Synthesis of Monoclinic Vanadium Dioxide via One-pot Hydrothermal Route

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Abstract: Pure monoclinic vanadium dioxide nanoparticles (VO2 NPs) with a controlled uniform size are considered essential for the preparation of thermochromic smart window coatings on desired substrates. Herein, we report a facile one-step hydrothermal synthesis of VO2(M) NPs without post-treatment of annealing, which may induce unwanted aggregation of NPs. In contrast with the annealed sample, the one-step processed VO2(M) NPs exhibit superior thermochromic performance with the solar modulation efficiency of 11.8% and luminous transmittance of 37.3%.

Keywords: hydrothermal; one-step; single-phase; thermochromic

1. Introduction

Vanadium dioxide (VO2), as a typical strongly electron-correlated transition metal oxide, has a first-order and reversible metal–insulator transition (MIT) at phase transition temperature (τc) ~340 K. The MIT was first discovered by Morin et al. in 1959 [1]. Since then, it has drawn extensive research [2]. At room temperature and unstrained, the crystal structure of VO2 is monoclinic (M, P21/c, a = 5.75 b = 4.54 c = 5.38, β = 122.64°) with zig-zag dimerized V-V pairs along c axis, while above the τc, a tetragonal structure (7 P42/mmm a = b = 4.55 c = 2.86, β = 90°) is favored. The MIT happens within 1 ps [3], accompanied by an abrupt electrical resistance change of approximately five orders of magnitude [4]. As well as changes of structure and electrical properties, the abrupt optical modulation in the wavelength of infrared [5], terahertz [6], and microwave [7] during MIT gives VO2 great potential for applications such as thermochromic smart windows [8], 3D-printed smart window [9], optical switching devices [10], light modulator [11], and infrared stealth [12].

The key to realizing these intensive applications depends on the controlled preparation of high-quality VO2 single/polycrystals powders or thin-film due to the multivalent nature of vanadium element, making it tough work to synthesize high purity VO2. Compared with some high-cost or complex methods, such as electrodeposition [13], sputtering [14], pulse laser [15], and sol-gel [16], hydrothermal synthesis is probably the most effective method to control the morphology, size, and phase structures of VO2. Recently, Li et al. summarized a detailed review on the hydrothermal synthesis of the VO2 phase and its application in thermochromic smart windows [17], from which we know that most of the reported one-step hydrothermal syntheses require a high temperature and long reaction
time. Meanwhile, in most cases, certain metal doping, such as tungsten [18,19], is necessary to obtain VO₂(M) nanoparticles (NPs). However, the doping elements that substitute vanadium elements normally deteriorate the crystallinity and hinder the thermochromic performance of VO₂. Son et al. prepared the VO₂(M) phase with different morphologies by changing hydrothermal temperatures, pH value, and duration [20]. However, the product was generally a mixture of the two phases, which is not suitable for the actual applications. Chen et al. synthesized the fine crystalline VO₂(M) NPs via one-step hydrothermal, and they found both a high latent heat of 43 J/g and good thermochromic property of the VO₂ in comparison to the bulk one [21]. However, the used high hydrothermal temperature, up to around 400 °C, leads to a high cost and uneven size distribution of VO₂ NPs. Alie et al. also reported the direct hydrothermal synthesis of VO₂ without doping via modifying the molar ratio of oxalic acid and V₂O₅ [22]. The obtained VO₂ microcrystals showed a mixture of star shape and hollow sphere shape. The use of seed-assisted one-step hydrothermal to form VO₂ composite has also been recently reported by Jin et al. They reported a novel VO₂-ZnO dandelion structure with the help of the TiO₂ seeds [23]. Li et al. synthesized TiO₂ seeds assisted Mo-doped VO₂ zero-dimensional NPs due to the low nucleation energy [24]. A novel one-step hydrothermal was invented by Guo et al., in which they separated the hydrogen peroxide from the precursor solution, providing a rational oxidizing hydrothermal system [25]. However, the duration of hydrothermal synthesis has been doubled at the same time. Powell et al. and Malarde et al. introduced a continuous hydrothermal flow synthesis method for the direct preparation of a large amount VO₂(M) without a post-annealing process, while the mixing temperature synthesis was more than 400 °C [26,27]. Although the continuous hydrothermal synthesis showed a great value towards the industrial procedure, the as-prepared VO₂ NPs exhibited inferior thermochromic performance, proving the poor crystallinity and quality of the product in general.

