PEG-Assisted Hydrothermal Synthesis of VO₂(A) Nanowires with Remarkable Optical Switching Properties

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Abstract. High quality single crystalline VO₂(A) nanowires were synthesized by a facile hydrothermal method using oxalic acid as reducing agent and polyethylene glycol 6000 as surfactant. It was found that polyethylene glycol 6000 can effectively accelerate the transformation from V₂O₅ precursor to VO₂(B), and there is no intermediate phase V₃O₇·H₂O formed. Thus less time and lower temperature were needed in our hydrothermal method. The investigation of growth mechanism indicates an oriented attachment growth process in the hydrothermal system. In addition, the temperature-dependent optical switching properties have been studied. The results show that VO₂(A) nanowires exhibit distinct temperature-dependent optical switching properties, which can be potentially explored for optical switching devices.

Introduction

Vanadium dioxide has an abundant and diverse family of polymorphs, including VO₂(R/M), VO₂(A), VO₂(B), and recently reported VO₂(C) [1-4]. Among them, VO₂(R/M) has been paid the most attention due to its reversible first-order metal-insulator transition (MIT) at around 68 °C [1]. Accompanied with the phase transition, VO₂(R/M) undergoes drastic changes in both electrical and optical properties, which can be promisingly developed for a wide range of practical applications, such as sensors, switching devices, and intelligent thermochromic windows [1, 5]. In recent years, VO₂(B) has received increased attention because of the potential candidate for the cathode materials in lithium-ion batteries. A great deal of studies have revealed that the layered structure of VO₂(B) is helpful to enhance the Li⁺ intercalation performance [6]. However, another layered structure of VO₂(A) polymorph, which also exhibits a similar structural phase transition from a low-temperature tetragonal structure (A_L, *P4/ncc*) to a high-temperature body-center tetragonal structure (A_H, *I4/m*) [7, 8], has gained much less attention. One of the main reasons is that VO₂(A) is usually absent during preparation of VO₂ polymorphs [9-11].

VO₂(A) polymorph was first reported by Théobald in studying the hydrothermal process of a V₂O₄-V₂O₅-H₂O system [2]. Decades later, Oka and Yao *et al.* investigated the electrical properties, crystal structures and phase transition mechanism [7, 12]. Subsequently, few works on VO₂(A) were reported. Recently, one-dimensional (1D) VO₂(A) nanostructures, *i.e.*, nanowires, nanorods, and nanobelts, attracted lots of interests owing to the novel physical and chemical properties [1]. Researchers studied the electric, optical, and electrochemical properties and demonstrated that VO₂(A) can be potentially used as sensors, optical switching and cathode materials [8, 13, 14]. However, the studies of VO₂(A) is still very limited because of the harsh growth conditions. To date, VO₂(A) has been obtained exclusively by hydrothermal process and the synthesis methods previously reported are complex. Therefore, more facile, effective, and easily controlled method to synthesize VO₂(A) micro-nanostructures is essential for theoretical research and practical applications. Herein, in this letter

we report a facial PEG-assisted hydrothermal method for single crystalline VO₂(A) nanowires. Meanwhile, we analyzed the growth mechanism of the PEG-assisted hydrothermal process. Moreover, the optical switching properties of as-synthesized VO₂(A) nanowires were investigated by a series of variable-temperature infrared spectra during heating and cooling process.

Experimental

All of the chemical reagents were used without further purification. V₂O₅ was used as vanadium source. Oxalic acid (H₂C₂O₄•H₂O) was working as a reducing agent. The organic reagents polyethylene glycol 6000 (PEG-6000) was acting as surfactant. VO₂(A) nanowires were hydrothermally synthesized by mixing of V₂O₅, H₂C₂O₄•H₂O, PEG-6000 and distilled water (17ml). Weight ratio of V₂O₅ to H₂C₂O₄•H₂O and PEG-6000 is 1:1. The mixtures were heated up to 85 °C with vigorous stirring. Then the mixtures were poured into a 25 mL Teflon-lined autoclave with stainless steel shell and heated in an oven with different time, temperatures and weight ratios between reducing agent and surfactant.

The nanowire structure, crystallization and morphology of as-synthesized products were characterized by X-ray diffraction (XRD, Rigaku D-MAX 2200 VPC), scanning electron microscope (SEM, Quanta FEG 250) and transmission electron microscope (TEM, FEI Tecnai G2 F30), respectively. The optical switching properties were studied by FT-IR analyzer (IR, Nicolet/Nexus 670) combined with a temperature controlled probe stage. Every temperature point was kept three minutes to reach thermal equilibrium during the IR measurements.

