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**HYDROTHERMAL SYNTHESIS OF VANADIUM DIOXIDE
NANOPARTICLES AND ITS APPLICATIONS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2021

HYDROTHERMAL SYNTHESIS OF VANADIUM DIOXIDE NANOPARTICLES AND ITS APPLICATIONS

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Dr. Long Yi

Authorship Attribution Statement

This thesis contains material from three papers including two papers published in the following peer-reviewed journal and other one has been submitted by the journal invitation in which I am listed as the first or co-first author.

Chapter 2 is published as Y. Ke⁺, S. Wang⁺, **G. Liu**⁺, M. Li, T. J. White, Y. Long (2018) Vanadium Dioxide: The Multistimuli Responsive Material and Its Applications. *Small*, 1802025. (Back cover, Equivalent first author)

The contributions of the co-authors are as follows:

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- I prepared the manuscript drafts of the electrical and strain-activated device parts. The manuscript was revised by Dr. Long Yi.
- Prof. T. J White read the manuscript.
- Y. Ke prepared the manuscript drafts of the part of the optical device.
- S. Wang prepared the manuscript drafts of the part of the thermo-activated device and assisted in the figure drafting.
- Dr. Li prepared the part of the electrochemical and magnetic device and revise the manuscript.

Chapter 4 is submitted as **G. Liu**, Z. Du, M. Li and Y. Long, (2021) Synthesis of Monoclinic Vanadium Dioxide Hydrothermal. *Colloids and Interfaces*. (Invited Submission, First author)

- Dr. Long Yi provided the initial project direction, revised and edited the manuscript drafts.
- I prepared the manuscript drafts, and revised together with Z. Du
- Dr. Long Yi and Dr, M Li instructed on the hydrothermal analysis and has revised the manuscript.

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- Dr. Long Yi provided the initial project direction, revised and edited the manuscript drafts.
- I wrote the drafts of the manuscript.
- S. Wang assisted in the paper figures drafting.
- Dr. M. Layani assisted in the preparation of dispersion and mesh printing techniques.
- Prof. A.I.Y. Tok, Prof. T.J. White, and Prof. C. Li has revised the manuscript
- Dr. Li assisted in the electronic study in the paper.

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Abstract

Vanadium dioxide (VO_2), as the typical phase transition material, has drawn an intensive study including the fabrication, stimuli to trigger the transition as well as the high-performance devices based on VO_2 with different applications. High-performance optical and electrical applications of VO_2 require the synthesis of the VO_2 nanoparticles (NPs) with pure phase, high crystallinity, as well as controlled morphology and facet. However, because the VO_2 has multiple polymorphs and $\text{VO}_2(\text{M})$ has higher formation energy than other polymorphs, the common products of the hydrothermal synthesis are metastable $\text{VO}_2(\text{A})$ or $\text{VO}_2(\text{B})$.

To address the above problems, one-step hydrothermal synthesis of pure phase $\text{VO}_2(\text{M})$ with high crystallinity has been successfully realized by systematically investigating the parameters of the hydrothermal process. A phase evolution mechanism has been proposed in the formation of the $\text{VO}_2(\text{M})$, and the process-microstructure-property relationship has been established in the optical and electrical devices further.

The obtained $\text{VO}_2(\text{M})$ NPs have been coated to be used as a thermochromic smart window. It is observed that the particle size below 60 nm exhibits the best thermochromic properties, which exhibit comparable 11.8% solar modulation with 37.3 % visible transmittance. Such performance is also related to crystallinity doping level and preferred growth of VO_2 NPs.

Furthermore, the $\text{VO}_2(\text{M})$ mesh structure was prepared via the self-assembly method. The mesh structure was further fabricated into the resistance switches device. The high transparency resistance switches exhibit up to 10^4 ON/OFF ratio with the visible transparency at 86%, which outperforms the reported devices.

Lay Summary

Vanadium dioxide (VO_2), as a typical inorganic oxide, may not be commonly seen in our daily lives, but it's going to be. Researchers have already put a lot of effort into studying its properties since Morin *et al.* found the phase transition phenomenon of this oxide. The first attractive property is the phase transition temperature at 68 °C, which is much closer to our environment temperature than other phase transition materials. Besides this feature, VO_2 has a drastic change on the optical transmittance, the electrical resistance as well as the crystallographic structure, etc., during its phase transition process. Thus, many devices based on these characteristics have been developed.

To fabricate the devices, the first thing that needs to be settled is to synthesize the VO_2 . However, there are several challenges currently facing. The first one is to control the VO_2 phases. As the VO_2 has multiple polymorphs, to control the synthesis of the target phase, $\text{VO}_2(\text{M})$ is the first task. The synthesis method, called hydrothermal, has been widely used in the field, which has excellent control of the obtained phase. However, due to the high formation energy of the $\text{VO}_2(\text{M})$, the current hydrothermal method generally obtains the metastable phases of VO_2 , such as $\text{VO}_2(\text{A})$ and $\text{VO}_2(\text{B})$, which need further high-temperature annealing to be converted to $\text{VO}_2(\text{M})$. During the annealing process, the obtained nanoparticles will aggregate as the particles have high surface areas in the high-temperature environment. Thus, one-step hydrothermal is in high demand for the VO_2 devices fabrications. In the thesis, the one-step hydrothermal of pure $\text{VO}_2(\text{M})$ with high crystallinity has been achieved. In addition, the hydrothermal duration can be largely reduced to 6 h by raising hydrothermal temperature beyond 300 °C, compared with normal hydrothermal, which requires up to 7 days process.

In the further study, the smart window application has been investigated by coating as-prepared VO_2 onto the normal glass side, and the comparable thermochromic properties have been achieved. Furthermore, the VO_2 mesh structure has been prepared and fabricated into resistance switches. The high transparency resistance switches are vital for next-generation devices, including skin sensors and neuromorphic electronics, etc.

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Table of Contents

Abstract	i
Lay Summary	iii
Acknowledgements	v
Table of Contents	vii
Table Captions	xiii
Figure Captions	xv
Abbreviations	xxiii
 Chapter 1 Introduction.....	 1
1.1 Hypothesis	2
1.2 Objectives and Scope	3
1.3 Dissertation Overview	3
1.4 Findings and Outcomes/Originality	5
References.....	6
 Chapter 2 Literature Review	 9
2.1 Overview	10
2.2 Hydrothermal synthesis of VO ₂	13
2.3 VO ₂ in thermochromic applications	15
2.3.1 VO ₂ MIT behavior in thermochromic applications	15

2.3.2	VO ₂ thermochromic smart window	16
2.4	VO ₂ in electrical applications.....	18
2.4.1	VO ₂ MIT behavior in electrical devices applications	18
2.4.2	Electrical Switch and FET	19
2.4.3	Single and Coupled VO ₂ oscillators	22
2.4.4	Memristor Based on VO ₂	24
2.4.5	Electrical-Stimulated Radio Frequency Switch	25
2.4.6	Electro-optical Devices	27
2.4.7	Electrothermal mechanical devices.....	28
	References.....	30
 Chapter 3 Experimental Methodology.....		41
3.1	Selection of Chemicals.....	42
3.2	Synthesis and Preparation	42
3.2.1	Hydrothermal synthesis of vanadium oxide (VO _x).....	42
3.2.2	Preparation of VO ₂ smart window coatings.....	46
3.2.3	Preparation of self-assembly VO ₂ mesh structure	47
3.3	Characterization	48
3.3.1	X-ray diffraction	48
3.3.2	Scanning Electron Microscope	50
3.3.3	Transmission Electron Microscope.....	51
3.3.4	Differential Scanning Calorimetry.....	52
3.3.5	UV-vis-NIR Spectrophotometer	54
	References.....	55

Chapter 4	Synthesis of Monoclinic Vanadium Dioxide via One-step Hydrothermal	59
4.1	Introduction	60
4.2	Experimental Methods	61
4.2.1	Materials and synthesis	61
4.2.2	Preparation of VO ₂ -based thermochromic film	62
4.2.3	Characterization	62
4.3	Results and Discussion.....	63
4.3.1	Effect of the amount of the reduction	63
4.3.2	Effect of the hydrothermal duration.....	66
4.3.3	Effect of the precursor concentration.....	68
4.3.4	Thermochromic performance of VO ₂ (M) NPs	70
4.3.5	Effect of the Cr doping	72
4.4	Conclusions	76
	References.....	77
Chapter 5	High-temperature Hydrothermal Synthesis	81
5.1	Introduction	82
5.2	Experimental Section	83
5.2.1	Materials	83
5.2.2	Hydrothermal synthesis of VO ₂ NPs	83
5.2.3	Preparation of the VO ₂ (M) nanocomposite film.....	84
5.2.4	Characterization	84
5.3	Results and Discussion.....	85
5.3.1	Effect of the hydrothermal temperature	85

5.3.2 Discussion of phase transition behavior and thermochromic property.....	89
5.3.3 Effect of the value of filling factor	93
5.4 Conclusions	95
References.....	95
 Chapter 6 Self-assembled VO₂ Mesh Film-based Resistance Switches.....	99
6.1 Introduction	100
6.2 Experimental Methods	101
6.3 Results and Discussions	103
6.3.1 Transparent VO ₂ mesh film fabrication and characterization.....	103
6.3.2 Affecting factors on VO ₂ mesh film fabrication.....	107
6.3.3 Performance of Transparent VO ₂ mesh resistance switches.....	109
6.4 Conclusions	113
References.....	114
 Chapter 7 Conclusions and Recommendations	119
7.1 Conclusions	120
7.1.1 Conclusions of one-step hydrothermal of VO ₂ and its application in thermochromic coatings.....	120
7.1.2 Fabrication of VO ₂ mesh structure and its application in resistance switches	124
7.2 Recommendations	126
7.2.1 Improvements on the VO ₂ smart window application.....	126
7.2.1.1 Enhance thermochromic performance	126
7.2.1.2 Improve the stability of VO ₂	126

7.2.2 Flexible VO ₂ electronic devices.....	127
References.....	129
Publication List	131

Table Captions

Table 2.1 Approaches to fabricate VO₂

Table 3.1 Water's dielectric constant, density, and viscosity data at different temperatures and pressure.

Table 5.1. Phase transition enthalpy (ΔH) and temperature (τ_c) of different hydrothermal duration and temperature.

Table 5.2. Thermochromic performance (T_{lum} and ΔT_{sol}) of high-crystallinity VO₂ NPs.

.

Figure Captions

Figure 1.1 Controllable Hydrothermal synthesis of various VO₂ polymorphs and its conversion to VO₂(M). Reproduced with permission, ^[7] Wiley-VCH.

Figure 2.1. Crystal structure in the a) metallic VO₂(R) and b) insulating states. V atoms are indicated in green, and O atoms in red. Reproduced with permission. ^[7] Copyright 2014, Nature. Schematic of the electronic band structure of c) VO₂(R) and d) VO₂(M). Reproduced with permission ^[8] Copyright 2013, Nature

Figure 2.2. Scheme for the VO₂ based devices, its respective input stimuli, and output response. As described in the lower left corner, the color represents the category of input stimuli and output response of the device.

Figure 2.3. VO₂ thermochromic applications. a) Optical constant n and k respective to the wavelength and the temperature. b) Transmittance and reflectance spectrum for intrinsic VO₂ sample. Reproduced with permission. ^[98] Copyright 2014, Royal Society of Chemistry. c) Schemes of five typical structures effectively improve the performance of the smart window.

Figure 2.4. a) Schematic and SEM image of fabricating two-terminal VO₂ switching device, with VO₂ thin film channel of 10 μm length, 6 μm width, and thickness of 10 nm, grown on the TiO₂ (001) substrate. b) I-V characteristics of two-terminal VO₂ devices at different temperatures from 230 K to 270 K with a current compliance of 500 μA. The VO₂ device switched to low resistance metallic state from a high resistance insulator state when the voltage reaches the threshold stage, reaching the compliance limit. Reproduced with permission. ^[105] Copyright 2016, American Chemistry Society. c) Schematic of VO₂ based field effect transistor. VO₂ films were grown on the single-crystalline Nb-doped TiO₂, which was also served as a bottom gate for FET device with Al wires bonded to the contact.

d) I-V characteristics of the Nb-doped TiO₂(101) gated VO₂ transistor. Fixed V_D of 0.2 V, the I_G (gate leakage current) and I_D (channel current) of FET were obtained at three different temperature as the function of applied gate voltage. Reproduced with permission.^[106] Copyright 2015, Nature Publishing Group. e) Schematic of the hyper-FET, with the VO₂ device of 4-μm length and 2-μm width in series with the conventional source channel of n-type Si device. f) I-V characteristics of the VO₂ based hyper-FET as the function of V_{GS}. The results exhibited the abrupt and reversible modulation corresponds to the IMT and MIT process of VO₂, respectively. Reproduced with permission.^[107] Copyright 2015, Nature Publishing Group.

Figure 2.5. Oscillation behavior of VO₂ based device due to MIT process. a) I-V characteristic in current-mode of the VO₂ (length of 25 μm and width of 18 μm) based device, exhibiting three states with current increasing. Negative differential resistance (NDR) appears in the transitive state. b) Schematic of the circuit used to obtain the transitive state in VO₂, by the series external resistor R_s. c) Results of VO₂ relaxation oscillator as a function of the time domain. The inset figure shows the time domain for one oscillation period, including the IMT process with τ₁ = 0.35 μs and MIT process with τ₂ = 0.65 μs. Synchronized oscillation in coupled VO₂ oscillators and its application. d) Schematic of two coupled VO₂ oscillators via one capacitor (C_c = 680 pF). The two oscillators were in series with the different resistor. (R_{s1} = 38 kΩ and R_{s2} = 47 kΩ) respectively. e) Experiment results of oscillators before and after coupling. Before coupling, two specific oscillators showed 48.43 kHz and 37.27 kHz with different output power. While after coupling, two coupled oscillators converged to a new single resonant frequency, 22.95 kHz. f) Results of visual saliency detection of images using coupled VO₂ oscillators systems, comparison with the conventional digital implementation. Reproduced with permission.^[113] Copyright 2014, Walter de Gruyter Publishing Group.

Figure 2.6. a) Schematic of the single VO₂ nanowire-based memristor device, with the external voltage source and the ampere meter (top), and a FESEM image of VO₂ nanowire (bottom). b) The characteristic performance of information storage applications. Applying

3 V and 5 V voltage pulses on the VO₂ nanowire-based device for writing as well as 0.3 V for reading and 0V for resetting, the results showed the non-volatile and stable switching of VO₂ single nanowire-based memristor. Reproduced with permission.^[116] Copyright, 2013, Wiley- VCH. c) Optical micrograph (top) and Schematic (bottom) of two-terminal VO₂ based radio frequency switching device. 120 nm VO₂ films with the length of 5-15 μm and width of 25 μm were grown single crystal (0001) Al₂O₃ substrates, with Ti/Au electrode as signal contacts. d) (1) Schematic of the setup of VO₂ RF test, using an Agilent N5214A vector network analyzer (VNA) and DC block for supplying parallel DC source for VO₂ device. (2) Insertion loss of VO₂ with increasing input current at 10 GHz. (3 and 4) Insertion loss (S_{21}) and Return loss (S_{11}) results as a function of frequency at input 70mA bias. (OFF state in black line and ON state in red line). Reproduced with permission.^[121] Copyright 2014, AIP Publishing.

Figure 2.7 a) Schematic of voltage controlled opto-memory device based on MIT process of VO₂, grown on the commercial n-type single crystal (0001) GaN/Al₂O₃ substrate via MOCVD. b) Demonstration of the optical memory device with different input V_{pulse} (0.5 and 1 V) and V_{dc} (4.5 and 5 V). Reproduced with permission.^[119] Copyright 2016, American Chemical Society. c) The false-colored SEM image of as fabricated VO₂ actuator. The exposed gap of VO₂ was 2 μm , grown on MgO substrate, with Ti/Au electrodes deposited. d) Converting electrical oscillation to mechanical actuation. With applying the 2 V external voltage, and the 10-20 k Ω series resistor, two different oscillation obtained in figure i) and ii). The corresponding actuation performance was shown in iii and iv), respectively. For generic f_{EO} (iii), the deflection showed limited, while for the specific f_{EO} (iv), the deflection was much larger and showed harmonic component. Reproduced with permission.^[127] Copyright 2017, Wiley-VCH.