In this paper, we successfully synthesize non-doping VO₂(M) NPs via one-step hydrothermal at a relatively low temperature within a short time by adjusting hydrothermal parameters, including the amount of the reduction, reaction time, and precursor concentration. The obtained VO₂(M) has evenly distributed uniform size and morphology without further annealing treatment, which displays high crystallinity and good thermochromic performance.

2. Materials and Methods
2.1. Materials and Synthesis

In the experiments, all chemicals of V₂O₅(Alfa Aesar, Ward Hill, MA, USA, 99.6%), N₂H₄·H₂O (Alfa Aesar, Ward Hill, MA, USA, 99.9%), and H₂O₂ (30 wt%, Sigma-Aldrich, St. Louis, MI, USA) were used as received without any further purification. In a typical hydrothermal process, 1 mmol commercial V₂O₅ powders were added into 5 mL preheated H₂O₂ (30 wt%) at 90 °C with 200 rpm stirring. After a vigorous reaction, a brownish V₂O₅-H₂O₂ precursor was obtained. A certain amount of deionized (DI) water was added subsequently. Afterward, the brownish precursor was chemically reduced by adding N₂H₄·H₂O solution dropwise with stirring for 10 min. After the precursor turned blue-black, it was transferred into a 50 mL PTFE liner and sealed in a stainless steel autoclave. The hydrothermal temperature was set at 260 °C for a certain period (12–168 h), and then the samples were cooled to room temperature in the air. The black precipitate was collected by centrifugation and washed several times in turn with DI water, acetone, and ethanol. After being dried at 50 °C in a vacuum oven, the final black powders were obtained. No further annealing process was performed on any of the products.

2.2. Preparation of VO₂-Based Thermochromic Film

The 50 mg of as-prepared VO₂ NPs were evenly dispersed into 5 mL ethanol and 5 mL concentrated Si-Al solution by one-hour ultrasonication bath. The synthesis of the Si-
Al solution has been reported in our previous work [8]. The VO₂ films were further prepared by spin coating on the soda-lime glass substrate with the same speed and coating times. The coated substrate was dried in the vacuum oven for one hour at 90 °C, then another one hour at 150 °C to remove the solvent and form the uniform coatings.

2.3. Characterization

The X-ray diffraction (XRD) patterns of the obtained powders were collected from a Shimazu Powder XRD-6000 X-ray diffractometer with Cu Kα radiation (λ = 0.15406 nm) under 40 KV voltage and 30 mA current. The surface morphology of the samples was characterized by field emission scanning electron microscope (FESEM, JSM-7600F, JEOL, Akishima, Tokyo, Japan). Differential Scanning Calorimeter (DSC Q10, TA instrument, New Castle, DE, USA) was used to characterize the phase transition behavior of the samples upon the heating and cooling rate of 10 °C/min under N₂ atmosphere. Variable temperature optical transmission spectra of the prepared VO₂ films were measured on a UV-Vis-NIR spectrophotometer (Cary 5000, Agilent Ltd., Santa Clara, CA, USA) in the wavelength of 250–2500 nm at 20 and 90 °C, respectively. A Linkam PE120 system Peltier heating and the cooling stage was attached to regulate the temperature of the substrates. The integrated luminance transmittance and solar transmittance were calculated using the below expression based on the transmittance data:

\[
T_{\text{lum/sol}} = \frac{\int \phi_{\text{lum/sol}}(\lambda) T(\lambda) d\lambda}{\int \phi_{\text{lum/sol}}(\lambda) d\lambda}
\]

\[
\Delta T_{\text{sol}} = \frac{\int \phi_{\text{lum/sol}}(\lambda) [T(\lambda) - \phi_{\text{sol}}(\lambda)] d\lambda}{\int \phi_{\text{lum/sol}}(\lambda) d\lambda}
\]

where T(λ) denotes the film transmittance data at wavelength λ, φ is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon). A more detailed discussion on the evaluation method was reported in [28].

3. Results and Discussion

3.1. Effect of the Amount of the Reduction

As discussed in our previous paper [29], the amount of reduction is the crucial factor for the synthesis of VO₂ phase. Thus, in a series of hydrothermal experiments, the amount of N₂H₄·H₂O solution was optimized first.

The XRD patterns of the hydrothermal samples under the same condition, but with different amounts of the reduction, are shown in Figure 1. The crystallography data are listed in Table 1. The phase evolution of the obtained vanadium oxide could be observed from the increment of the reduction. When the initial amount of N₂H₄·H₂O was 30 μL, the hydrothermal product was still V₂O₅, which is the same phase as the raw material. This is due to the fact that the reduction was mainly consumed by the residual H₂O₂ in the precursor. After the amount of N₂H₄·H₂O increased to 50 μL, the V₂O₅ was reduced to pure V₆O₁₃. When 60 μL of N₂H₄·H₂O was selected, a high crystalline pure phase of VO₂(M) (JCPDS #43-1051) was synthesized. The pure VO₂(M) was still retained when the amount of reduction increased to 70 μL, but from the XRD pattern, the crystallinity of the product became much lower. As shown in Figure 1e,f, the powders were reduced to V₆O₁₁ and V₃O₅, upon which the amount of reduction was further raised to 80 and 90 μL. Additionally, the crystallinity of the powders gradually decreased with increment of N₂H₄·H₂O no matter what kind of vanadium oxide phase it was. Therefore, to synthesize the VO₂ NPs with high crystallinity, 60 μL reduction was chosen as the standard amount for the consequent hydrothermal synthesis.
Figure 1. (a–f) XRD patterns of hydrothermal samples with different amounts of the reductive reagent N$_2$H$_4$·H$_2$O at 260 °C and 24 h duration.

Table 1. The crystallography data of the obtained phases with different amounts of the reductive reagent.

| Obtained Sample | Space Group | Cell Parameters a, b, c (Å) | β(°) |
|-----------------|-------------|----------------------------|------|
| V$_2$O$_5$ (30 μL) | Pmmn | 11.516, 3.565, 4.3727 | 90 |
| V$_4$O$_{13}$ (50 μL) | C2/m | 11.960, 3.713, 10.070 | 100.9 |
| VO$_2$(M) 60 μL, 70 μL | P2/c | 5.752, 4.538, 5.383 | 122.64 |
| V$_3$O$_5$ (80 μL) | P-1 | 5.440, 6.990, 23.660 | 120.9 |
| V$_3$O$_5$ (90 μL) | P2/c | 9.835, 5.031, 6.9742 | 109.46 |

