemical and physical properties, as well as their promising potential applications in nanodevices [1–3], which is different from their bulk materials. Moreover, the hydrothermal approach is an effective method to fabricate one-dimensional nanostructures not only because of its critical temperature and pressure, but also the low cost, large scale and high chemical and physical properties, which made them have a wide range of practical applications, such as catalysts, cathode materials for reversible lithium-ion batteries, gas sensors, optical switching devices, intelligent thermochromic windows, and so on [7–12]. As a family of vanadium oxides, vanadium dioxide (VO$_2$) is a representative binary compound with different polymorphs, for example, VO$_2$(M), VO$_2$(R), VO$_2$(B), VO$_2$(A) [13], recently reported VO$_2$(C) [14], and so on. Among them, a great deal of attention has been paid to VO$_2$(B), VO$_2$(M) and VO$_2$(R) for the reason that VO$_2$(B) can be used as the promising cathode materials in lithium-ion batteries [15], while VO$_2$(M/R) undergo a semiconductor-to-metal transition at 68°C, accompanied with drastic changes in both electrical and optical properties [16, 17]. However, other polymorphs of VO$_2$, which may also have scientific importance, novel chemical and physical properties, and potential applications, have been reported less well, comparatively [18]. Thus, the study on other polymorphs of VO$_2$ is urgent necessary and the discovery of their novel properties and potential applications is a challengeable task for materials scientists. Until now, the research on VO$_2$(A) has not been sufficiently conducted in the literature. In this Letter, we put emphasis on the synthesis, the chemical and optical switching properties of VO$_2$(A).

The presence of VO$_2$(A) was first reported by Théobald [13] in his extensive studies on the hydrothermal reaction of the VO$_2$−VO$_2$$_5$−H$_2$O system. Several decades later, Oka and his co-workers [19–21] reported that VO$_2$(A) was prepared by the hydrothermal method using VO(OH)$_2$ or VOCl$_2$ as the precursors. The structures of VO$_2$(A) were determined as low-temperature phase (LTP) and high-temperature phase (HTP) before and after the phase transition temperature ($T_c$), respectively. They also found that VO$_2$(A) underwent a metal–semiconductor transition at around 162°C (P4/ncc, 130 below 162°C and I4/m, 87 above 162°C) in the case of VO$_2$(M/R). Thereafter, there were few references about VO$_2$(A) reported. Recently, VO$_2$(A) nanorods were synthesised by the reduction of VO$_2$(A) with oxalic acid under hydrothermal treatment [18]. Thus, the synthesis, property and application of VO$_2$(A) are very deserved to be studied. Besides, the optical switching properties of VO$_2$(A) are not reported to the best of authors’ knowledge.

Herein, we developed a facile way to synthesise VO$_2$(A) nanobelts by the reduction of peroxovanadium complexes ([VO(O$_2$)$_{2-x}$]$^x^+$) with ethanol without any surfactants or templates under the hydrothermal treatment. Furthermore, the optical switching properties of VO$_2$(A) were studied by the variable-temperature infrared spectra for the first time to the best of authors’ knowledge.

2. Experimental: All reagents used in the experiments were of analytical grade and used without any further purification. In a typical synthesis, 0.45 g of bulk VO$_2$ was dispersed in 37 mL of redistilled water with magnetic stirring. Then 2 mL of H$_2$O$_2$ (30 wt%) and 1 mL of absolute ethanol were successively added into the above solution. The solution was still stirred for 1 h at room temperature to get good homogeneity. After mixing, the mixture was transferred into a 60 mL stainless steel autoclave, then sealed and maintained at 300°C for 48 h. When the reaction was finished, the blue–green precipitate was filtered off, washed with distilled water and anhydrous alcohol several times, respectively, and dried in vacuum at 75°C for future characterisation and application.