Figure 3.1 Temperature dependence (up to 400 °C) of water's saturation vapor pressure

Figure 3.2 Parr hydrothermal autoclave, vessel model 4749

Figure 3.3 Schematic illustration of the different growth situations based on the rate

comparison

Figure 3.4 (a) Photopic luminosity function versus visible wavelength region (380 – 780 nm), (b) Hemispherical tilted irradiance data at 250- 2500 nm wavelength corresponding to the sun standing 37° above the horizon.

Figure 3.5 Schematic diagram of the solvent evaporation process.

Figure 3.6 The schematic diagram of the X-ray diffractometer system

Figure 3.7 Bragg's law is seen by the constructive interference of reflected waves.

Figure 3.8 Schematic configuration of a scanning electron microscope instrument. (JSM-5410)

Figure 3.9 The two basic operation modes of the TEM imaging: (A) projecting the diffraction pattern onto the screen; (B) projecting the image of the specimen on the viewing screen.

Figure 3.10 (a) the diagram of a typical heat flux disk-type DSC system. (b) the schematic curve of measured heat flow rate versus temperature.

Figure 3.11 The diagram of the mechanism of the UV-Vis-NIR spectrophotometer

Figure 4.1. (a-f) XRD patterns of hydrothermal samples with different amounts of the reductive reagent $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ at 260 °C and 24 h duration

Figure 4.2. SEM images of hydrothermal samples with different amounts of the reduction at 260 °C and 24 h duration.

Figure 4.3. (a-d) XRD patterns of hydrothermal samples with different duration at 260 °C with 60 μl $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$.

Figure 4.4. (a-d) SEM images of hydrothermal samples with different duration at 260 °C with 60 μl $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ with the size distribution analysis attached below.

Figure 4.5. (a-d) XRD patterns of hydrothermal samples with different precursor concentrations at 260 °C with 60 μl $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and 24 h duration

Figure 4.6. (a-d) SEM images of hydrothermal samples with different precursor concentrations at 260 °C with 60 μl $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ and 24 h duration.

Figure 4.7. (a) DSC curves of the hydrothermal VO_2 powders at different hydrothermal duration at 260 °C with 60 μl $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$; (b) phase change enthalpy (ΔH) and transition temperature (τ_c) versus hydrothermal duration.

Figure 4.8. Transmittance spectra of fabricated VO_2 films with VO_2 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.

Figure 4.9. (a-d) XRD patterns of hydrothermal samples with different doping concentrations at 260 °C with 60 μl $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ for 24 h.

Figure 4.10. (a-d) SEM images of the hydrothermal samples with different doping concentrations at 260 °C with 60 μl $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ for 24 h.

Figure 4.11 DSC curves of the hydrothermal VO_2 powders at different Cr doping concentrations at 260 °C with 60 μl $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$.

Figure 4.12 Transmittance spectra of fabricated VO₂ films with non-doped and Cr doped VO₂ NPs synthesized.

Figure 5.1. (a) XRD patterns of the different duration (6 and 12 hrs) hydrothermal samples with different hydrothermal temperature (260-350 °C). The standard VO₂(M) XRD peaks are indicated. (b) FWHM of peak (011) and the intensity ratio of peak (110) to peak (011) versus different hydrothermal conditions.

Figure 5.2. (a-h) SEM images of different duration (6 and 12 hours) hydrothermal samples with hydrothermal temperature from 260-350 °C.

Figure 5.3. The average particle size (left) and SD (right) versus different hydrothermal temperature and duration.

Figure 5.4. DSC curves of the different duration (6 and 12 h) hydrothermal VO₂ samples: (a) 6h hydrothermal duration with different hydrothermal temperature; (b) 12h hydrothermal duration with different hydrothermal temperature.

Figure 5.5. Transmittance spectra of fabricated VO₂ films with short duration hydrothermal synthesis VO₂ powder samples. The circles in the figure indicate the appearance of the crosspoints.

Figure 5.6. XRD patterns of the hydrothermal samples with different filling factors.

Figure 5.7. SEM images of the hydrothermal samples with different filling factors with size distribution results attached below.

Scheme 6.1 Schematic diagram for the fabrication of self-assembly transparent VO₂ mesh film.

Figure 6.1 Characterization of transparent VO₂ mesh film. a) photography of VO₂ mesh sample within the blue circle. b) SEM image of the VO₂ mesh film; c) Visible transmittance spectrum of VO₂ mesh film and a bare glass slide.

Figure 6.2 EDX mapping result of the distributed vanadium (red) overlapping with the SEM picture of (a) the frame and (b) the specific knot of VO₂ mesh.

Figure 6.3 Surface profiler characterizations of VO₂ mesh (550 X 550 μm), below with the roughness of indicated line in surface.

Figure 6.4 (a) TEM and SAED results of VO₂ NPs (b) XRD results of VO₂ NPs and VO₂ mesh c) Raman result of VO₂ mesh film d) Infrared transmittance results of wavelength between 1000 - 2500 nm at 20 °C (blue) and 90 °C (red).

Figure 6.5 Surface tension vs. (a) surfactant concentration and (b) VO₂ NPs concentration

Figure 6.6 Optical microscope images for VO₂ mesh with different mixture percentage, inset with enlarged mesh structure (a) 1 wt. % VO₂, 0.01 vol. % BYK; (b) 2 wt. % VO₂, 0.01 vol. % BYK; (c) 3 wt. % VO₂, 0.01 vol.% BYK; (d) 3 wt. % VO₂, no BYK.

Figure 6.7 Characterization of VO₂ mesh resistance switch. Optical images of Au/Ti electrode deposited on the (a) VO₂ mesh, (b) bare glass substrate.

Figure 6.8 I-V characteristic of the VO₂ mesh resistive switch and bare glass slide.

Figure 6.9 Current vs Time curve of VO₂ mesh switches during the I-V characterization

Figure 6.10 the retention result of the VO₂ resistive switch.

Figure 6.11 XRD comparison data of VO₂ mesh switches before and after 50 cycles.

Figure 6.12 Visible transmission of the transparent VO₂ mesh resistance switches with voltage from 0-5 V applied.

Figure 6.13 Comparison between the result of our work and recently reported resistance switches based on PVP,⁴⁰ ZnSnO₃,³⁷⁻³⁸ WO_x,⁴¹ SnO₂/ZnO,³⁶ SrTiO₃,³⁹ TiO₂,⁴² BTCO,⁴³ and Fe: SnO₂.²⁷

Figure 7.1 (a) Schematic diagram of the core-shell structure to improve the stability (b) Extra upper protective layer for the separation of the VO₂ film. Reproduced with permission from the Royal Society of Chemistry.^[7]

Figure 7.2 Different types of NP-based flexible sensors. (a) NP-based strain gauge for sensing deformation via the change of NPs distance. (b) NP-based strain gauge via the tuning of the surface coverage. (c) NP-based flexible sensors for ambient conditions such as temperature or relative humidity (RH) (d) different sensitivity was achieved by the different load applied. (e) Flexible sensor not affected by the deformation. (f) high durability of the NP-based flexible sensor with continuous deformation. Reproduced with permission,^[10] American Chemistry Society

Abbreviations

AC	alternating current
ALD	atomic layer deposition
ANN	artificial neural networks
BSE	Backscattered Electron
CNT	carbon nanotube
CVD	chemical vapor deposition
DC	direct current
DI	Deionized
DOS	density of states
DSC	differential scanning calorimetry
EBSD	backscattered diffraction
E-MIT	Electrical-stimulating MIT
FESEM	field emission scanning electron microscope
FET	field effect transistor
FF	filling factor
HRS	high resistance state
HTP	high-temperature phase
ITO	indium tin oxide
LRS	low resistance state
LTP	low-temperature phase
MBE	molecular beam epitaxy
MIT	Metal-Insulator Transition
NB	nanobeam
NIR	near infrared
NP	nanoparticle

PAD	polymer-assisted deposition
PLD	pulsed laser deposition
RF	Radio Frequency
ReRAM	random-access memory
RS	resistance switching
SD	standard deviation
SE	secondary electrons
SEM	scanning electron microscope
SPT	structural phase transition
TEM	transmission electron microscope
TF	thin film
TMO	transition metal oxide
UV	ultraviolet
XRD	X-ray diffraction

Chapter 1

Introduction

Although VO₂ has been extensively studied since Morin discovered the phase transition, the synthesis of the high crystallinity VO₂ free-standing powder for multiple applications still faces tremendous challenges. To avoid the aggregation during high-temperature post-annealing and the deterioration of the performance due to doping, one-step hydrothermal synthesis has been developed and parameters to improve the VO₂. Furthermore, the VO₂ nanoparticles have been further fabricated into mesh structure to increase the transparency as well as exhibits the high resistance change. The objective of the thesis is to provide a one-step hydrothermal synthesis without doping and study the influence of the hydrothermal parameters such as the amount of the reducing agent to obtain the high crystallinity VO₂ powder and to enhance the thermochromic performance. Moreover, electrical changes during MIT are exploited via self-assembling VO₂-based mesh structure, exhibiting high transparency for the next-generation electronics applications. In the final part, the dissertation of the thesis was outlined, then the findings and outcomes in the thesis are overviewed.

1.1 Hypothesis

Vanadium dioxide (VO_2), as a typical strongly correlated electron material, has drawn an extensive scale of researches since Morin et al. found discovered the metal-insulator transition (MIT) in 1959. ^[1] They demonstrated that this reversible transition happened at the critical temperature (τ_c) of ~ 340 K, accompanied by a structural phase transition (SPT). ^[2-4] Besides the discovery led to understand the fundamental study of the VO_2 and to explain the transition behavior, researches on technique for the growth of the VO_2 has been another focus. Various techniques have developed into the synthesis of VO_2 nanoparticles (NPs) and thin films (TFs). ^[5, 6] The hydrothermal process has been a widely used method to synthesize the VO_2 NPs, because of its competent control on the phase, size, and morphology of the final product. ^[7] As shown in Fig. 1.1, controllable hydrothermal synthesis of various VO_2 polymorphs has conducted by intensive researchers, including $\text{VO}_2(\text{A})$, ^[8] $\text{VO}_2(\text{B})$, ^[9] $\text{VO}_2(\text{D})$, ^[10] $\text{VO}_2(\text{P})$, ^[11] and $\text{VO}_2(\text{M})$. The phase that undergoes MIT at ~ 340 K is the $\text{VO}_2(\text{M})$. Thus, additional annealing needs to be done for the conversion to $\text{VO}_2(\text{M})$. As illustrated in the figure, $\text{VO}_2(\text{A})$ or $\text{VO}_2(\text{B})$ need high annealing temperatures up to 700°C . Such high-temperature annealing conditions caused the obtained VO_2 NPs coarsening and aggregation. ^[12]

Figure 1.1 Controllable Hydrothermal synthesis of various VO_2 polymorphs and its conversion to

VO₂(M). Reproduced with permission, ^[7] Wiley-VCH.

To avoid the aggregation of the NPs, the one-step hydrothermal method has been proposed. However, due to the high formation energy of VO₂(M), the one-step hydrothermal needs the assistance of the seeds or doping elements such as W, Mg. ^[13]. In such doping cases, the distorted VO₂ structure would deteriorate the crystallinity and stability of the VO₂ NPs. ^[14] Thus, the one-step hydrothermal synthesis of pure phase VO₂(M) without seeds and doping is vital in the study of the VO₂ applications.

1.2 Objectives and Scope

In this thesis, the hydrothermal synthesis of VO₂ has been studied, and the obtained samples are further applied in several applications:

- a) One-step hydrothermal synthesis of pure phase VO₂(M) without the assist of doping and post-annealing and its application in the smart window coatings.
- b) High-temperature hydrothermal synthesis of VO₂(M) within a short duration and improved crystallinity and its thermochromic property study.
- c) Fabrication of self-assembled VO₂-based mesh and its application in the electrical switches.

1.3 Dissertation Overview

The thesis studied the different parameters to achieve the one-step hydrothermal synthesis of single-phase VO₂(M) NPs with high crystallinity. The obtained VO₂(M) NPs were applied in the thermochromic coatings in the smart window application. And the VO₂(M) NPs were prepared into mesh structure by combing mesh printing and self-assembly methods. The high transparency VO₂ mesh structure was further fabricated as the resistance switches, which exhibits ab abrupt resistance ON/OFF ratio up to 10⁴.

Chapter 1 provides a rationale for the research and outlines the goals and scope. VO₂, as the typical phase transition material, has been synthesized via various methods. Among the kinds of methods, the hydrothermal is controllable of the size, phase, and morphology.

However, the post-annealing results in the obtained NPs coarsening and aggregation. The seeds and doping assist methods decreased the crystallinity of the NPs. The mixture phases of the obtained NPs via one-step hydrothermal are common. Thus, the work to synthesis the pure VO₂(M) NPs with high crystallinity is necessary for the VO₂ applications.

Chapter 2 carefully reviews the recent literature concerning the phase transition properties and its mechanism debate, as well as the multistimuli and various application exploiting the phase transition process of the VO₂(M). The current hydrothermal strategies to synthesize the VO₂(M) NPs were discussed, including the one-step hydrothermal and post-annealing methods. In the last part, the applications in smart windows and electronics, including two/three-terminal switches, oscillators, etc., were introduced systematically.

Chapter 3 first discussed the preparation methods carried out in the thesis. The origin, mechanism, and development of the hydrothermal method and apparatus are introduced first. Next, the preparation method of VO₂ smart window coatings is discussed, as well as the calculations of the thermochromic performance evaluation, including solar modulation and visible transmittance. Thirdly, the mechanism of the self-assembly method is illustrated. At last, the mechanisms of characterization techniques, including XRD, SEM, TEM, DSC, UV-Vis-NIR spectrophotometer, are briefly introduced.

Chapter 4 is the first result chapter. In this chapter, the one-step hydrothermal synthesis is conducted without the assist of seeds and doping. The hydrothermal parameters, including the amount of the reduction, the hydrothermal duration, and the precursor concentration, are systematically studied. The phase transition of the obtained VO₂(M) was studied. Furthermore, the thermochromic performance of the prepared VO₂(M) coatings has been investigated, including the different thickness and different hydrothermal duration. In the last part, the Cr doping hydrothermal is studied as a comparison. The doping concentration is chosen from 1% to 10%.

Chapter 5 still discussed one-step hydrothermal synthesis. As to obtain the VO₂(M) NPs within a short duration using one-step hydrothermal synthesis, the hydrothermal

temperature has increased from 260 °C in the last chapter to 350 °C. However, due to the limitation of the PTFE liner, quartz liner, which has a higher melting point, is used in the high-temperature hydrothermal synthesis. In addition, due to the adjustment of the volume of the liner, the filling factor is studied.

Chapter 6 prepared the VO₂ mesh structure by the mesh printing method. The mesh structure is successfully formed due to the “coffee ring” effect via self-assembly. The concentration of the VO₂ dispersion, as well as the amount of the surfactant, are adjusted accordingly. The high transparency VO₂ mesh structure is further fabricated into resistance switches.

Chapter 7 summarised the results of the projects, including (1) one-step hydrothermal synthesis of VO₂(M) NPs without the assist of the seeds and doping and its application in the thermochromic smart window. (2) High-temperature hydrothermal synthesis is carried out beyond 300 °C. (3) high transparent VO₂ mesh structure preparation and its fabrication into the resistance switches application.