The morphology of the above samples is shown in Figure 2a–e. With the phase evolution of the obtained vanadium oxides, the morphology of these samples changes from nanowires/microwires dramatically into sub-100 nm NPs and further growth into larger particles. In Figure 2a, the length of V$_2$O$_5$ nanowires is up to several micrometers, which is different from the sheet structure of V$_2$O$_5$·H$_2$O$_2$ precursor both in size and shape reported before [30]. Figure 2b shows the microbelt structure of the obtained V$_4$O$_{13}$ powder, which is caused by the aggregation of the initially formed nanowires under hydrothermal conditions. Simultaneously, small amounts of the NPs could be observed at the edge of the microwire. From Figure 2c, the morphology of the VO$_2$ product is the uniform NPs with a diameter around 100 nm. No nanowire or micrometer was observed. Upon further adding the reduction, the size of the particles is getting larger and irregular, from NPs to micrometer bulks, as shown in Figure 2d,e. The irregular morphology also causes a decrease in the crystallinity, as discussed in Figure 1 of the XRD results.
Based on Figures 1 and 2, a hydrothermal synthesis mechanism could be speculated. With the high temperature and pressure, the sheet structure of the precursor turned into nanowires at the initial stage. The reduction process began with the increased amount of N₃H₆·H₂O. The nanowires grew together into the microwires via an oriented attachment mechanism, and then the NPs gradually appeared at the edge of the microwires. The final morphology using N₃H₆·H₂O as the reduction of the VO₂ was NPs, which is similar to the previous reports. Herein, N₃H₆·H₂O plays a crucial role in the hydrothermal process of VO₂ (M), which provides a reducing environment and controls the phase and morphology of the NPs. Gui et al. speculated a molecular coordination mechanism, and the hydrazine and vanadium could be assembled as a building block and promote the growth of the particle-shape VO₂ nanocrystalline [31]. The same group further synthesized nanorod VO₂(R) via adding hydrazine, and they further postulated that hydrazine could serve as a soft template. Both Santulli et al. and Son et al. found the potential of N₃H₆ as the coordination agent in central vanadium ions into one-dimensional nanorod, nanoneedle morphologies [20]. Additionally, Ji et al. postulated that with the existence of N₃H₆, the [V₂O₇]⁴⁻ was the main vanadium complex, while with the presence of H₂C₂O₄, the dominant vanadium complex was larger volume [V₁₀O₂₈]⁶⁻, in which micro-size particles were favorably produced [32].

3.2. Effect of the Hydrothermal Duration

The second parameter discussed in the series of the hydrothermal preparation was the hydrothermal duration while keeping N₃H₆·H₂O at 60 μL. The XRD results in Figure 3 show that the hydrothermal samples with different duration increased from 12 h to 168 h. It can be found that all samples are single-phase VO₃(M) when the reduction amount was kept constant. The XRD peaks of the VO₃(M) gradually intensified with the increase of the hydrothermal duration.
Figure 3. (a–d) XRD patterns of hydrothermal samples with different duration at 260 °C with 60 μL N₂H₄·H₂O.

Figure 4a shows a large amount of the hollow half-sphere shape within 12 h hydrothermal synthesis, which indicates that a short time less than 12 h was far from enough for the growth of uniform NPs, and the size of the particles were rather uneven, ranging from 20 nm to 130 nm. With the increase in hydrothermal duration to 24 h, the uniform NPs morphology is shown in Figure 4b, with an average size of 60.2 nm. As shown in Figure 4c,d, the hydrothermal duration continued to be extended, the shape of the NPs remained the same, and the size grew larger. The average size was 75.9 nm for the 72 h sample, while the size of NPs grew to nearly 90 nm at an even longer duration at 168 h.
3.3. Effect of the Precursor Concentration

Besides the reduction amount and hydrothermal duration, the precursor concentration is the last hydrothermal parameter we were concerned with in our experiment. The preparation of the precursor was introduced in the experimental section. To adjust the precursor concentration, the volume of the solvent, including H₂O₂ and DI water, was kept unchanged, while the amount of the raw material of V₂O₅ powder was tuned from 1 mmol up to 2 mmol accordingly.