X-ray photoelectron spectroscopy (XPS, VGESCALAB MK II with Mg K$_{α}$, 1253.6 eV) was used to confirm the composition and the oxidation state of the vanadium. X-ray powder diffraction (XRD) was carried out on a D8 X-ray diffractometer equipment with Cu K$_{α}$ radiation, A = 1.54060 Å. The morphology of the products was observed by scanning electron microscopy (SEM, Quanta 200) and transmission electron microscopy (TEM, JEM–100CXII). The phase transition temperature of the samples was measured by differential scanning calorimetry (DSC, DSC822°, METTLER TOLEDO) in a heating rate at 5°C/min with a liquid nitrogen cooling system. Optical properties of the samples were tested by Fourier transform infrared spectroscopy (FTIR, NICOLET 5700).
with an adapted heating controlled cell. FTIR patterns of the solid samples were measured using KBr pellet technique from 4000 to 400 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). About 1 wt% of the samples and 99 wt% of KBr were mixed homogeneously, and then the mixture was pressed to a pellet.

3. Results and discussion: Important information about the surface composition and the chemical element valence of the as-obtained sample can be provided by the XPS measurement, as shown in Fig. 1. Fig. 1a shows the survey spectrum of the as-obtained sample. It can be seen that no peaks of elements other than V, O and C can be observed, which is corresponding with the results of other vanadium oxides, for example, VO\(_2\)(B) [22], V\(_3\)O\(_7\)-H\(_2\)O [23] and V\(_2\)O\(_3\) [24]. The C\(_{1s}\) peak is owing to some CO\(_2\) absorbed on the surface of the sample and can be disregarded. The V\(_{2p}\) core-level spectrum (Fig. 1b) illustrates that two peaks at 516.3 and 523.8 eV are attributed to the spin-orbit splitting of the components, V\(_{2p3/2}\) and V\(_{2p1/2}\), which is the characteristic of vanadium in the +4 oxidation state in the bulk [23, 25, 26].

Fig. 2 represents a typical XRD pattern of the VO\(_2\)(A) obtained by our designed hydrothermal conditions. All the diffraction peaks from Fig. 2b can be readily indexed to the tetragonal crystalline phase (space group: P4\(_2\)/nmc 138) of VO\(_2\)(A), in agreement with the literature values (JCPDS no. 42-0876, \(a = 8.450 \text{ Å}, c = 7.686 \text{ Å}\)) [19], whose plots are shown in Fig. 2a. No peaks of any other phases are detected, indicating the as-prepared sample with high purity.

Based on the above results, VO\(_2\)(A) was successfully prepared though two steps in our synthetic route. In the first step, the bulk V\(_2\)O\(_5\) powders were completely dissolved in dilute H\(_2\)O\(_2\) aqueous solution to form the deep orange solution and the [VO(O\(_2\))\(_2\)]\(^2-\) was formed [27]. The reaction equation is as follows:

\[
V_2O_5 + 4H_2O_2 \rightarrow 2[VO(O_2)_2]^- + 3H_2O + 2H^+ \quad (1)
\]

In the second step, all of vanadium atoms in the +5 oxidation state ([VO(O\(_2\))\(_2\)]\(^-\)) were reduced to that of +4 oxidation state in the presence of ethanol, and the crystal nuclei of vanadium oxides appeared and constituted freely to form VO\(_2\)(A) under the hydrothermal conditions. In this progress, the ethanol served as the reducing agent. A portion of ethanol was oxidised to aldehyde, which was experimentally confirmed through chemical analysis (silver mirror reaction and GC analysis) of the final solution mixture and also in agreement with the literature [22, 23, 28]. Thus, the reaction equation of VO\(_2\) through the reaction of V\(_2\)O\(_5\), H\(_2\)O\(_2\), EtOH and H\(_2\)O under the hydrothermal condition can be expressed as follows:

\[
2[VO(O_2)_2]^- + 2H^+ + CH_3CH_2OH \rightarrow 2VO_2 + CH_3CHO + 2H_2O + 2O_2 \quad (2)
\]

The morphology of the as-obtained VO\(_2\)(A) was investigated by SEM and TEM tests. Fig. 3a shows a representative SEM image, which illustrates that VO\(_2\)(A) predominantly consists of a large quantity of uniform nanostructures with well-defined facets. We can occasionally see some rectangular cross-sections at the end of the sample, indicating the product is belt-like morphology. A representative TEM image (Fig. 3b) further confirms the results of SEM analysis. The as-obtained VO\(_2\)(A) nanobelts are with typical lengths up to several tens of micrometres, widths about 180 nm and
thickneses about 45 nm in average from the SEM and TEM images. The phase and dimension of the as-prepared products are sensitively dependent on the reaction conditions (e.g. the reaction time, the reaction temperature and the ratio of EtOH/H₂O) through our extensive experiments.