1.4 Findings and Outcomes

The research in the thesis led to several impactful findings and outcomes:

1. The single-phase VO₂(M) NPs without seeds and doping assist were successfully obtained by the one-step hydrothermal synthesis. The size of the nanoparticles ranges from around 60 nm to 90 nm, with the highest ΔH at 49.4 J/g. The results suggest the high crystallinity of the samples. The prepared, smart window coatings exhibit comparable thermochromic properties, with the best result of ΔT_{sol} at 11.8% and T_{lum} at 37.3%.
2. The high-temperature hydrothermal was carried out in the research. The VO₂(M) NPs could be synthesis at a short duration of 6 h with the hydrothermal temperature beyond 300 °C.
3. The high transparency continuous VO₂ mesh structure was successfully prepared via the self-assembly method with 86% visible transmittance. The mesh structure was

further fabricated into the resistance switches, which exhibit up to 10^4 ON/OFF ratio with the V_{th} at 1.5 V.

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Chapter 2

Literature Review

The reversible, ultrafast, and multistimuli responsive phase transition of monoclinic phase VO₂ makes it an intriguing material. It has intensive studies on its mechanism of the transition process, the diverse stimuli methods, its preparation techniques, as well as various applications. In this chapter, first, the long-standing mechanism of the VO₂ MIT was briefly introduced, as well as the band structure and crystallographic structure transition. Next, the various VO₂ synthesis methods were discussed with the hydrothermal method introduced in detail. The hydrothermal preparation mainly has two strategies: one-step direct hydrothermal with the assist of doping element or seeds and post-annealing combined with the hydrothermal process to produce VO₂(M). In the final part, the various smart applications based on the MIT of VO₂(M) are discussed, including thermochromic smart window coatings and various electronic devices including two/three-terminal switches, oscillators, memristors, and electro-optic/electrothermal devices.

Yujie Ke, Shancheng Wang*, **Guowei Liu***, Ming Li, Timothy J. White, and Yi Long. "Vanadium dioxide: The multistimuli responsive material and its applications." *Small* 14, no. 39 (2018): 1802025. (Back cover, Co-first author). Reproduced with permission, Wiley-VCH.

2.1 Overview

In 1959, the pioneering work of Morin demonstrated that vanadium dioxide (VO_2) shows a reversible metal-insulator transition (MIT) at the critical temperature (τ_c) of ≈ 340 K,^[1] where a structural phase transition (SPT) happened simultaneously. During the SPT, VO_2 undergoes a displacive transformation from high-temperature rutile $\text{VO}_2(\text{R})$ to low-temperature monoclinic $\text{VO}_2(\text{M})$. For $\text{VO}_2(\text{R})$, the vanadium ions are linearized on the 1a Wyck off position with an average nearest V–V distance of $2.88 \text{ \AA}$ along the c_{R} axis, which is smaller than the critical V–V interaction distance of $2.94 \text{ \AA}$. Therefore, the d -orbital electrons are shared by all of the vanadium atoms in $\text{VO}_2(\text{R})$, resulting in metallic behavior. While for $\text{VO}_2(\text{M})$, due to the structure distortion, there are two different V–V distances of 0.262 and 0.316 nm , which results in the formation of the zigzag-type vanadium atom chains along the a_{M} axis (or c_{R} axis). The larger V–V (0.316 nm) distance results in the localization of d -orbital electrons inside the V–V dimer and gives rise to the insulating behavior of $\text{VO}_2(\text{M})$,^[2] as illustrated in Fig. 2.1a and 2.1b. The above-mentioned SPT can be classified as the Peierls model to describe the nature of phase transition in VO_2 . In addition, according to the crystal field theory, Goodenough theoretically described the electronic band structures. For $\text{VO}_2(\text{R})$, the density of states (DOS) depends on the combining of anti-bonding π^* orbitals and $d_{\parallel}$ orbitals. After phase transition to $\text{VO}_2(\text{M})$, the V–V ion dimerization splits the $d_{\parallel}$ band, resulting in the state of filled bonding and empty anti-bonding. Furthermore, the anti-bonding orbitals π^* move up, and opens up the gap between anti-bonding π^* orbitals and $d_{\parallel}$ orbitals. (Fig. 2.1c,d) Zylbersztejn and Mott attributed the MIT to the Mott–Hubbard model by considering the strong electron-electron correlations, and concluded that the MIT would happen when the electron density (n_e) and Bohr radius (a_{H}) satisfy $n_e^{1/3} a_{\text{H}} \approx 0.2$.^[3, 4] As summarized in the most recent review,^[5] the physical nature of the MIT remains a long-standing debate, and the difficulty in assigning it to a separate mechanism lies in the challenge of decoupling the structural and electronic portions of the ultrafast phase transition. Indeed, it is difficult to understand the MIT of VO_2 completely using only one model, and the cooperation of these two mechanisms is strongly supported by considering the phase transition kinetics.^[6]

Figure 2.1. Crystal structure in the a) metallic $\text{VO}_2(\text{R})$ and b) insulating states. V atoms are indicated in green, and O atoms in red. Reproduced with permission.^[7] Copyright 2014, Nature. Schematic of the electronic band structure of c) $\text{VO}_2(\text{R})$ and d) $\text{VO}_2(\text{M})$. Reproduced with permission.^[8] Copyright 2013, Nature

Across the MIT, VO_2 offers reversible and dramatic changes in physical properties (electrical resistance, optical transmittance, and thermal conductivity) in response to different external stimuli, including photons, temperature, electric field, magnetic field, electrical chemistry, and stress (Fig. 2.2). Manipulating the MIT of VO_2 by external stimuli is an active research area, making VO_2 a material of great interest for novel electronic and optical devices.^[9-11] Device functional performance is largely dependent on the size, morphology, doping, and crystallinity of VO_2 , and several chemical and physical techniques have been exploited to fabricate VO_2 .

Figure 2.2. Scheme for the VO₂ based devices, its respective input stimuli, and output response.

As described in the lower left corner, the color represents the category of input stimuli and output response of the device.

Table 2.1 lists the approaches that have been developed to synthesize the VO₂, and some of these fabrication processes are recently reviewed ^[12] with polymer assisted deposition methods, ^[13] hydrothermal, ^[14] sol-gel, ^[15] and chemical vapor deposition (CVD),^[16] discussed in details and those approaches simply and economically permit controlled synthesis of VO₂ deployed in thermochromic smart windows. Meanwhile, sputtering, ^[17-19] pulsed laser deposition (PLD), ^[8, 20, 21] and molecular beam epitaxy (MBE) ^[22-24] are generally used to prepare high-quality VO₂ thin films that can be integrated into microelectronic circuits for memory and field effect transistor (FET) devices. Besides, thermal evaporation deposition is an effective route to prepare the single-domain VO₂ nanowires that can be employed to explore the fundamental properties. ^[25-28] Moreover, for the purpose of the practical application, scalable production of VO₂ nanoparticles, ^[29-31]

wafer-scale VO₂ thin films,^[32-35] and large-scale hybridized VO₂ films^[36, 37] are developed by various synthesis techniques. Among these fabrication methods, the hydrothermal process has proven very successful and is widely used for free-standing VO₂ nanostructures with controlled size and morphology.

Table 2.1 Approaches to fabricate VO₂

Reaction Media	Method
Solid-state reaction	Thermolysis, ^[38] thermal oxidation ^[39]
Solution-based deposition	Hydrothermal, ^[40] solvothermal, ^[41] sol-gel, ^[42] polymer-assisted deposition (PAD), ^[43] electrochemical ^[44]
Gas-based deposition	Chemical vapor deposition (CVD), ^[45] thermal evaporation, ^[46] atomic layer deposition (ALD), ^[47] pulsed laser deposition (PLD), ^[48] magnetron sputtering ^[49]

2.2 Hydrothermal Synthesis of VO₂

As recently reviewed by Li. et al., VO₂ has multiple polymorphs, including VO₂(A), VO₂(B), VO₂(D), VO₂(M), VO₂(P), and hydrate VO₂.^[14] It is common to obtain the metastable phase or multiphases in the hydrothermal product. Many researches have been conducted to study the mechanism of hydrothermal reaction to prepare high purity phase of the VO₂, especially the pure VO₂(M), as its standout properties in the various application.^[50] Two main strategies have been carried out for the VO₂(M) hydrothermal synthesis, the one-step direct method,^[51] and the post-synthetic annealing aided the hydrothermal process.^[52]

As compared with multiple procedures, one-step hydrothermal synthesis is facile and economical. Son et al. prepared the VO₂ (M) phase with different morphologies by modifying hydrothermal temperatures, pH value, and duration^[53] However, the product was generally a mixture of two phases, which is not suitable for the actual applications.

Alie et al. also reported the direct hydrothermal synthesis of VO₂ without doping via modifying the molar ratio of oxalic acid and V₂O₅.^[54] The obtained VO₂ microcrystals showed a mixture of star-shape and hollow sphere shape. High-temperature synthesis was performed to overcome the multiple phases and morphologies for the hydrothermal product of VO₂. Chen et al. synthesized the fine crystalline VO₂(M) nanoparticles via one-step hydrothermal with temperature up to around 400 °C, 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.^[55] Malarde et al. firstly introduced a continuous hydrothermal flow synthesis method for the direct preparation of a large amount of VO₂(M) NPs without a post-annealing process at a mixing temperature above 400 °C. The continuous hydrothermal flow method shows a great value towards the industrial procedure, but at present, the as-prepared VO₂ nanoparticles exhibited an inferior thermochromic performance, proving the poor crystallinity and quality of the product in general.^[56] On the other hand, the seed-assisted one-step hydrothermal to prepare VO₂ is also reported recently. Jin et al. successfully synthesized a novel VO₂-ZnO dandelions structure with the help of the TiO₂ seeds.^[57] And Li et al. synthesized Mo-doped VO₂ zero-dimensional nanoparticles with the assist of TiO₂ seeds by reducing the low nucleation energy.^[58] A recently novel one-step hydrothermal method was published by Guo et al., where they separated the hydrogen peroxide from the precursor solution, providing a rational oxidizing hydrothermal system.^[51] However, the duration of hydrothermal synthesis has been doubled.

Due to the various polymorphs of VO₂, it is common to obtain some metastable phases apart from VO₂(M) by hydrothermal. Thus, besides scrupulously designed one-step hydrothermal synthesis, metastable-phase VO₂ hydrothermal combined post-heat treatment has been proposed, as the metastable phase is typically obtained first via the hydrothermal process. The most common phase obtained in hydrothermal is VO₂(B), which usually has the one-dimensional nanobelt or nanorod morphology.^[59, 60] Through changing the hydrothermal parameters, such as precursor, reduction, or pH value, other morphologies like nanoring,^[61] mesocrystal,^[62] the hollow microscope^[63] could be obtained. VO₂(B) has been widely studied and used as the cathode material for the battery industry due to the layered structure.^[64, 65] VO₂(B) can be completely transformed into the thermodynamically stable phase of VO₂(M) under the suitable atmosphere and temperature

environment, ^[66, 67] and unlike VO₂(R) to VO₂(M), the phase transition from VO₂(B) to VO₂(M) via high-temperature annealing is irreversible. According to the in-situ temperature-dependent X-ray diffraction (XRD) characterization, VO₂(B) is stable in vacuum up to 400 °C, and it can be transformed to VO₂(M) completely at 600 °C ^[67] Corr et al. prepared pure VO₂(M) by annealing VO₂(B) at 700 °C for 1 h under argon atmosphere. ^[68] The obtained VO₂(M) particles are much larger compared with parent VO₂(B) after such a high-temperature process. Another metastable phase obtained from hydrothermal synthesis is VO₂(A), which also undergoes a phase transition accompanied with a dramatic change in electric and magnetic properties. ^[69] However, the phase transition happens upon heating at a temperature around 162 °C, and the crystal structure changes from the low-temperature phase (LTP, P4₂/nmc) to the high-temperature phase (HTP, I4/m). ^[70] The morphology of the hydrothermal obtained VO₂(A) normally in nano/microrods and belts. ^[71, 72] Xie et al. discovered theoretically that VO₂(A) has lower formation energy than VO₂(B) during the phase transition to VO₂(M). ^[72] The conversion from VO₂(A) to VO₂(M) is irreversible and coarsening with the high-temperature annealing process as the conversion of VO₂(B). Under such conditions, a rapid low-temperature heating treatment of metastable VO₂(D) and VO₂(P) has been developed recently. ^[73, 74] The morphology of the obtained VO₂(M) could be highly maintained as the starting materials. Li. et al. successfully synthesized kilogram scale VO₂(D) NPs via large-scale hydrothermal process. The pure VO₂(M) with fine crystallinity and without coarsening could be obtained at a annealing temperature below 400 °C. ^[29] Paramontroseite VO₂(P) is another metastable phase of VO₂, which was firstly synthesized via the hydrothermal method by Xie et al. ^[75, 76] The conversion from VO₂(P) to VO₂(M) happened under the ultrafast annealing process (within 1 min) at 400 °C. ^[74]

2.3 VO₂ in thermochromic applications

2.3.1 VO₂ MIT behavior in thermochromic applications

The MIT of VO₂ could be triggered as the ambient temperature reaches 68 °C. Across the MIT, several properties such as optical constants, lattice structure, lattice parameter, and

electrical conductivity of VO₂ will change abruptly, and such thermal-induced properties changing prompts the application of VO₂ in thermal-activation devices. For example, the thermo-optical devices such as smart windows and camouflage are based on the significant changing of refractive index (n) and extinction coefficient (k) during the MIT (Fig. 2.3a), and which leads to the optical responses such as the changing of transmittance and reflectance (Fig. 2.3b) at the different wavelength. Meanwhile, the thermomechanical devices like resonator and actuator are based on the crystal contraction along the c -axis ($\approx 1\%$) and expansion in the a -axis direction ($\approx 0.6\%$) when MIT happens.^[77] Moreover, as the conductivity of VO₂ changes up to five magnitudes upon the MIT due to the overlapping and separation of the energy band in the crystal,^{[2],[34]} the fabrication of temperature sensor and other thermal activated electrical device becomes possible.

2.3.2. VO₂ thermochromic smart window

VO₂ based smart windows used to cut energy consumption for indoor temperature regulation attracted lots of attention since the concept was first discussed in 1985.^[78] Artificial buildings consume up to 40% of the energy produced globally, and contribute up to 30% of global greenhouse gas emission^[79] and a large portion of artificial building energy consumption is used to regulate the indoor temperature. As VO₂ possesses a relatively “silent” way to regulate the amount of infrared transmits through the window with a negligible optical property change in visible spectrum range,^[80] it becomes an ideal candidate for smart window application. However pure VO₂ does not meet the requirement of the smart window due to high τ_c ($\approx 68^\circ\text{C}$), low luminous transmittance, (T_{lum} , lower than 40%) and poor solar modulation ability (ΔT_{sol} , the difference between solar transmittance at low temperature and high temperature, less than 10%).^[81] Therefore, the thermochromic performance of VO₂ needs to be improved to meet the requirement of the smart window. There are two approaches for the performance enhancement, reduce τ_c via dopant and enhance both ΔT_{sol} and T_{lum} via structure engineering. Tungsten (W), molybdenum (Mo), and rare-earth elements have been investigated to decrease τ_c by introducing distorting lattice and charge balance.^{[28],[82]} Some other dopants like titanium (Ti), fluorine (F), and magnesium (Mg) are used to improve T_{lum} and ΔT_{sol} .^[83-85] Because the majority of dopants

can merely improve the individual thermochromic property and recent trend turns to co-dope multiple dopants to achieve overall performance improvement.^[86, 87] On the other hand, structure engineering on nano- or microscale tends to ameliorate the unsatisfied properties as summarized in Fig. 2.3c namely multilayered VO₂,^[88] biomimetic structure,^[89, 90] nanothermochromism^[91] and porous,^[92] and gridded structure,^[93, 94] respectively. For example, the multilayered structure can not only introduce antireflection to enhance T_{lum} , but also grant multifunctionality (antioxidation ability and self- cleaning) to the devices and solve the mild toxicity issue in VO₂.^[95] Biomimetic moth-eye nanostructuring can enhance both T_{lum} and ΔT_{sol} simultaneously as such structure gives rise to antireflection as well as more VO₂ surface area for solar modulations.^[89] The best reported T_{lum} (66.4%) and ΔT_{sol} (26.5%) comes from the nanothermochromism category from both calculation and experiment.^[94, 96, 97]

Figure 2.3. VO₂ thermochromic applications. a) Optical constant n and k respective to the wavelength and the temperature. b) Transmittance and reflectance spectrum for intrinsic VO₂ sample. Reproduced with permission.^[98] Copyright 2014, Royal Society of Chemistry. c) Schemes

of five typical structures effectively improve the performance of the smart window.