Results and Discussion

During hydrothermal process, the growth time, reaction temperature, and weight ratio of reaction reagents are significantly important for VO₂(A) nanowires synthesis. Fig. 1A presents the XRD patterns of samples prepared at 220 °C for different growth time with a weight ratio of 2:1 between reducing agent and surfactant. As the growth time increasing, the products experience a evolution from V₂O₅ precursor (Fig. 1A(e)), VO₂(B) (JCPDS 81-2392) polymorph (Fig. 1A(d)) [4], hybrid of VO₂(B) and VO₂(A) (JCPDS 42-0876) polymorphs (Fig. 1A (b) and (c)) [13], to the finally pure VO₂(A) phase (Fig. 1A(a)). There are no V₃O₇•H₂O nanostructures formed which are usually as intermediate phase in the hydrothermal synthesis process [4]. The absence of V₃O₇•H₂O nanostructures is mainly resulted from the addition of PEG-6000 surfactant, which should play an important role on the transformation from V₂O₅ precursor to VO₂(B) structures. It has been proved that PEG-6000 can be used as reducing agent, which is helpful to improve the transformation from V₂O₅ precursor to VO₂(B) [11]. Fig 1B reveals the effect of reaction temperature on the phase structure. At low temperatures (Fig. 1B (c) and (d)), most peaks are consistent with VO₂(B) phase. When the temperature increasing to 210 °C, some peaks of VO₂(B) vanish and peaks belonging to VO₂(A) appear (Fig. 1B (b)), which means that a small parts of VO₂(B) transform to VO₂(A) as the growth time increases. Pure and highly crystalline VO₂(A) nanowires are synthesized when the reaction temperature increases to 220 °C. It has been proved that in hydrothermal synthesis process reaction temperature is significantly important to enhance crystallinity of VO₂(A) nanostructures [4, 10, 11]. In our studies, the reaction temperature is relatively low compared with previous reports because of the surfactant PEG-6000, which accelerate the shift from V₂O₅ to VO₂(B) [4, 10-14]. The effect of weight ratio between reducing agent and surfactant is shown in Fig. 1C. It can be seen from the figure that V₃O₇ and V₆O₁₃ nanostructures appear when the reducing agent is lower (Fig. 1C (b) and (d)), which also indicates that PEG-6000 can work as reducing agent [11]. However, there is only VO₂(B) nanostructures with enough reducing agent shown in Fig. 1C(c). Obviously, oxalic acid is mainly responsible for reducing action, while surfactant PEG-6000 is very helpful to improve the transformation from V₂O₅ to VO₂(B). Owing to the surfactant PEG-6000, our hydrothermal synthesis of VO₂(A) nanowires needs less time and lower temperature compared with the previous reports [4, 10-14].

Fig. 1 XRD patterns of samples synthesized at different growth time, temperatures and weight ratios between reducing agent ($\text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$) and surfactant (PEG-6000), (A) growth temperature is 220°C and weight ratio is 2:1, (a) 48 h, (b) 24 h, (c) 12 h, (d) 6 h and (e) 0 h; (B) growth time is 48 h and weight ratio is 2:1, (a) 220°C , (b) 210°C , (c) 200°C and (d) 180°C ; (C) growth time and temperature are 48 h and 220°C respectively, (a) 2:1, (b) 1:2, (c) 3:0 and (d) 0:3.

Fig. 2(a)-(f) show the morphological evolution of samples with different growth time. Fig. 2(a) shows that the morphology of V_2O_5 precursor is irregular sheets at 0 h. The short nanowires exfoliating from V_2O_5 precursor sheets appear at 3 h (Fig. 2(b)). As the growth time increasing, more and more nanowires form. These nanowires are $\text{VO}_2(\text{B})$ structure as depicted in Fig. 1A. Gradually, $\text{VO}_2(\text{B})$ structure converts into $\text{VO}_2(\text{A})$ structure, and the short nanowires progressively elongate with increased growth time. Finally, ultra-long $\text{VO}_2(\text{A})$ nanowires with lengths up to tens of micrometers form as shown in Fig. 2(f). In the following the crystallinity and elemental analysis of an individual $\text{VO}_2(\text{A})$ nanowire are determined by TEM and EDS measurements presented in Fig. 2 (g) and (h). High-resolution TEM (HRTEM) image with regular textures and corresponding select area electron diffraction (SAED) patterns suggest the single crystal feature of the $\text{VO}_2(\text{A})$ nanowire. In addition, the SAED patterns keep unchanged when the electron beam moved along the length of the nanowire, which further confirms its single-crystalline nature [4]. Careful analysis of the HRTEM image and SAED patterns indicates that the growth axis of the $\text{VO}_2(\text{A})$ nanowire is along [001] growth direction.