When the phase transition of VO₂(A) occurs, it exhibits a noticeable endothermic profile in the DSC curve. The temperature of this endothermic profile corresponds to that of the VO₂(A) phase change. The DSC curve of VO₂(A) nanobelts is depicted in Fig. 4. The endothermic peak representing the phase transition temperature of the VO₂(A) nanobelts appears at 160.9 °C on the curve. The explanation can be that the structure of VO₂(A) is converted from LTP (P4/ncc, 130) to HTP (I4/m, 87) at this temperature, accompanying with the endothermic profile, which corresponds to the previous report of VO₂(A) [21] and is similar with the VO₂(M/R).

According to the DSC result of the as-obtained VO₂(A) nanobelts, it undergoes a noticeable endothermic peak at about 161 °C. However, there are no references reported about the optical property of VO₂(A) before and after the phase temperature. Therefore the as-obtained VO₂(A) nanobelts were explored as an optical switching device in this Letter. The optical switching property of VO₂(A) nanobelts was investigated by a series of variable-temperature infrared spectra of heating and cooling, as shown in Fig. 5. Fig. 5a shows all the curves obtained with the variable-temperature IR tests. It can be clearly observed from Fig. 5a that VO₂(A) has the optical switching property at different vibratory absorption bands, revealing that it has potential applications in optical switching devices at the vibratory absorption bands from 700 to 650 cm⁻¹ and from 600 to 550 cm⁻¹. To obtain a noticeable view, two typical results below and up Tₘ were selected to make Fig. 5b. Fig. 5c reveals the process of the phase transition of VO₂(A) before and after Tₘ, indicating its phase transition is at around 161 °C. The transmission of the sample is also different before and after the phase temperature, as shown in Figs. 5a and b. These properties of VO₂(A) verify that it is beneficial for the development and application of an optical switching material, which is similar with that of VO₂(M/R) [8, 29, 30].

It was reported [29, 31–33] that the optical spectrum is usually interpreted as that the observed bands are related to the electromagnetic resonance between incident photons (with a specific wave number) and variation of chemical bond polarisation associated with a specific vibration mode. The V⁴⁺–V⁴⁺ bonding in LTP of VO₂(A) with a distance of 2.7695(8) Å is dissociated in HTP with a distance of 3.0794(3) Å reported by Oka [21]. At low temperature (T < 162 °C) the electrons involving in the V⁴⁺–V⁴⁺ bonds between VO₂ octahedra are localised, whereas these electrons are delocalised at high temperature (T > 162 °C). In the metal state at T > Tₘ, these electrons are delocalised: this delocalisation involves a screening effect for the incident photons, which occurs at the surface of the sample [31]. The results show that no vibrational absorption bands can be observed. The variable-temperature infrared spectra confirm the strong reversible metal–semiconductor phase transition at around 161 °C (Figs. 4 and 5). Therefore the changes in the vibration bands from 700 to 650 cm⁻¹ and from 600 to 550 cm⁻¹ are observed while the structures of VO₂(A) nanobelts turn from LTP (P4/ncc, 130) to HTP (I4/m, 87) during heating and cooling. However, the heating and cooling curves are asymmetric in Fig. 5, which indicates the hysteresis behaviour in the sample.

Figure 5 Variable-temperature infrared spectra of VO₂(A) nanobelts
a All of IR curves with different temperatures
b Selected two IR curves from a
b Selected some typical IR curves from a to clearly observe the process of the phase transition of VO₂(A) before and after Tₘ.
4. Conclusion: VO$_2$(A) nanobelts were successfully synthesised through a facile hydrothermal approach using peroxovanadium (V) complexes and green solvent (ethanol) as the reducing agent without using any surfactants or templates. The as-obtained VO$_2$(A) nanobelts were with typical lengths up to several tens of micrometres, widths about 180 nm and thicknesses about 45 nm on average. The phase transition properties of VO$_2$(A) were investigated by differential scanning calorimetry (DSC), indicating that it exhibits a strong phase transition at around 160.9°C. Furthermore, the optical switching properties of VO$_2$(A) were studied by the variable-temperature infrared spectra for the first time, and it was found that VO$_2$(A) nanobelts could be used as the optical switch at different vibratory absorption bands.

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6 References

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