2.4 VO₂ in electrical applications

2.4.1 VO₂ MIT behavior in electrical devices applications

Electrical-stimulating MIT (E-MIT) of VO₂ based devices create the potential for low power-supplied electronics, while the mechanism for E-MIT is still under debate.

The first mechanism relates to direct electrons or holes injection via the electric field. Stefanovich *et al.* reported the MIT of VO₂ was initiated by electron injection with an applied electrical field. They compared the experiment switching time with the calculated delay time (the time required for the channel temperature reaching τ_c from ambient temperature), and found three orders of magnitude difference between experiment switching time (1.5 ns) and calculated delay time (900 ns). They referred that the increased electron density induced MIT other than heating the lattice.^[99]

Another mechanism triggering the E-MIT in VO₂ is Joule heating or electrothermal mechanism by locally melting the insulators as the current passing through VO₂.^[100] This phenomenon was recently confirmed by optically monitoring the MIT process in two-terminal in-plane VO₂ electrical switching that stacking on the single-mode silicon waveguide,^[101] and they found the filamentary behavior induced by Joule heating instead of the electrons injection is the main reason to induce the E-MIT.^[102] Cavalleri *et al.* found that the formation of the rutile unit cell was essential for the metallic behavior of VO₂, even when the correlated *d* band was highly depleted (holes injection) and confirmed that the dominant mechanism of MIT was thermal triggering through ultrafast spectroscopy.^[103]

Moreover, some researchers believe that the E-MIT of VO₂ results from the coupling induction of electrical and thermal mechanisms. Lee *et al.* utilized the quantum driven-dissipative model, simulating the main process of VO₂ MIT via effective temperature description.^[101] Although the nucleation or shrinking of conductive filament could be explained via the joule heating mechanism, the strongly hysteretic MIT behavior of VO₂

cannot be demonstrated by the pure thermal effect. A bistable insulator-metal phase due to the electric field effect was also considered.

2.4.2. Electrical Switch and FET

Due to the abrupt resistance change of VO₂ during MIT as well as the programmable switching time and degree, the VO₂-based devices exhibit the great advantage and potential in switching, FET, oscillator, and memory devices.

Two-terminal switching

Stefanovich et al. constructed a planar VO₂ switch on Si substrate, with a dielectric buffer layer of ≈ 70 nm SiO₂ in between.^[99] The length and width of the VO₂ channel were 0.2 mm and 5–10 μ m, respectively, and the thickness was about 0.1–1 μ m. When applying the bias voltage at room temperature, the device showed the S-shaped voltage-current characteristic, and the MIT occurred at around 2 V which acted as threshold voltage (V_{th}). However, the switching time was in tens of microseconds, and the “ON/OFF” resistance ratio was less than one order of magnitude. Ultrafast two-terminal VO₂ switching, exhibiting phase transition within 2 ns and “ON/OFF” ratio more than two orders of magnitude, was fabricated by Zhou et al. recently.^[104] Fig. 2.4a shows another VO₂ based lateral switch to study the temperature dependent switching performance, in which the VO₂ epitaxial thin film was grown on TiO₂ (001) substrate. This device exhibited MIT induced by applying direct current (DC) and pulse bias at different temperature. I–V curves in Fig. 2.4b demonstrate the V_{th} varies from 15.8 V at 230 K to 3.7 V at 270 K and the dissipated power at the onset of MIT also decreased linearly with increasing temperature.^[105]

Three terminal field effect transistors

In the three-terminal FET, the main mechanism for rectifying characteristics is electrostatic doping through field effect because the joule heating is highly limited due to the low gate-drain current. Integrating the VO₂ channel with gate electric makes itself a three-terminal

FET like device. The conductivity of the VO₂ channel can be switched between the insulating state and the metallic state when the external gate voltage is applied. Such device is called Mott FET, by replacing the conventional semiconductor channel with a Mott insulator.

Akira et al. achieved a positive-bias gate-controlled MIT near the τ_c of VO₂.^[106] They fabricated the VO₂ thin film on the (101)-oriented Nb-doped TiO₂ substrate with silver paste used as the Ohmic contacts onto the VO₂ channel and aluminum wires bonded to the Nb-doped TiO₂ substrate (Fig. 2.4c). The electrical properties (gate current I_G and drain current I_D as a function of gate voltage V_G) of the FET device were studied at three different temperatures, 306.3, 315, and 325.3 K in Fig. 2.4d. I_G was around three orders of magnitude smaller than I_D , suggesting that the Joule heating effect in the device is negligible. The results showed that channel current changed negligibly with increasing V_G at 306.3 or 325.3 K; however, a large current modulation occurred at 315 K which is close to τ_c . The channel current I_D was almost nonlinear with two orders of magnitude increment as the V_G increasing from 0 to 9 V, which is attributed to the electrostatic mechanism discussed above.

Nikhil et al. designed a novel type of Mott FET by integrating VO₂ as a source terminal.^[107] Fig. 2.4e illustrates the schematic of the hyper-FET device consisting of a two-terminal VO₂ device in series with the channel of a conventional Si n-FET. The transport results of the hyper FET performed at room temperature ($T = 300$ K) are shown in Fig. 2.4f, which showed an abrupt and reversible transition of the channel current I_D as a function of the V_G . When I_D is above the critical current threshold as V_G increased, the MIT of VO₂ occurs, resulting in the abrupt increment in I_D .

It is worth mentioning that the quality of the interface between VO₂ films and dielectric layers relates to the I_G , which may limit the phase transition in VO₂ in an electric field. For example, VO₂ bottom-gated FET devices were prepared on Si substrates with two different kinds of dielectric layers: 300 nm SiO₂ and 500 nm hybrid Al₂O₃/SiO₂. In the 500 nm hybrid layer, I_G remains low with the increment of V_G , while in the 300 nm SiO₂ layer, the I_G increased noticeably.^[108]

Two-terminal switch

Mott transistor

Figure 2.4. a) Schematic and SEM image of fabricating two-terminal VO₂ switching device, with VO₂ thin film channel of 10 μm length, 6 μm width, and thickness of 10 nm, grown on the TiO₂ (001) substrate. b) I-V characteristics of two-terminal VO₂ devices at different temperatures from 230 K to 270 K with a current compliance of 500 μA. The VO₂ device switched to low resistance metallic state from a high resistance insulator state when the voltage reaches the threshold stage, reaching the compliance limit. Reproduced with permission.^[105] Copyright 2016, American Chemistry Society. c) Schematic of VO₂ based field effect transistor. VO₂ films were grown on the single-crystalline Nb-doped TiO₂, which was also served as a bottom gate for FET device with Al wires bonded to the contact. d) I-V characteristics of the Nb-doped TiO₂(101) gated VO₂ transistor. Fixed V_D of 0.2 V, the I_G (gate leakage current) and I_D (channel current) of FET were obtained at three different temperature as the function of applied gate voltage. Reproduced with permission.^[106] Copyright 2015, Nature Publishing Group. e) Schematic of the hyper-FET, with the VO₂ device of 4-μm length and 2-μm width in series with the conventional source channel of n-type Si device. f) I-V characteristics of the VO₂ based hyper-FET as the function of V_{GS}. The results exhibited the abrupt and reversible modulation corresponds to the IMT and MIT process of VO₂, respectively. Reproduced with permission.^[107] Copyright 2015, Nature Publishing Group.

2.4.3. Single and Coupled VO₂ Oscillators

An electronic oscillator is widely used in the electronic circuit, such as resistor-capacitor/inductor circuits, in which a periodic repeated signal is produced. Oscillators can convert applied DC to the different frequency alternating current (AC) signal. Till now, two kinds of oscillators have been widely used, harmonic (linear) and relaxation (nonlinear) oscillator. Due to the characteristics of the nonlinear MIT process, VO₂ based oscillators would exhibit relaxation behavior under applying external current/voltage.

Relaxation oscillator based VO₂ switches

It is known that one of the prerequisite properties for obtaining the current/voltage oscillations is in the presence of clear negative differential resistance (NDR) regime in the I-V characteristic as shown in Fig. 2.5a. The current-controlled NDR was obtained in the nonlinear I-V characteristic in the transitive state during MIT of VO₂, between 4 and 7 mA.^[109] A typical circuit used to obtain the current-controlled NDR (Fig. 2.5b) is to

connect a VO₂ based device with external resistance (R_s) in series to form a relaxation oscillator (Fig. 2.5c). The inset is the two switching time constants, $\tau_1 = 0.35 \mu s$ and $\tau_2 = 0.651 \mu s$ represents the insulator-to-metal transition (IMT) and MIT time respectively, and the frequency of the oscillation could be calculated, $f_{osc} = 1 \text{ MHz}$.^[110] The frequencies of these self-sustained oscillations can range from several kHz to 1 MHz and could be tuned by simply altering R_s , thereby adjusting the injected current.^[111]

Coupled VO₂ oscillator

Besides the single VO₂-based oscillator, experiments of coupled VO₂ oscillators have been also carried out by connecting a resistor, capacitor, or FET between two oscillators.^[110] As shown in Fig. 2.5d, the typical schematic of two VO₂ oscillators with different oscillating frequency coupled by a capacitor. Fig. 2.5e shows the frequency of two separated oscillators are $f_{osc,1} = 48.43 \text{ kHz}$ and $f_{osc,2} = 37.27 \text{ kHz}$, respectively, while after coupling of these two oscillators, a single resonant frequency of 22.95 kHz could be obtained. This process is called synchronization, which plays a crucial role both in elementary nervous systems (neural pairs) and neural networks with a very large number of elements. Therefore, VO₂ coupled oscillators show promising application in neuromorphic oxide electronics.^[112] Such function of coupled oscillators has also been applied to encode computing, showing the associative computing features with the applications in image or pattern recognition (detection), visual saliency, and template matching. For example, Fig. 2.5f shows the application of coupled VO₂ oscillators for visual saliency approximations (detecting parts of the image that visually stand out).^[113] It is evident that the oscillators show higher sensitivity to image contrast in comparison to a complementary metal-oxide-semiconductor application-specific integrated circuit accelerator.

Figure 2.5. Oscillation behavior of VO₂ based device due to MIT process. a) I-V characteristic in current-mode of the VO₂ (length of 25 μm and width of 18 μm) based device, exhibiting three states with current increasing. Negative differential resistance (NDR) appears in the transitive state. b) Schematic of the circuit used to obtain the transitive state in VO₂, by the series external resistor R_s . c) Results of VO₂ relaxation oscillator as a function of time domain. Inset figure shows the time domain for one oscillation period, including IMT process with $\tau_1 = 0.35 \mu\text{s}$ and MIT process with $\tau_2 = 0.65 \mu\text{s}$. Synchronized oscillation in coupled VO₂ oscillators and its application. d) Schematic of two coupled VO₂ oscillators via one capacitor ($C_c = 680 \text{ pF}$). The two oscillators were in series with the different resistor. ($R_{s1} = 38 \text{ k}\Omega$ and $R_{s2} = 47 \text{ k}\Omega$) respectively. e) Experiment results of oscillators before and after coupling. Before coupling, two specific oscillators showed 48.43 kHz and 37.27 kHz with different output power. While after coupling, two coupled oscillators converged to a new single resonant frequency, 22.95 kHz. f) Results of visual saliency detection of images using coupled VO₂ oscillators systems, comparison with the conventional digital implementation. Reproduced with permission.^[113] Copyright 2014, Walter de Gruyter Publishing Group.

2.4.4. Memristor Based on VO₂

As discussed in Section 2.4.2, the two-terminal VO₂ device exhibits non-volatile resistive switching when applied external voltage/ current, which can also be fabricated into memory devices used for memristor^[114] and memcapacitor.^[115] The memristor is a nonlinear two-terminal device whose resistance is determined by the dynamic net charge of the system instead of instant applied voltage (current). Wang et al. reported a two-terminal memristor based on a single VO₂ nanobeam, which exhibits MIT when external voltage was applied. A schematic of the single VO₂ nanowire memristor is shown in the upper figure in Fig. 2.6a with the corresponding scanning electron microscope (SEM) image below. Before applying the voltage pulses, the VO₂ nanowire was an insulator with resistance around $10^{11} \Omega$. After applying the voltage pulse to the VO₂ nanowire, the resistance decreased to a lower value due to the MIT of VO₂. To quantitatively study the switchable and retainable resistance of the device, they applied two different voltage pulses of 3 and 5 V for 0.25 s under the bias voltage of 0.3 V and the resistance of the device could be decreased to 10^9 and $10^8 \Omega$ respectively (Fig. 2.6b). Additionally, the VO₂ nanowire can be reset to the initial state when applying zero voltage bias, as the metallic phase is totally switched back to the insulator phase. The resistance switching behavior makes the VO₂ based device a high-performance non-volatile memristor.^{[116],[117]} Pellegrino et al. fabricated the free-standing VO₂/TiO₂ cantilever, exhibiting two types of data retention that is the non-volatile resistive memory with self-heating erasing and the volatile memory with current erasing.^[117] Additionally, the MIT in VO₂ showing volatile threshold switching behavior can also be used as Mott selectors in the resistive random-access memory (ReRAM) devices and 3D memory array.^[118, 119]

2.4.5. Electrical-Stimulated Radio Frequency Switch

Compared with the conventional RF switching devices, VO₂ RF switching exhibits a short response time and high reliability. ^[120] Treadway et al. fabricated the VO₂-based RF switching device on single-crystal Al₂O₃ (0001) substrate and Ti/Au electrodes are patterned on the top and sides of VO₂ as signal and ground contacts respectively.^[121] Fig. 2.6c shows the optical micrograph of the co-planar waveguide device as well as the schematic side view. The RF characterization was held at room temperature, and S

parameters (return loss ($|S_{11}|$) and insertion loss ($|S_{21}|$) were measured by an Agilent vector network analyzer with a -5 dBm signal. The circuit of the test configuration is shown in Fig. 2.6d1. S_{11} and S_{21} of RF characteristics of VO₂ coplanar waveguide were recorded in OFF and ON states, as shown in Fig. 2.6d2–d4. Fig. 2.6d2 demonstrates how the insertion loss at 10 GHz varied as a function of compliance current. As indicated by the decrease in insertion loss, the device was turned on with $I = 10$ mA and showed negligible improvement when the current is higher than 70 mA. As illustrated in Fig. 2.6d3 and d4, both S_{21} and S_{11} showed a significant difference between ON and OFF state at frequency up to 13.5 GHz, due to the abrupt change in conductivity of VO₂ across MIT.

Memristor

Electrical-stimulated radio frequency switch

Figure 2.6. a) Schematic of the single VO₂ nanowire-based memristor device, with the external voltage source and the ampere meter (top), and a FESEM image of VO₂ nanowire (bottom). b) The characteristic performance of information storage applications. Applying 3 V and 5 V voltage pulses on the VO₂ nanowire-based device for writing as well as 0.3 V for reading and 0V for

resetting, the results showed the non-volatile and stable switching of VO₂ single nanowire-based memristor. Reproduced with permission.^[116] Copyright, 2013, Wiley- VCH. c) Optical micrograph (top) and Schematic (bottom) of two-terminal VO₂ based radio frequency switching device. 120 nm VO₂ films with the length of 5-15 μm and width of 25 μm were grown single crystal (0001) Al₂O₃ substrates, with Ti/Au electrode as signal contacts. d) (1) Schematic of the setup of VO₂ RF test, using an Agilent N5214A vector network analyzer (VNA) and DC block for supplying parallel DC source for VO₂ device. (2) Insertion loss of VO₂ with increasing input current at 10 GHz. (3 and 4) Insertion loss (S_{21}) and Return loss (S_{11}) results as a function of frequency at input 70mA bias. (OFF state in black line and ON state in red line). Reproduced with permission.^[121] Copyright 2014, AIP Publishing.