Fig. 2 SEM images of samples prepared at 220 °C for different growth time with a weight ratio of 2:1 for reducing agent to surfactant, (a) 0 h, (b) 3 h, (c) 6 h, (d) 12h, (e) 24 h and (f) 48 h; TEM images of as-synthesized VO₂(A) nanowire, (g) low-resolution TEM of a single nanowire and its EDS spectrum, (h) HRTEM image, inset is the corresponding SAED patterns.

A schematic of the growth process for VO₂(A) nanowires is presented in Fig. 3. Originally, V₂O₅ precursor has a large surface energy in reactive solution. It tends to recrystallize and exfoliate from the V₂O₅ precursor in the help of the surfactant PEG-6000, which results in formation of short VO₂(B) nanowires as shown in Fig. 3 (f) and (b). In addition, PEG-6000 works as surfactant and reducing agent in the hydrothermal system [11]. As the growth time increases, there are a few VO₂(A) structures formed. It can be seen from Fig. 3(g) that plenty of nanowires are composed of several interconnected nanowires, and the top part of the nanowires clearly indicates the oriented attachment growth phenomenon [10, 11, 15]. At this point, both VO₂(A) and VO₂(B) structures exist as depicted in Fig. 3 (d) and (g). The oriented attachment spontaneously proceeds and meanwhile VO₂(B) gradually converts into VO₂(A) with the increase of reaction time [16]. Finally, ultra long and well crystalline VO₂(A) nanowires form by self-assembling. Accordingly, the growth mechanism of VO₂(A) nanowires can be described as a recrystallizing (exfoliating)-oriented attachment-self-assembling process.

Fig. 3 Schematic of the formation mechanism for VO₂(A) nanowires, (a) V₂O₅ precursor at 0 h; (b) short VO₂(B) nanowires at 6 h; (c) hybrid VO₂(A) and VO₂(B) nanowires at 24 h; (d) VO₂(A) long nanowires after 48 h. SEM of samples in different periods, (e) 0 h, (f) 6 h, (g) 24 h, (h) 48 h.

The optical switching properties of as-synthesized VO₂(A) nanowires were studied by a series of variable-temperature infrared spectra during heating and cooling process respectively presented in Fig. 4. Clearly, VO₂(A) nanowires exhibit good switching property at different vibratory absorption bands, such as from 550 cm⁻¹ to 600 cm⁻¹, 650 cm⁻¹ to 700 cm⁻¹, and 920 cm⁻¹ to 950 cm⁻¹. During heating process, the vibratory absorption bands from 650 cm⁻¹ to 700 cm⁻¹ gradually disappear, while for another two vibratory absorption bands they decrease as the temperature increases. Conversely, the vibratory absorption bands experience an opposite trend when cooling down. Additionally, there are slight red shift in heating cycle and blue shift in cooling cycle, implying a phonon mode soften behavior in VO₂(A) nanowires. These distinct switching properties of VO₂(A) nanowires can be potentially explored for optical switching devices [13].

Fig. 4 Typical IR curves with different temperatures ranging from 80 °C to 200 °C, (a) heating process, (b) cooling process. The red arrows point high temperature during heating process, and the blue arrows point low temperature during cooling process.

Conclusion

In summary, we have successfully developed a facile hydrothermal route to synthesize VO₂(A) nanowires. The surfactant of PEG-6000 is found to be useful to improve the recrystallizing and exfoliating of VO₂(B) nanowires from V₂O₅ precursor. So intermediate phase V₃O₇·H₂O is not formed in the hydrothermal synthesis process, which effectively reduces the reaction temperature and growth time. By analysis of the evolution of structure and morphology of samples, we found that the growth mechanism of VO₂(A) nanowires is well consistent with oriented attachment growth process. Furthermore, the as-synthesized VO₂(A) nanowires exhibit remarkable optical switching properties which is useful in designing optical switching devices.

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