Figure 5 shows the XRD patterns of the hydrothermal samples with different precursor concentrations. The crystallography data are listed in Table 2. Note that the concentration of V₂O₅ powder was kept at 1 mmol in our experiment as mentioned above. As shown in Figure 5b, all of the XRD peaks are attributed to the standard VO₂(M) peaks. Two uncertain peaks marked with the star, around 18.7° and 37.8°, turned up as we increased the concentration of V₂O₅ up to 1.25 mmol (Figure 5b). Upon further increasing the V₂O₅ concentration to 1.5 mmol, Figure 5c exhibits that most of the peaks are assigned to VO₂(B), although a small number of peaks attributed to VO₂(M) could still be observed. When the concentration of V₂O₅ powder was increased to 2 mmol, V₆O₁₃ was synthesized, as shown in Figure 5d. However, there were still VO₂(M) peaks. This suggests that the reduction amount is significant to synthesize the VO₂(M), while the precursor concentration must be controlled within the corresponding range.

Figure 4. (a–d) SEM images of hydrothermal samples with different duration at 260 °C with 60 μL N₂H₄·H₂O, inset with the size distribution analysis.
Figure 5. (a–d) XRD patterns of hydrothermal samples with different precursor concentrations at 260 °C with 60 μL N₂H₄·H₂O and 24 h duration.

Table 2. The crystallography data of the obtained phases with different precursor concentrations.

| Obtained Sample | Space Group | Cell Parameters a, b, c (Å) | β(°) |
|-----------------|-------------|-----------------------------|------|
| VO₂(M)          | P2₁/c       | 5.752, 4.538, 5.383         | 122.64|
| VO₂(B)          | C2/m        | 12.152, 3.719, 6.347        | 107.58|
| V₆O₁₃           | C2/m        | 11.960, 3.713, 10.070       | 100.9 |

The SEM images in Figure 6 shows morphologies of the above samples, which highly coincided with the XRD results. Figure 6a shows the highly uniform NPs, which is the pure VO₂(M) phase. In Figure 6b, two shapes of the particles are clearly shown. The NPs are VO₂(M), while the thicker nanobeams mostly belong to the unknown phase indicated in the XRD pattern (Figure 5b). Two different kinds of morphology in NPs and ultralong nanowires are shown in Figure 6c. According to the XRD results, the nanowires with lengths up to several micrometers belong to VO₂(B), while the NPs are VO₂(M). In Figure 6d, it is found that besides the VO₂(M) NPs, microbelts are observed. The microbelts comprise V₆O₁₃, based on the XRD result, which is completely identified as the V₆O₁₃ in Figure 2b.
3.4. Thermochromic Performance of VO₂(M) NPs

Figure 7 shows the DSC of the synthesized VO₂ NPs from different hydrothermal durations in the hydrothermal process. In general, endothermic peaks are observed in the heating segment, while exothermic peaks are found during the cooling process, and the thermal hysteresis indicates that the VO₂ possesses first-order and fully reversible phase transition. The transition temperature and enthalpy of the samples were integrated by the collected data and determined by the TA analysis software.

In Figure 7a, the 12 h hydrothermal sample barely exhibits any peaks. The bump appears at 66.2 °C during the heating ramp and at 43.4 °C during the cooling ramp. The transition temperature was 54.8 °C, and the latent heat is 7.6 J/g, much lower than the reported data [17]. This suggests a large number of defects in the samples, and it further proves that the insufficient hydrothermal time for the VO₂ synthesis, as discussed in Figure 4a. As the duration increased to 24 h, the endothermic and exothermal peaks were both shifted towards the higher temperature, that is, 70.2 °C and 56.5 °C, which brought the $\tau_c$ to 63.4 °C, and the enthalpy increased to 37.3 J/g. As for the 72 h hydrothermal
sample, the position of the peaks barely shifted, while the enthalpy further increased to 43.3 J/g. A more significant change for DSC peaks could be observed for the 168 h duration sample. The endothermic peak appeared at 77.4 °C and the exothermal bump at 59.2 °C, which puts the $\tau_c$ at 68.3 °C. The obtained enthalpy value was 49.4 J/g. In contrast, the endothermic or exothermal peaks for 72 h and 168 h are sharper, indicating the larger particle size for these samples (Figure 4). The trend that $\Delta H$ and $\tau_c$ both increased with the longer hydrothermal duration is further shown in Figure 7b.