2.4.6. Electro-optic Devices

Due to the thermal sensitive property and corresponding abrupt change of infrared transmission, the electrical produced joule heating can also be utilized to regulate optical properties of VO₂ by combining it with some transparent conductive electrode materials such as Ag nanowires, indium tin oxide (ITO), carbon nanotube and so on.^[122, 123]

A novel opto-electronic memory device, utilizing abrupt transmission change in the infrared region, was fabricated by Fan *et al.*^[119] Fig. 2.7a shows the scheme of the device: high-quality VO₂ epitaxial film was grown on the center area of commercial high conductive n-GaN/Al₂O₃ (0001) crystal substrate via molecular beam epitaxy method, and Au electrode was deposited on the edges of GaN layer. Different from the above mentioned “electrical writing-electrical reading” memristor, by effectively regulating the infrared transmittance via applied pulse voltage, they realized the VO₂ based infrared memory device, which could be operated as the “electrical writing–optical reading” type. As shown in Fig. 2.7a, two voltage sources have been applied on the VO₂ based infrared memory device: a constant DC voltage (V_{dc}) was used to heat VO₂ to a temperature close to the τ_c , and a pulsed voltage (V_{pulse}) acting as the “writing” power. The optical “reading” behavior was recorded via the transmission at 1.8 μm by the UV-vis spectrometer. The performance of the VO₂ based infrared memory device was shown in Fig. 2.7b. At first, two different initial V_{dc} of 4.5 V and 5 V were applied on the GaN layer separately, which has no effect

on the transmittance within 50 s (I green area). For the state of $V_{dc}=5.0$ V in pink region II, VO_2 changed to metallic phase swiftly and exhibit low infrared transmission, then an additional applied $V_{pulse}=1$ V gives rise to a limited memory effect. For the case of $V_{dc}=4.5$ V, if no additional pulse voltage was added (blue region III), the transmission would eventually end at a stable state; However, when a voltage pulse $V_{pulse}=0.5$ V was applied (blue curve in region III), the transmission would decrease step-by-step, showing the memory features in optical response. If the pulse of voltage was increased to 1 V, the variation of the memory step would be larger. By modifying the applied DC voltage and pulse voltage, the performance of VO_2 based optoelectronic memory device could be modulated easily

2.4.7. Electrothermal mechanical devices

The MIT in VO_2 leads to the thermal expansion coefficient change between VO_2 and other materials, which make it can be used in some novel mechanical devices.^[124, 125] Joule heating generated by current passing VO_2 can also cause a huge flexural and mechanical change of the VO_2 composite device.^[126]

As discussed in the oscillator part, by converting small input DC voltage to AC signal (oscillator output), the electrical oscillator frequency (f_{EO}) could be controlled precisely in circuit, and the resonant motion could be triggered in VO_2 based microstructure device fabricated by Manca *et al.*^[127] Fig. 2.7c₁ shows the false-colored SEM image of the whole device and the exposed VO_2 gap is 2 μm . The electrical circuit used to characterize the electrical oscillation when applying DC voltage source (V_0) on the VO_2 microbridge and the external load resistor (R_0), as shown in Fig. 2.7c₂. Fig. 2.7d shows the performance of VO_2 microbridge actuator. For a generic combination of V_0 and R_0 , the mechanical motion showed the limited amplitude of VO_2 microbridge (panels i, iii). However, for the selective values of the parameters, a strong harmonic mechanical response was observed (panels ii, iv). Based on the phase change of VO_2 , this device can be employed to selectively excite the different mechanical modes of the microstructures by modifying the input voltage.

Another interesting application for electro-thermally triggering VO_2 phase transition is to integrate the resistive heater with the VO_2 -based MEMS mirror device. This novel device exhibited the programming vertical displacement and tilting angle due to VO_2 mechanical change along with the hysteretic MIT behavior under low voltage input, showing the potential applications in MEMS reflector, raster, or micro-size projector, etc.

E-MIT VO_2 has been widely discussed and fabricated into the kinds of devices, utilizing the ultrafast MIT process, accompanying with the up to four orders of magnitude resistance abrupt change as well as the optical and mechanical response.

Electro-optic modulator

Electrothermal actuator

Figure 2.7 a) Schematic of voltage controlled opto-memory device based on MIT process of VO_2 , grown on the commercial n-type single crystal (0001) $\text{GaN}/\text{Al}_2\text{O}_3$ substrate via MOCVD. b) Demonstration of the optical memory device with different input V_{pulse} (0.5 and 1 V) and V_{dc} (4.5 and 5 V). Reproduced with permission.^[119] Copyright 2016, American Chemical Society. c) The false-colored SEM image of as fabricated VO_2 actuator. The exposed gap of VO_2 was 2 μm , grown on MgO substrate, with Ti/Au electrodes deposited. d) Converting electrical oscillation to

mechanical actuation. With applying the 2 V external voltage, and the 10-20 k Ω series resistor, two different oscillation obtained in the figure i) and ii). The corresponding actuation performance was shown in iii and iv), respectively. For generic f_{EO} (iii), the deflection showed limited, while for the specific f_{EO} (iv), the deflection was much larger and showed the harmonic component. Reproduced with permission.^[127] Copyright 2017, Wiley-VCH.

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Chapter 3

Experimental Methodology

In this chapter, the selection of the materials in the hydrothermal synthesis is reviewed first. Next, the hydrothermal synthesis of VO₂ is introduced in the detailed procedures, as well as the preparation of the VO₂ mesh structure. The fabrication methods for the applications of the thermochromic smart window coatings and electronic switches are discussed. Furthermore, the principles of the materials characterization techniques used in the thesis have been briefly explained, including X-ray Diffraction, Scanning electron microscopy, Raman spectroscopy, UV-Vis-NIR spectrophotometer, etc., to study the phases, morphologies, and the thermochromic/electrical properties of the prepared samples.

3.1 Selection of Chemicals

Vanadium pentoxide (Alfa Aesar, 99.6%) was chosen to be the vanadium source in the hydrothermal process. In the Cr-doping hydrothermal preparation, Chromium (III) oxide (Alfa Aesar, 99%) was selected as the additive. Hydrogen peroxide (Sigma-Aldrich, 30%) and hydrazine monohydrate (99.9%, Alfa Aesar) was added during the precursor preparation. It is worth mentioning that the high concentration of H_2O_2 is corrosive, and $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and V_2O_5 are toxic. ^[1, 2] The chemicals used in the experiment must be highly cautious. In addition, AZ 5214E photoresistor (photoresist image reversal, MicroChemicals GmbH) and AZ Developer (AZ Electronic Materials GmbH) were used in the preparation process of VO_2 based resistance switches.

3.2 Synthesis and Preparation

3.2.1 Hydrothermal synthesis of vanadium oxide (VO_x)

Throughout the thesis, the main method for vanadium oxide sample synthesis is hydrothermal due to its effective control of the size, morphology, and phase structures of the obtained samples besides the low cost compared with sputtering or pulse laser.

Back in 1845, the hydrothermal technique was a powerful tool to simulate the natural conditions underneath the earth crust's and to achieve them in the laboratory environment, as the term *hydrothermal* purely origins from geology. ^[3] Until the late 1940s, the hydrothermal method became more important in the synthesis of inorganic compounds, such as zeolites by Barrer. ^[4] The key of hydrothermal synthesis is to achieve the supercritical water condition in the elevated temperature and pressure as of "hydrothermal origin." ^[5] In addition, in recent years, the hydrothermal technique is evolved to the solvothermal, as the water is substituted by the organic solvents. ^[6] The hydrothermal method was chosen instead of solvothermal, as water is the most accessible, environmentally friendly of all the solvents, and intensively studied in the synthesis process. However, in the high temperature and pressure, the viscosity (η) of water decreases as the

polarity of water drops, resulting in higher molecular mobility. In addition, due to the decrease of the density (ρ) and dielectric constant (ϵ), the ionic hydration endures the dramatic change. Table 3.1 lists the data of the viscosity, density and dielectric constant of water at different high temperature and pressure conditions.^[7]

Table 3.1 Water's dielectric constant, density, and viscosity data at different temperatures and pressure.

p/MPa	Parameter	t/°C					
		200	250	300	350	400	450
10	ϵ_r	35.1	27.4	20.4	1.2	1.2	1.1
	ρ	0.871	0.806	0.715	0.045	0.038	0.034
	η	0.136	0.108	0.087	0.022	0.025	0.027
20	ϵ_r	35.3	28.0	21.2	14.1	1.6	1.4
	ρ	0.878	0.816	0.733	0.600	0.101	0.079
	η	0.139	0.110	0.091	0.070	0.026	0.028
30	ϵ_r	35.9	28.4	22.0	15.7	5.9	2.1
	ρ	0.885	0.826	0.751	0.646	0.357	0.148
	η	0.141	0.113	0.094	0.076	0.044	0.031
40	ϵ_r	36.3	28.9	22.6	16.7	10.5	3.8
	ρ	0.891	0.835	0.765	0.672	0.523	0.271
	η	0.114	0.115	0.097	0.080	0.062	0.039
50	ϵ_r	36.6	29.3	23.1	17.6	12.2	6.6
	ρ	0.897	0.843	0.777	0.693	0.278	0.402
	η	0.146	0.118	0.099	0.083	0.068	0.051
60	ϵ_r	37.0	29.7	23.6	18.2	13.3	8.5
	ρ	0.903	0.850	0.788	0.711	0.612	0.480
	η	0.148	0.120	0.101	0.086	0.073	0.059
70	ϵ_r	37.3	30.0	24.0	18.8	14.2	9.9
	ρ	0.909	0.857	0.798	0.726	0.638	0.528
	η	0.150	0.122	0.104	0.089	0.077	0.065

The temperature dependence of saturation vapor pressure is shown in Fig. 3.1. Below 200 °C, the saturation vapor pressure is far low, and above 200 °C, the pressure increases dramatically and hits around 20 bar at 400 °C. In such conditions, the hydrothermal temperature normally sets at 200 to 400 °C. The temperature was set at 260 °C in chapter 4, one-step hydrothermal synthesis of VO₂, and the temperature was slightly higher is due to the different formation energy among different VO₂ phases, which is discussed further in the following chapter, while in the high-temperature hydrothermal synthesis, the temperature was set up to 350 °C.

Figure 3.1 Temperature dependence (up to 400 °C) of water's saturation vapor pressure

The design for hydrothermal apparatus, widely known as the autoclave, has been studied alongside the hydrothermal method itself since the 19th century. The most successful materials used for autoclave design are corrosion resistant alloys ^[7] due to the critical conditions during the hydrothermal synthesis. In our hydrothermal synthesis, the stainless-steel autoclaves from the Parr company are chosen. The typical design of the autoclave is shown in Fig 3.2.

Figure 3.2 Parr hydrothermal autoclave, vessel model 4749.

In the typical hydrothermal process, the first step is to start with the preparation of the precursor. The V_2O_5 powder was added into the preheated H_2O_2 solution with stirring. Significant heat was generated during the vigorous process. Thus, it is worth mentioning the reaction should be carried out in the big flask or beaker. Finally, The DI water was added after the mixture turned to dark brown color. The second step is to transfer the precursor to the liner of the autoclave. Quartz liner was chosen for the high-temperature hydrothermal in this thesis, as the commonly used Polytetrafluoroethylene (PTFE) liner has a much lower melting temperature. As the temperature and pressure increased, the precursor started to decompose to nuclei, and the monomers were created at the same time, which assisted in the growth of nuclei to create a supersaturated reaction environment. [8] The rate of the precursor decomposition (r_d) and the growth of the nuclei (r_g) are crucial to the final samples, thus the control of the temperature and pressure of the hydrothermal process is evitable in the thesis, as shown in Fig. 3.3. In addition, to obtain the ideal VO_x samples, the other hydrothermal parameters such as the duration, the filling factor are also critical. The details are discussed in the following chapters.

Figure 3.3 Schematic illustration of the different growth situations based on the rate comparison.

3.2.2 Preparation of VO₂ smart window coatings

First, the obtained pure-phase, high crystallinity, and uniform VO₂ nanoparticles were evenly dispersed with alcohol and concentrated Si-Al solution for a one-hour ultrasonication bath. The synthesis of the Si-Al solution has been reported in our previous work.^[9] The prepared VO₂ based dispersion was cast on the pre-cleaned soda-lime glass substrates by spin-coating. The thickness of the VO₂ film was controlled by the concentration of the prepared VO₂ dispersion and the speed and times of the spin-coating. The coated substrates were further dried for each one hour at 90 °C and 150 °C separately to remove the solvent, and the uniform coating was achieved in the end.

To evaluate the thermochromic performance of VO₂ based coatings for the smart window application, the calculation of the integrated optical quantity is widely accepted for the precise description and comparison, including the luminous transmittance at the wavelength range at 380 to 780 nm and the solar transmittance from 250 to 2500 nm. The integral luminous transmittance (T_{lum}) is calculated by equation (1):

$$T_{\text{lum}} = \frac{\int_{380}^{780} \Phi_{\text{lum}}(\lambda) T(\lambda) d\lambda}{\int_{380}^{780} \Phi_{\text{lum}}(\lambda) d\lambda} \quad (1)$$

Where $T(\lambda)$ represents the film transmittance data at wavelength λ , $\Phi_{\text{lum}}(\lambda)$ denotes the standard luminous efficiency function in the wavelength range of 380- 780 nm for photopic vision. ^[10]

The integral solar transmittance (T_{sol}) and solar modulation (ΔT_{sol}) are calculated by the following equations:

$$T_{\text{sol}} = \frac{\int_{250}^{2500} \Phi_{\text{sol}}(\lambda) T(\lambda) d\lambda}{\int_{250}^{2500} \Phi_{\text{sol}}(\lambda) d\lambda} \quad (2)$$

$$\Delta T_{\text{sol}} = T_{\text{sol, lt}} - T_{\text{sol, ht}} \quad (3)$$

Where $\Phi_{\text{sol}}(\lambda)$ stands for the standard solar irradiance spectrum for air mass 1.5 in Fig. 3.4b, which is corresponding to the sun standing 37° above the horizon. ^[11] The $T_{\text{sol, lt}}$ denotes the integral transmittance at low temperature when VO_2 is at the monoclinic phase, while the $T_{\text{sol, ht}}$ represents at high temperature when VO_2 is in the rutile phase.

Figure 3.4 (a) Photopic luminosity function versus visible wavelength region (380 – 780 nm), (b) Hemispherical tilted irradiance data at 250- 2500 nm wavelength corresponding to the sun standing 37° above the horizon.

3.2.3 Preparation of self-assembly VO_2 mesh structure

The self-assembly closely packed VO_2 nanoparticle mesh film was fabricated based on the utilization of the mesh printing ^[12] technique and the caterpillar force in the “coffee ring effect” via solvent evaporation. ^[13] As shown in Fig. 3.5, via controlling the concentration of the nanoparticles suspension, the pattern of the mask, as well as the separate height

between the mask and film (h_g), the different film patterns, were achieved. Fig 3.5(c) is the discrete pattern fabricated via the dilute dispersion, while the continuous film was formed in Fig 3.5(d) from a concentrated dispersion. ^[14]

Figure 3.5 Schematic diagram of the solvent evaporation process.

In the thesis, the transparent VO₂ mesh structure was prepared through the procedures below. First, the VO₂ nanoparticles were added into the DI water and the surfactant. After 10-min sonication, the uniform VO₂ dispersion was obtained. A sonicator (Elmasonic S60H, Elma Ultrasonic) with the ultrasonic frequency of 37 kHz with 550 W power consumption was used. Next, the VO₂ dispersion was dropped onto the pre-cleaned glass substrates via the screen-printing mesh (Ponger 2000, Israel) above. Upon contact, the liquid immediately wetted the mesh walls and space between the mesh and glass slide. Then, with the evaporation of the DI water, the VO₂ nanoparticles moved towards the edge of the mesh walls due to the caterpillar force. After removing the mesh, the VO₂ mesh film was heated at 60 °C for 2 h in the vacuum oven for further sintering. Finally, the transparent VO₂ mesh film was achieved.

3.3 Characterization

3.3.1 X-ray diffraction

In this thesis, X-ray diffraction (XRD) characterization method via Shimadzu X-ray powder diffractometer with Cu K α radiation ($\lambda = 0.1541$ nm) was mainly used to determine the crystal phases and structures of the prepared hydrothermal samples.

From first discovered by W.C. Rontgen in 1895, X-ray has developed the field of crystallography until the wave character was confirmed from a single crystal by Max von Laue in 1912. ^[15] X-rays are beams with short-wavelength at 0.01 to 10 nm and high-energy of 10 – 100 KeV of electromagnetic radiation. Among these, only those with a wavelength between 0.01 nm and 0.1 nm are used to determine the crystal structures, which are called hard X-rays. The development of the X-ray powder diffractometer has begun since 1935 by Le Gallery, and the first commercial equipment was introduced in 1947. ^[16] Fig 3.6 shows the schematic configuration of the X-ray diffractometer of Bruker D5000.

Figure 3.6 The schematic diagram of the X-ray diffractometer system.

As shown in Fig 3.7, the parallel X-ray beams will be reflected by certain crystal planes. The crystal phases are identified by Bragg's law, $n \cdot \lambda_{e1} = 2 d_{hkl} \sin \theta$. λ_{e1} is the wavelength of the incident X-ray, while θ is the incident angle, and d_{hkl} denotes the distance between the plane (h k l). The constructive interference only occurs when the Bragg's law meets, thus the diffracted X-ray has high intensities compared with other incident X-ray directions.

The intensity and width of the peak reflect accordingly the details of the crystal planes as well as the particle size.

Figure 3.7 Bragg's law is seen by the constructive interference of reflected waves.

3.3.2 Scanning Electron Microscope

The scanning electron microscope (SEM) was widely used in the thesis to examine and analyze the morphology of the hydrothermal samples as well as the microstructure of the VO₂ mesh, etc.

Fig 3.8 is a typical schematic diagram of the SEM. ^[17] At the top of the column is the electron gun, which generates the electrons and accelerates to the 0.1 to 30 keV level. 5 keV is selected as the standard voltage in the thesis. Next, the electromagnetic apertures and lenses (condenser lenses) are used to form the focused electron spot with a size of 1 to 100 nm, which requires a high vacuum environment. Scanning coils are used to deflect the electron beam in order to shift along the x and y-axis. In the final part, several detectors are placed to collect different signals. The image information is based on the produced signals, while a focused electron beam was used to interact with the surface of the targeted sample. However, there are several signals yielded when the surface of the specimen was engaged, including auger electrons, backscattered electrons (BSE), and secondary electrons (SE). In general, as well in this thesis, the image information is based on the secondary electrons, as they have lower energy thus expected to bear richer information

about topography. As for the backscattered electrons, the yield is dependent upon the atomic number of the sample, as heavier element generates more yield. The classic BSEs have much lower lateral resolution compared with SEs, as they have larger energy producing the larger region of the specimen. The newly developed electron is able to determine the nanoscale crystals.

Figure 3.8 Schematic configuration of a scanning electron microscope instrument.(JSM-5410) ^[17]

3.3.3 Transmission Electron Microscope

Compared with SEM, electron sources are accelerated by high voltage (200 kV) in the transmission electron microscope (TEM) and focused by several electromagnetic apertures and lens. With the higher energy of the electron beam and smaller wavelength, the TEM

can achieve the atomic resolution, which also means the very spot of the specimen could be observed each time. As the electrons will pass through the specimen when the electron beams interact with the sample, thus the specimen needs to be prepared thin enough (<100 nm) to let the electrons pass through. As shown in Fig. 3.9, TEM has different working modes based on the signals that have been collected by the detectors. Fig. 3.9a is the SAED mode, as the SAD aperture is inserted into the system, and the objective aperture is removed. In this thesis, the obtained hydrothermal samples were characterized by TEM JOEL 2010 UHR with an accelerating voltage at 200 kV. The morphology of the samples at higher magnifications was revealed with the objective aperture inserted and the SAD aperture removed. (Fig. 3.9b)

Figure 3.9 The two basic operation modes of the TEM imaging: (A) projecting the diffraction pattern onto the screen;(B) projecting the image of the specimen in the viewing screen. ^[18]

3.3.4 Differential Scanning Calorimetry

Besides the crystal phases identification and morphology study of the sample, the heat capacity (C_p), the phase transition temperature, and the crystallinity degree of the samples, etc., were revealed by the differential scanning calorimetry. (DSC) There two basic types of DSCs, including heat flux and power compensation DSC. The latter one measures the thermal power difference by the compensated joule heat controlled as the sample and reference are set at the same temperature. In the thesis, the heat flux disk-type Q10 DSC (TA instrument, USA) at constant pressure was used as the characterization equipment, which directly measures the temperature difference (ΔT) between the sample and reference, and the sample heat flow (q) is determined by the Ohm's law, $q = \Delta T/R$, where R denotes the resistance of the disk. ^[19] Fig. 3.10a shows the diagram of a typical heat flux disk-type DSC system. The S denotes the place where the sample is placed, and R stands for the reference. And the number 1 is the thermoelectric disk where the sample and reference place and 2 is the furnace and 3 is the lid to maintain the heat of the system, the number 4 is the thermocouple to measure the temperature, and the last number 5 represents the controller the DSC system. To determine the heat capacity of the sample (C_s), the basic equation is ^[20] $\Delta q_{sr} = q_s - q_r = C_s \frac{dT_s}{dt} - C_r \frac{dT_r}{dt} = (C_s - C_r)\beta$

Where q_s and q_r stand for the measured heat flow of the sample and reference, and β is the heating. Thus, with the known capacity of the reference (C_r), the C_s is calculable. Fig 3.10b is the schematic curve of the measured heat flow versus the temperature as an example.

For phase transition materials like VO₂, there are endothermic peaks during the heat process and exothermic peaks in the cooling process to calculate the phase transition temperature. (τ_c) And for the crystallinity degree of the samples is to compare the enthalpy value of the targeted with the pure crystallinity sample at the crystallinity temperature. ^[21]

A UV-Vis-NIR spectrophotometer (Cary 5000, Agilent Ltd, USA) is used throughout the thesis. The transmittance spectra with the range of 250 – 2500 nm wavelength were

measured. As the targeted VO₂-based thermochromic coatings undergo the phase change at the critical temperature, the spectrophotometer was additionally equipped with a PE120 Peltier heating and cooling stage (Linkam, UK), as well as the water-circulating cooling system. The prepared VO₂-based coatings samples were mounted on the stage during the measurement. The low temperature is set at 20 °C when the VO₂ sample is at the monoclinic phase, while the high temperature is at 90 °C and stable for several minutes until the phase transition process is complete.

As shown in Fig 3.11, the light emits from the source, passing the entrance slit then is split by the dispersion device. After the exit slit, the single-wavelength light was obtained. The Cary 5000 model used in this thesis is the dual-beam type. Thus, the single wavelength beam is reflected by the mirrors to pass through the reference and sample. After the reflection and absorption of the light, the remaining light signals are collected by the detectors. The wavelength of the light is modified by the slits and the dispersion device.

Figure 3.11 The diagram of the mechanism of the UV-Vis-NIR spectrophotometer. ^[22]

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Chapter 4

Synthesis of Monoclinic Vanadium Dioxide via One-step Hydrothermal

Pure monoclinic vanadium dioxide nanoparticles (VO_2 NPs) with the 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 $\text{VO}_2(\text{M})$ NPs without posttreatment of annealing, which may induce unwanted aggregation of NPs. In contrast with the annealed sample, the one-step processed $\text{VO}_2(\text{M})$ NPs exhibits superior thermochromic performance with the solar modulation efficiency of 11.8% and luminous transmittance of 37.3%. Under the same hydrothermal conditions, we also find Cr doping is in favor of the growth of the metastable phase of $\text{VO}_2(\text{A})$ other than the common $\text{VO}_2(\text{B})$ or the stable thermodynamic phase of $\text{VO}_2(\text{M})$. From what we know, $\text{VO}_2(\text{A})$ is firstly reported in the morphology of NPs, apart from the typical one-dimensional nano or micrometer belt shape.

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4.1 Introduction

Vanadium dioxide (VO_2), as a typical strongly electron correlated transition metal oxide, has a first-order and reversible metal-insulator transition (MIT) at phase transition temperature (τ_c) ~ 340 K. The MIT was first discovered by Morin et al. in 1959.^[1] Since then, it has drawn extensive researches.^[2] At room temperature and unstrained, the crystal structure of VO_2 is monoclinic (M, $P2_1/c$, $a = 5.75$ $b = 4.54$ $c = 5.38$, $\beta = 122.64^\circ$) with zig-zag dimerized V-V pairs along c axis, while above the τ_c , the tetragonal structure ($P4_2/mnm$ $a = b = 4.55$ $c = 2.86$, $\beta = 90^\circ$) 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 makes VO_2 a great potential for the 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 those intensive applications depends on the controlled preparation of high-quality VO_2 single/polycrystals powders or thin-film due to the multivalent nature of vanadium element, making it tough work to synthesize high purity VO_2 . Compared with some high-cost or complex methods, such as electrodeposition,^[13] sputtering,^[14] pulse laser,^[15] sol-gel,^[16] hydrothermal synthesis is probably the most effective method to control the morphology, size, and phase structures of VO_2 . Recently, Li et al. summarized a strenuous and elaborate review on the hydrothermal synthesis of the VO_2 phase and its application in thermochromic smart windows.^[17] From which we know that most of the reported one-step hydrothermal synthesis requires a much high temperature and long reaction time. Meanwhile, in most cases, certain metal doping, such as tungsten,^[18, 19] is necessary to obtain $\text{VO}_2(\text{M})$ nanoparticles (NPs). However, the doping elements that substitute vanadium elements normally deteriorate the crystallinity and hinder the thermochromic performance of VO_2 . Son et al. prepared the $\text{VO}_2(\text{M})$ 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] But the used high hydrothermal temperature, up to around 400 °C, leads to the 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 seed-assisted one-step hydrothermal to form VO₂ composite is also reported by Jin et al. recently. They reported a novel VO₂-ZnO dandelions structure with the help of the TiO₂ seeds.^[23] While 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., where they separated the hydrogen peroxide from the precursor solution, providing a rational oxidizing hydrothermal system.^[25] But, the duration of hydrothermal synthesis has been doubled at the same time. Malarde et al. firstly introduced a continuous hydrothermal flow synthesis method for the direct preparation of large amount VO₂(M) without a post-annealing process while the mixing temperature synthesis was more than 400 °C.^[26] 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.

4.2. Experimental Section

4.2.1 Materials and synthesis

In the experiments, all chemicals of V_2O_5 (Alfa Aesar, 99.6%), $N_2H_4 \cdot H_2O$ (Alfa Aesar, 99.9%), and H_2O_2 (30 wt%, Sigma-Aldrich) were used as received without any further purification. In a typical hydrothermal process, 1 mmol commercial V_2O_5 powders were added into 5 ml preheated H_2O_2 (30 wt%) at 90 °C with 200 rpm stirring. After a vigorous reaction, a brownish $V_2O_5 \cdot H_2O_2$ precursor was obtained. A certain amount of deionized (DI) water was added subsequently. Afterward, the brownish precursor was chemically reduced by adding $N_2H_4 \cdot H_2O$ solution dropwise with stirring for 10 min. After the precursor turned blue-black, it was transferred into a 50 ml PTFE liner and sealed into a stainless-steel autoclave. The hydrothermal temperature was set at 260 °C for a certain period (12-168 h), 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 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.

4.2.2 Preparation of VO_2 -based thermochromic film

The 50 mg of as-prepared VO_2 NPs were evenly dispersed into 5 ml ethanol and 5 ml concentrated Si-Al based solution by one-hour ultrasonication bath. The synthesis of the Si-Al solution has been reported in our previous work. The VO_2 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 hour at 150 °C to remove the solvent and form the uniform coatings.

4.2.3 Characterization

The X-ray diffraction (XRD) patterns of the obtained powders were collected from a Shimadzu Powder XRD-6000 X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15406$ 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, JOEL, Japan). Differential Scanning Calorimeter (DSC Q10, TA instrument, USA) was used to characterize the phase transition behavior of the samples upon the heating and cooling rate

of 10 °C /min under the N₂ atmosphere. Variable temperature optical transmission spectra of the prepared VO₂ films were measured on a UV-Vis-NIR spectrophotometer (Cary 5000, Agilent Ltd, USA) in the wavelength of 250~2500 nm at 20 °C 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:

$$T_{\text{lum/sol}} = \frac{\int \phi_{\text{lum/sol}}(\lambda) T(\lambda) d\lambda}{\int \phi_{\text{lum/sol}}(\lambda) d\lambda} \quad (1)$$

$$\Delta T_{\text{sol}} = T_{\text{sol}}(20\text{ }^{\circ}\text{C}) - T_{\text{sol}}(90\text{ }^{\circ}\text{C}) \quad (2)$$

Where $T(\lambda)$ 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 of the evaluation method was reported.^[27]

4.3 Results and Discussion

4.3.1 Effect of the amount of the reduction

As discussed in our previous paper,^[28] the amount of reduction is the crucial factor for the synthesis of the desired VO₂ phase. Thus, in the series of hydrothermal experiments, the amount of N₂H₄·H₂O solution was optimized firstly.

The XRD patterns of the hydrothermal samples under the same condition, but with different amounts of the reduction, are shown in Fig. 4.1. The phase evolution of the obtained vanadium oxide could be observed from the increment of the reduction. When the initial amount of N₂H₄·H₂O is 30 μl, the hydrothermal product is still V₂O₅ that is the same phase as the raw material. It is due to that the reduction was mainly consumed by the residual H₂O₂ in the precursor. After the amount of N₂H₄·H₂O increasing to 50 μl, the V₂O₅ was reduced to pure V₆O₁₃. As 60 μl of N₂H₄·H₂O was selected, a high crystalline pure phase of VO₂(M) (JCPDS #43-1051) was synthesized. The pure VO₂(M) is still retained with increasing the amount of reduction to 70 μl, but from the XRD pattern, the crystallinity of the product became much lower. As shown in Fig. 4.1e and 1f, the powders will be reduced to V₆O₁₁ and V₃O₅, when the amount of reduction was further raised to 80 and 90

μL . Additionally, the crystallinity of the powders is gradually decreased with increment of the $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ no matter what kind of vanadium oxide phase it is. So, to synthesize the VO_2 NPs with high crystallinity, 60 μL reduction was chosen as the standard amount for the consequent hydrothermal synthesis.

Figure 4.1. (a-f) XRD patterns of hydrothermal samples with different amounts of the reductive reagent $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ at 260 °C and 24 h duration.

The morphology of the above samples is shown in Fig. 4.2a-e. With the phase evolution of the obtained vanadium oxides, the morphology of these samples changes from nanowires/microwires dramatically into sub-100nm NPs and further growth into larger particles. In Fig. 4.2a, the length of V_2O_5 nanowires is up to several micrometers, which is different from the sheet structure of the $\text{V}_2\text{O}_5\text{-H}_2\text{O}_2$ precursor both in size and shape reported before.^[29] Fig. 4.2b shows the microbelt structure of the obtained V_6O_{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 Fig. 4.2c, the morphology of the VO₂ 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 Fig. 4.2d-e. The irregular morphology also causes a decrease in the crystallinity, as discussed in Fig. 4.1 of the XRD results.