The thermochromic property is evaluated through the temperature-dependent UV-Vis-NIR spectra, as shown in Figure 8. The solid and dotted lines demonstrate the high temperature and low-temperature optical transmittance, respectively, of the prepared VO$_2$ films. Figure 8a shows all three samples with different concentrations of VO$_2$ dispersion prepared from the non-doped single-phase VO$_2$ NPs. The concentration of the prepared VO$_2$ dispersion was adjusted by the added amount of the VO$_2$ powders, and the volume of the solvent, including alcohol and Si-Al gel, was kept the same. The thickness of the three samples was also kept the same by controlling the same speed and time of the spin-coating process. For the 1% film, the integrated luminous transmittance ($T_{\text{lum}}$) was calculated to be 44.4%, and the solar modulation ($\Delta T_{\text{sol}}$) was 10.4%. With the higher concentration of the dispersion, the solar modulating ability was improved alongside the degradation of the $T_{\text{lum}}$ (2% sample, $T_{\text{lum}} \sim 37.3\%$, $\Delta T_{\text{sol}} \sim 11.8\%$, and 3% sample, $T_{\text{lum}} \sim 13.8\%$, $\Delta T_{\text{sol}} \sim 13.6\%$). The thermochromic performances of the hydrothermal samples of different durations are exhibited in Figure 8b. All samples were made with the same concentration of VO$_2$ dispersion, as well as the same film thickness. With the duration increased to 72 h and 168 h, the blueshift of the crosspoint between the low and high temperature can be observed in the transmittance spectra, as shown in the circles of Figure 8b. This is caused by the different optical scattering properties between the room temperature VO$_2$(M) and high-temperature phase VO$_2$(R). The higher transmittance in the visible wavelength range is due to the less light scattered in the high-temperature VO$_2$(R). With the longer hydrothermal duration, crosspoints appear for the 72 h sample with particle size at 75.9 nm and the 168 h sample with 86.1 nm. This phenomenon deteriorates the thermochromic performance of the longer duration sample (72 h sample, $T_{\text{lum}} \sim 31.7\%$ $\Delta T_{\text{sol}} \sim 11.0\%$, and 168 h sample, $T_{\text{lum}} \sim 35.7\%$ $\Delta T_{\text{sol}} \sim 5.7\%$) compared with the 24 h sample at the same thickness and dispersion concentration ($T_{\text{lum}} \sim 37.3\%$, $\Delta T_{\text{sol}} \sim 11.8\%$).

![Figure 8](https://example.com/figure8.png)

**Figure 8.** Transmittance spectra of fabricated VO$_2$ films with VO$_2$ nanoparticles (NPs) synthesized: (a) different concentrations of prepared VO$_2$ dispersion; (b) different duration of the hydrothermal samples. The circles in the figure indicate the appearance of the crosspoints.

### 4. Conclusions

In this paper, pure VO$_2$(M) NPs with uniform morphology were prepared via one-step hydrothermal synthesis without doping or annealing treatment. The raw material of V$_2$O$_5$ was gradually reduced to microbelt V$_6$O$_{13}$ and then to desired VO$_2$ NPs, and eventually to larger and irregular morphology V$_6$O$_{11}$ and V$_3$O$_5$ with the increment of the
N2H4·H2O addition. Furthermore, hydrothermal duration and precursor concentration have been studied carefully to obtain the pure and high crystallinity NPs. The obtained VO2 powders were dispersed and spin-coated onto glass substrates to prepare VO2 films, which exhibited comparable thermochromic performance. This provides an alternative way to understand the hydrothermal process mechanism for synthesizing the multi-phase and multi-valence vanadium oxides. The proposed hydrothermal method could be extended for various vanadium oxides synthesis in applications beyond smart window coatings.

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