Based on Fig. 4.1 and 4.2, a hydrothermal synthesis mechanism could be speculated. With the high temperature and pressure, the sheet structure of the precursor turns into nanowires at the initial stage. The reduction process begins with an increased amount of N₂H₄·H₂O. The nanowires grow together into the microwires via an oriented attachment mechanism, and then the NPs gradually appear at the edge of the microwires. The final morphology using N₂H₄·H₂O as the reduction of the VO₂ is NPs, which is similar to the previous reports. Herein, N₂H₄·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.^[30] The same group further synthesized nanorod VO₂(R) via adding hydrazine, and they further postulate the hydrazine could serve as a soft template. Both Santulli et al. and Son et al. found the potential of N₂H₄ 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 N₂H₄, 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.^[31]

Figure 4.2. SEM images of hydrothermal samples with different amounts of the reduction at 260 °C and 24 h duration.

4.3.2 Effect of the hydrothermal duration

The second parameter discussed in the series of the hydrothermal preparation was the hydrothermal duration while keeping $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ at 60 μl . The XRD results in Fig.4.3 show the hydrothermal samples with different duration increased from 12 h to 168 h. It can be found that all samples are single-phase $\text{VO}_2(\text{M})$ when the reduction amount was kept constant. The XRD peaks of the $\text{VO}_2(\text{M})$ gradually intensified with the increase of the hydrothermal duration.

Figure 4.3. (a-d) XRD patterns of hydrothermal samples with different duration at 260 °C with 60 μl $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.

Fig. 4.4a 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 is far from enough for the growth of uniform NPs, and the size of the particles are rather uneven, ranging from 20 nm to 130 nm. When the hydrothermal duration increases to 24 h, the uniform NPs morphology is shown in Fig. 4.4b, with an average size of 60.2 nm. In Fig. 4.4c and 4.4d, the hydrothermal duration continues to be extended, the shape of the NPs remains the same, while the size is getting larger. The average size is 75.9 nm for the 72 h sample, while the size of NPs grows to nearly 90 nm at an even longer duration at 168 h.

Figure 4.4. (a-d) SEM images of hydrothermal samples with different duration at 260 °C with 60 μl $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ with the size distribution analysis attached below.

4.3.3 Effect of the precursor concentration

Besides the reduction amount and hydrothermal duration, the precursor concentration is the last hydrothermal parameter we are concerned with within our experiment. The preparation of the precursor was introduced in the experimental section. To adjust the precursor concentration, the volume of the solvent, including H_2O_2 and DI water, was kept unchanged, while the amount of the raw material of V_2O_5 powder was tuning from 1 mmol up to 2 mmol accordingly.

Fig.4.5 shows the XRD patterns of the hydrothermal samples with different precursor concentrations. Note that the concentration of V_2O_5 powder is kept at 1 mmol in our experiment mentioned in the above parts. As shown in Fig.4.5b, all of the XRD peaks are attributed to the standard $\text{VO}_2(\text{M})$ peaks. Two uncertain peaks marked with the star, around 18.7° and 37.8° , turn up as we increased the concentration of V_2O_5 up to 1.25 mmol (Fig. 4.5b). Upon further increasing the V_2O_5 concentration to 1.5 mmol, Fig. 4.5c exhibits that most of the peaks are assigned to $\text{VO}_2(\text{B})$, while a small number of peaks attributed to $\text{VO}_2(\text{M})$ still could be observed. When the concentration of V_2O_5 powder was increased to 2 mmol, V_6O_{13} was synthesized, as shown in Fig. 4.5d. However, $\text{VO}_2(\text{M})$ peaks are still in existence. It suggests the reduction amount is significant to synthesize the $\text{VO}_2(\text{M})$, while the precursor concentration must be controlled within the corresponding range.

Figure 4.5. (a-d) XRD patterns of hydrothermal samples with different precursor concentrations at 260 °C with 60 μl $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and 24 h duration.

The SEM images in Fig. 4.6 shows morphologies of the above samples, which are highly coincided with the XRD results. Fig. 4.6a shows the highly uniform NPs, which is the pure $\text{VO}_2(\text{M})$ phase. In Fig. 4.6b, two shapes of the particles are clearly shown. The NPs are the $\text{VO}_2(\text{M})$, while the thicker nanobeams mostly belong to the unknown phase indicated in the XRD pattern (Fig.4.5b). Two different kinds of morphology in NPs and ultralong nanowires are shown in Fig. 4.6c. According to the XRD results, the nanowires with lengths up to several micrometers belong to $\text{VO}_2(\text{B})$, while the NPs are $\text{VO}_2(\text{M})$. In Fig. 4.6d, it was found that besides the $\text{VO}_2(\text{M})$ NPs, microbelts are observed. The microbelts are V_6O_{13} based on the XRD result, which is completely identified as the V_6O_{13} in the Fig. 4.2b.

Figure 4.6. (a-d) SEM images of hydrothermal samples with different precursor concentrations at 260 °C with 60 μl $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and 24 h duration.

4.3.4 Thermochromic performance of $\text{VO}_2(\text{M})$ NPs

Fig. 4.7 shows the DSC of the synthesized VO_2 NPs from different hydrothermal duration in the hydrothermal process. In general, endothermic peaks are observed in the heating segment, while exothermal peaks are found during the cooling process, and the thermal hysteresis indicates that the VO_2 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 Fig. 4.7a, the 12 h hydrothermal sample barely exhibits unappealing peaks. The bump appears at 66.2 °C during the heating ramp, while at 43.4 °C during the cooling ramp. The transition temperature is 54.8 °C, and the latent heat is 7.55 J/g, much lower than the reported data. This suggests a large number of defects in the samples, and it further proves that the insufficient hydrothermal time for the VO_2 synthesis, as discuss in Fig. 4.4a. With the duration increases to 24 h, the endothermic and exothermal peaks are both shifted towards the higher temperature, which is 70.2 °C and 56.5 °C, which brings the τ_c to 63.4

°C. The enthalpy increases to 37.3 J/g. As for the 72 h hydrothermal sample, the position of the peaks barely shifts, while the enthalpy further increases to 43.32 J/g. The more significant change for DSC peaks could be observed for the 168 h duration sample. The endothermic peak appears at 77.4 °C, and the exothermal bump at 59.2 °C, which gives the τ_c at 68.3 °C. The obtained enthalpy value is 49.4 J/g. By contrast, the endothermic or exothermal peaks for 72 h and 168 h are sharper, indicating the larger particle size for these samples (Fig. 4.4). The trend that ΔH and τ_c both increased with the longer hydrothermal duration is further shown in Fig. 4.7b.

Figure 4.7. (a) DSC curves of the hydrothermal VO₂ powders at different hydrothermal duration at 260 °C with 60 μ l N₂H₄·H₂O; (b) phase change enthalpy (ΔH) and transition temperature (τ_c) versus hydrothermal duration.

The thermochromic property is evaluated through the temperature-dependent UV-Vis-NIR spectra, as shown in Fig. 4.8. The solid and dotted demonstrates the high temperature and low-temperature optical transmittance of the prepared VO₂ films. In Fig. 4.8a, all three samples with different concentrations of VO₂ dispersion are prepared from the non-doped single-phase VO₂ NPs. The concentration of the prepared VO₂ dispersion was adjusted by the added amount of the VO₂ powders, and the volume of the solvent, including alcohol and Si-Al gel, was kept the same. The thickness of the three samples is 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_{lum}) is calculated to be 44.4%, and the solar modulation (ΔT_{sol}) is 10.4%. With the higher concentration of the dispersion, the solar modulating ability was improved alongside the degradation of the T_{lum} (2 % sample, T_{lum} ~ 37.3%, ΔT_{sol} ~ 11.8%, and 3 % sample, T_{lum} ~ 13.8%, ΔT_{sol} ~ 13.6%). The thermochromic

performance of the different duration hydrothermal samples is exhibited in Fig. 4.8b. All samples were made with the same concentration of VO₂ 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. It is caused by the different optical scattering properties between the room temperature VO₂(M) and high-temperature phase VO₂(R). The higher transmittance in the visible wavelength range is due to the less light scattered in the high-temperature VO₂(R). With the longer hydrothermal duration, crosspoints appear at 72 h sample with particle size at 75.9 nm and 168 h sample with 86.1 nm. This phenomenon deteriorates the thermochromic performance of the longer duration sample (72 h sample, $T_{lum} \sim 31.7\%$, $\Delta T_{sol} \sim 11.0\%$, and 168 h sample, $T_{lum} \sim 35.7\%$, $\Delta T_{sol} \sim 5.7\%$), compared with the 24 h sample at the same thickness and dispersion concentration. ($T_{lum} \sim 37.3\%$, $\Delta T_{sol} \sim 11.8\%$).

Figure 4.8. Transmittance spectra of fabricated VO₂ films with VO₂ NPs synthesized: (a) different concentrations of prepared VO₂ dispersion; (b) different duration of the hydrothermal samples. The circles in the figure indicate the appearance of the crosspoints.

4.3.5 Effect of the Cr doping

Besides the non-doping VO₂(M) synthesis, the Cr doped VO₂ samples were also studied to further understand the growth mechanism of the vanadium oxide during the hydrothermal. The Cr doping concentration was adjusted by the amount of the Cr₂O₃ powder added into the precursor. The Cr doping percentage was calculated based on the ratio of the Cr element over the Cr and V elements.

Fig.4.9 shows the XRD patterns of the hydrothermal samples with different doping concentrations. In Fig. 7a, only 1 % Cr element was added into the precursor. Besides the $\text{VO}_2(\text{M})$ peaks, the $\text{VO}_2(\text{A})$ peaks and the small peaks attributed to Cr_2O_3 are clearly shown. However, when the Cr doping increases to 3%, $\text{VO}_2(\text{A})$ peaks vanished, left with $\text{VO}_2(\text{M})$ and Cr_2O_3 peaks. It is the same as the 5% and 10% Cr doping samples, while the Cr_2O_3 peaks are becoming intensifier.

Figure 4.9. (a-d) XRD patterns of hydrothermal samples with different doping concentrations at 260 °C with 60 μl $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ for 24 h.

In Fig 4.10, SEM images of all the Cr doping samples are shown. The morphology of all the samples is in high uniform NPs, despite the slightly different XRD results. The average size of the hydrothermal particles is 55.9 nm, slightly smaller than the size of the non-

doping 24 h VO₂ sample (around 60.1 nm), as the Cr element is slightly smaller than the V element. Due to the presence of the Cr₂O₃, the NPs are the mixture of the obtained VO₂(M) and excessive Cr₂O₃. For the 1 % Cr doping sample, the NPs are the mixture of the VO₂(M) and VO₂(A). The VO₂(A) NPs morphology is first reported, although the sample is not in the pure phase.

Figure 4.10. (a-d) SEM images of the hydrothermal samples with different doping concentrations at 260 °C with 60 μ l N₂H₄.H₂O for 24 h.

DSC curves for different doping concentration samples are shown in Fig. 4.11. As discussed in Fig. 4.9 and Fig. 4.10, the XRD peaks and morphology attributed to VO₂(M) are kept similar with the doping concentration from 1% increasing up to 10%, while the Cr₂O₃ peaks are intensifier. The discussion applied in DSC curves as well. In Fig. 4.11, the position of the endothermic and exothermic peaks is barely shifted except for the 10% doping samples. The exothermic peaks are at 52 °C, 51.5 °C, and 52.6 °C separately, while the endothermic peaks are at 67.5 °C, 68.9 °C, and 66.9 °C. Thus, the transition temperature for these three samples is 59.8 °C, 60.1 °C and 59.7 °C. As for the highest doping concentration, the transition temperature is slightly increased to 62.8 °C. From these DSC curves, we can conclude that with higher doping concentration, the transition temperature

increased despite the doped Cr element distorted the VO_6 octahedral structure and increased defects, causing τ_c decrease at first. [32] On the enthalpy wise, the heat latent is 33.2 J/g, 32.7 J/g, and 31.1 J/g for 1%, 3%, and 5% doping, slightly decreased from the non-doping sample with the enthalpy of 37.3 J/g. However, based on the XRD results in Fig. 4.9, due to the increment of the peak intensity of Cr_2O_3 with the higher doping concentration, it suggests that the low doping efficiency in the hydrothermal process. The final product is mostly the mixture of the Cr_2O_3 and $\text{VO}_2(\text{M})$. Thus, it could be another reason that the morphology and DSC have changed in the smaller range.

Figure 4.11 DSC curves of the hydrothermal VO_2 powders at different Cr doping concentration at 260 °C with 60 μl $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$.

Due to the low doping efficiency of the hydrothermal synthesis, the lowest doping concentration sample was prepared for the smart window applications, as the higher doping concentration samples have a lower ratio of the thermochromic VO_2 NPs. As shown in Fig. 4.12, the film prepared with 1% Cr doped VO is compared with the non-doped VO_2 sample. The thermochromic property of the 1% Cr-doped film is calculated to be $T_{\text{lum}} \sim 35.1^\circ\text{C}$ and $\Delta T_{\text{sol}} \sim 11.3\%$, slightly inferior to the non-doped film ($T_{\text{lum}} \sim 37.3^\circ\text{C}$, $\Delta T_{\text{sol}} \sim 11.8\%$), despite the

smaller size of the Cr-doped samples with the average size at 55.9 nm compared with the non-doped samples at 60.1 nm. On the other hand, with the smaller average size, the τ_c also slightly decreased to 59.8 °C for Cr-doped samples from 63.4 °C for non-doped samples.

Figure 4.12 Transmittance spectra of fabricated VO₂ films with non-doped and Cr doped VO₂ NPs synthesized.

4.4 Conclusion

In this paper, pure VO₂(M) NPs with uniform morphology were prepared via one-step hydrothermal synthesis without doping or annealing treatment. The raw material of V₂O₅ was gradually reduced to microbelt V₆O₁₃ and then to desired VO₂ NPs, eventually to larger and irregular morphology V₆O₁₁ and V₃O₅ 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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Chapter 5

High-temperature Hydrothermal Synthesis

Hydrothermal synthesis is the most investigated approach to fabricate high crystallinity vanadium dioxide nanoparticles (VO_2 NPs). The upper limit of the temperature most reported in the literature is 260 °C and the synthesis duration is no less than 24 hours. In this report, the synthesis temperature up to 350 °C was systematically studied. The pure phase monoclinic $\text{VO}_2(\text{M})$ NPs were firstly prepared at 290 °C with the 12 h hydrothermal duration. With the hydrothermal temperature raised to 320 °C, the high crystallinity $\text{VO}_2(\text{M})$ was obtained with only 6 h hydrothermal duration. However, the compromised thermochromic performance of the $\text{VO}_2(\text{M})$ based films is observed which could be due to the larger NPs size and faceted growth.

5.1 Introduction

Vanadium oxide (VO_x) has attracted tremendous attraction among the transition metal oxides.^[1] This is not only due to its rich solid phases in the V-O system, including the presence of Wadsley ($\text{V}_n\text{O}_{2n+1}$) and Magneli ($\text{V}_2\text{O}_{2n-1}$) phases, but also the novel properties and various potential applications.^[2] Among them, the monoclinic phase $\text{VO}_2(\text{M})$ has been intensively studied, which shows great potential for energy savings in buildings.^[3] $\text{VO}_2(\text{M})$ undergoes the reversible phase transition to the tetragonal $\text{VO}_2(\text{R})$ at the critical temperature (τ_c) at 68 °C, which is accompanied by abrupt changes both in the optical and electrical properties.^[4]

The hydrothermal method plays an important role in the controllable synthesis of VO_2 . Recently, Li et al. reviewed the hydrothermal synthesis of VO_2 and found that the long hydrothermal duration is necessary to obtain VO_2 directly.^[5] Cao et al. developed the one-step hydrothermal synthesis of $\text{VO}_2(\text{M})$ with the oxalic acid reduction of the raw material V_2O_5 .^[6] The hydrothermal process went through 7 days at 240 °C. Different combination of the raw materials and reductions results in the different hydrothermal process. However, even with the doping element^[7] or the seed assisted^[8], the duration of the hydrothermal process for pure phase $\text{VO}_2(\text{M})$ synthesis is still no less than 15 h. ^[5] It is worth noting that most hydrothermal synthesis is conducted at a temperature of 240-280 °C. It was reported that higher crystallinity of the obtained $\text{VO}_2(\text{M})$ with increasing processing temperature and larger NP particles and large NP size with longer duration.^[9] Thus, to obtain high crystallinity $\text{VO}_2(\text{M})$ with the smaller particle size, the rapid hydrothermal method at higher process temperature is worth studying.

Srinivasa et al. reported the rapid one-step hydrothermal synthesis of VO_2 within 1 h under 220 °C using V_2O_5 and citric acid, but the obtained product is $\text{VO}_2(\text{B})$, which requires further high-temperature annealing to convert to $\text{VO}_2(\text{M})$.^[10] It also suggests that the low hydrothermal temperature promotes the growth of the metastable phase of $\text{VO}_2(\text{B})$. To synthesize $\text{VO}_2(\text{M})$ in a rapid way, a higher hydrothermal temperature is selected in our experiment without posttreatment of annealing.

In this study, the one-step rapid hydrothermal was introduced to the synthesis of pure phase VO₂ (M). The pure phase VO₂ (M) was successfully synthesized with a short duration of 12h at the hydrothermal temperature of 290 °C. However, despite the high crystallinity, the thermochromic performance is degraded compared with most of the reported results due to the blueshift of the crosspoint between the transmittance spectra of VO₂ (M) and VO₂ (R). Such an abnormal phenomenon also suggests that the thermochromic property is influenced not only by the crystallinity, particle sizes but also the other factors such as different preference crystallographic orientation, which has not been reported in the literature before.

5.2 Experimental Section

5.2.1 Materials

All the chemical reagents in the experiments, vanadium pentoxide (V₂O₅, Alfa Aesar, 99.6%), hydrazine hydrate (N₂H₄·H₂O, Alfa Aesar, 99.9%), and Hydrogen peroxide (H₂O₂, 30 wt%, Sigma-Aldrich) were of analytical grade and used as received without any purification. Deionized (DI) water was used as the solvent during the precursor preparation and hydrothermal synthesis.

5.2.2 Hydrothermal synthesis of VO₂ NPs

1 mmol V₂O₅ powder was quickly added into the 5 ml H₂O₂ with continuous stirring at 200 rpm, and the mixture was heated at 90 °C. Next, 15 ml DI H₂O was added to the brownish mixture obtained from the above reaction. The solution then was stirred continuously for another 30 mins. Afterward, the reduction of N₂H₄·H₂O was added dropwise into the solution with stirring for another 10 mins. For comparison, a certain amount of DI water was further added into the precursor to regulate the filling factor (FF) of hydrothermal synthesis. Finally, the precursor was transferred into the quartz liner and sealed into the stainless-steel autoclave for a certain period (6 - 12 h) at different temperatures ranges from

260 to 350 °C. The product was washed several times with DI water and acetone and collected by centrifugation. The final powder was obtained after drying in the vacuum oven.

In the typical one-step hydrothermal synthesis of VO₂(M), the hydrothermal duration usually is usually more than 24 h or even up to several days for the complete phase evolution from the intermediate metastable phase to the thermodynamically stable phase of VO₂(M).^[11] Moreover, for hydrothermal reactors, the liner is generally made of polytetrafluoroethylene (PTFE), of which the melting temperature is around 327 °C.^[12] Therefore the hydrothermal temperature is typically set below 300 °C, which also caused the longer duration for the synthesis of VO₂(M).^[13] In our hydrothermal experiment, the liner was changed to quartz liner, which has the melting temperature up to 1670 °C that provides the possibility for the high-temperature hydrothermal synthesis of VO₂(M).

5.2.3 Preparation of the VO₂(M) nanocomposite film

VO₂ dispersion was prepared via the ultrasonication of a mixture of VO₂ NPs, ethanol, and Si-Al solution. The Si-Al solution was prepared and reported in our previous work.^[14] The VO₂ dispersion was cast on the 2.5 cm* 2.5 cm clean soda-lime glass by spin-coating. The speed and coating time are constant. The films were dried in the vacuum oven through a two-stage heating treatment. The heating process was firstly conducted at 90 °C for 1h, and then the temperature was set at 150 °C for another hour to eliminate the excess solvent. After cooling to room temperature, the uniform VO₂(M) nanocomposite films were obtained.

5.2.4 Characterization

The obtained hydrothermal powders were first characterized by X-ray diffraction (XRD, Shimadzu Powder XRD-6000) under 40 KV voltage and 30 mA current with Cu K α radiation ($\lambda = 0.15406$ nm). The morphology of the samples was determined by the field emission scanning electronic microscope (FESEM, JSM-7600F, JOEL, Japan). The phase transition behaviors of the samples were characterized and analyzed via the differential

scanning calorimeter (DSC Q10, TA instrument, USA). The heating and cooling rate remained at 10 °C/min among all tests under the N₂ atmosphere. The vis-infrared transmission spectra of the prepared VO₂ films were recorded by a UV-Vis-NIR spectrophotometer (Cary 5000, Agilent Ltd, USA) equipped with a Linkam PE120 system Peltier heating and the cooling stage. The temperature of the films was set at 20 °C and 90 °C separately. The range of the spectra was collected from 250 to 2500 nm.

As discussed in the previous paper, the main parameters to assess the thermochromic properties of the VO₂ films are T_{lum} and ΔT_{sol} .^[15] These two parameters were calculated based on the transmission data according to the following equations:

$$T_{lum/sol} = \frac{\int \phi_{lum/sol}(\lambda) T(\lambda) d\lambda}{\int \phi_{lum/sol}(\lambda) d\lambda} \quad (1)$$

$$\Delta T_{sol} = T_{sol}(20\text{ }^{\circ}\text{C}) - T_{sol}(90\text{ }^{\circ}\text{C}) \quad (2)$$

where $T(\lambda)$ denotes the film transmittance at wavelength λ , ϕ_{sol} is the solar irradiance spectrum for air mass 1.5 corresponding to the sun standing 37 ° above the horizon and ϕ_{lum} is spectral sensitivity in the wavelength from 380-780 nm.

5.3 Results and Discussion

5.3.1 Effect of the hydrothermal temperature

Fig. 5.1a shows the XRD patterns of the hydrothermal samples obtained at the temperature from 260 to 350 °C with a temperature interval of 30 °C. The duration was set at 6 h and 12 h separately. From Fig. 5.1(i-iv), the XRD patterns exhibit weak peaks, despite the increase of the hydrothermal duration. Additionally, there are two unknown peaks at 23.3° and 31.5° marked with stars in the XRD patterns of the 260 °C hydrothermal samples. When the temperature was increased to 290 °C, these two peaks are starting to diminish. With the duration raised to 12 h, these two peaks almost disappear with the appearance of the peak at 27.8° which is corresponding to the (011) face and is the main characteristic peak corresponding to the VO₂(M). In addition, all the other peaks are assigned to VO₂(M)

(PDF card: 43-1051), as shown in Fig. 5.1iv, and no other phases are observed at this hydrothermal condition. As the temperature was further increased to 320 °C with the 6h duration, all of the XRD peaks are matched well with the standard VO₂(M). When the duration increases to 12 h at 320 °C, the VO₂(M) phase remains, while the peak at 26.8° corresponding to (110/11 $\bar{1}$) with the square marked exhibits abnormal high intensity (Fig. 5.1vi). This phenomenon is rarely seen in the reported XRD pattern of VO₂(M). The intensity ratio between 26.8° and 27.8° and the FWHM of (011) is plotted against temperatures (Fig. 5.1b). It could be observed that the intensity ratio increases with the increasing temperature from 320 °C 6 h to 350 °C 6 h, as well as the increasing duration from 6 h to 12 h, which suggests that higher temperature or longer duration promote the (110/11 $\bar{1}$) growth direction, which is consistent with the observation of Chen et al. [16] Furthermore, based on full width at half maximum (FWHM) of the peak (011), the estimated nanocrystallite size can be calculated using the Debye-Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where D denotes the size of the nanocrystallites. K stands for the Scherrer constant and λ is the wavelength of the X-ray sources. β is the calculated FWHM and θ is the peak position. With the larger FWHM, the estimated size of the nanocrystallites is smaller. Thus, according to Fig. 5.1b, the higher hydrothermal temperature exhibits the larger FWHM, and the longer duration also gives the larger FWHM. It implies that in the temperature range of 320-350 °C, the higher hydrothermal temperature and the longer duration, the smaller size of the obtained NPs, which is different from the previous reported that the NPs size is bigger with the higher temperature. [9]

Figure 5.1. (a) XRD patterns of the different duration (6 and 12 hrs) hydrothermal samples with different hydrothermal temperature (260-350 °C). The standard VO₂(M) XRD peaks are indicated. (b) FWHM of peak (011) and the intensity ratio of peak (110) to peak (011) versus different hydrothermal conditions.

The study of the morphology and nanostructure of the as synthesized powders is shown in Fig 5.2, inset with the analyzed grain size distribution. In Fig. 5.2(a-b), the morphology of the sample obtained at 260 °C of 6 h are relatively uniform NPs with an average diameter of 55.1 nm, and the size of the NPs slightly increased to 67.2 nm at the longer duration of 12 h. However, according to Fig. 5.1(i-ii), these uniform NPs have not yet grown into VO₂(M). As the temperature increased to 290 °C, the morphology of the resulting sample is still uniform NPs, and the average diameter of NPs is nearly 80 nm (Fig. 5.2c, d). As analyzed in Fig. 5.1iv, these samples have evolved into VO₂(M). With the temperature further increased to 320 °C and 350 °C, the morphology of the samples is still NPs. The average size of 6 h and 12 h duration at above temperature is all among 90-95 nm. Based on the XRD and SEM results, the VO₂(M) NPs formed when the size was grown into around 80 nm, with the temperature reached at 320 °C, the average size reached its maximum at 95.1 nm. (Fig. 5.2e) From that condition, the size of NPs gradually decreased to 93.3, 93.1 and eventually to 90.6 nm. (Fig. 5.2f-h)

Figure 5.2. (a-h) SEM images of different duration (6 and 12 hours) hydrothermal samples with hydrothermal temperature from 260-350 °C.

Fig. 5.3 further exhibits the average NPs size distribution and standard deviation (SD) versus hydrothermal temperature. The NPs growth process can be divided into two parts.

The first stage is before the formation of $\text{VO}_2(\text{M})$. The particle size grows apparently from 55.1 nm to above 90 nm within the hydrothermal duration at 6 h and 12 h with the temperature increased from 260 to 320 °C. While the second phase is from 320 to 350 °C, as the $\text{VO}_2(\text{M})$ already formed, however, the longer duration and higher temperature, the size of the obtained NPs gets slightly smaller while still above 90 nm. The change of the NPs size can be observed at the upper lines in Fig. 5.3. The lower lines show the trend of the SD change, which is similar to the change of the average size. As the temperature increased from 260 to 320 °C, the SD value is bigger and gets smaller beyond 320 °C. It implies that with longer duration and higher temperature, the size is getting more uniform. Compared with 6 h and 12 h duration lines, the size is more uniform at a higher duration at 12 h in general, as the dotted line (12 h) is always below the solid line. (6 h)

Figure 5.3. The average particle size (left) and SD (right) versus different hydrothermal temperature and duration.

5.3.2 Discussion of phase transition behavior and thermochromic property

The phase transition behavior is shown in Fig. 5.4. As discussed in Fig. 5.1a, the samples obtained at the hydrothermal temperature of 260 °C within 6 h and 12 h are not grown into

VO₂(M), so there are no endothermic and exothermic peaks corresponding to the phase transition in the DSC curves. As the temperature increased to 290 °C, both the 6 h and 12 h duration samples start evolving into VO₂(M), and the exothermal and endothermic peaks appear. The latent heat for the 6 h sample is 2.7 J/g with τ_c at 65.8 °C, while for the 12 h sample, the higher peak exhibits the higher latent heat of 5.6 J/g and slightly higher τ_c at 66.8 °C. When the temperature is further increased to 320 °C, both the endothermic and exothermal peaks get much higher and sharper. Meanwhile, the latent heat increases to 31.6 J/g at 6h duration and 38.4 J/g at 12h duration with τ_c at 64.7 °C and 64.9 °C separately. As for the 350 °C samples, the peaks drop instead during the heating and cooling process for both samples in contrast to the samples obtained at 320 °C. Accordingly, the latent heat decreases to 20.2 J/g and 25.6 J/g for the 6 h and the 12 h samples respectively, but the τ_c for both samples was nearly unchanged compared with the samples obtained at 320 °C. It is worth mentioning changes of latent heat follow the changing trend of XRD peak in intensity at the 26.8° in Fig. 5.1v-viii. That is the highest XRD peak exhibits the highest latent heat during phase transition, which implying the crystallinity-dependent phase transition property.

Figure 5.4. DSC curves of the different duration (6 and 12 h) hydrothermal VO₂ samples: (a) 6h hydrothermal duration with different hydrothermal temperature; (b) 12h hydrothermal duration with different hydrothermal temperature.

Table 5.1 lists the ΔH and τ_c results that discussed above. As the VO₂(M) is not formed until the hydrothermal is raised to 290 °C, the data is not applicable at 260 °C. At 290 °C, the value of ΔH is relatively small which is corresponding to the weak (011) peak as shown in Fig. 5.1iii-iv. As the VO₂(M) formed at 320 and 350 °C, the value of ΔH increased

drastically. However, the value at 350 °C is smaller compared with 320 °C. This phenomenon could be the result of the smaller size of the obtained NPs. (Fig. 5.3) The crystallinity decreased with the smaller NPs. Thus, the highest crystallinity NPs obtained is at 320 °C and 12 h hydrothermal condition.

Table 5.1. Phase transition enthalpy (ΔH) and temperature (τ_c) of different hydrothermal duration and temperature.

Temp.(°C)	Duration		ΔH (J/g)		τ_c (°C)	
	6 h	12 h	6 h	12 h	6 h	12 h
260	Not applicable		Not applicable		Not applicable	
290	2.7	5.6	65.8	66.8		
320	31.6	38.4	64.7	64.9		
350	20.2	25.6	64.1	64.6		

The thermochromic performance for the short duration samples is further studied. As discussed in Fig. 5.1(i-ii), the sample obtained at 260 °C has not grown into VO₂(M), while the samples exhibit inferior phase transition performance at 290 °C as shown in Fig.5.4. Thus, VO₂(M) obtained at 320 °C and 350 °C were chosen to prepare VO₂ film used for thermochromic performance studies. The preparation procedures are discussed in the experimental section. The optical transmittance spectral of these films are shown in Fig.5.5. As compared with our previous VO₂ film coating,^[17, 18] the thermochromic performance for all VO₂(M) samples synthesized at high-temperature hydrothermal within the short duration is rather mediocre. Firstly, the transmittance contrast at 2500 nm, before and after the phase transition of VO₂, is not obvious, and the highest contrast of 10.8% is observed on the sample prepared by hydrothermal at 320 °C for 12 h sample. While in the previous long-duration hydrothermal samples,^[18] the optical transmittance contrast at 2500 nm is generally about 30- 40%, and some specific samples can reach up to 50-60%. Secondly, there is always a crosspoint between transmittance spectra of VO₂(M) and VO₂(R) in the wavelength around 1000 nm (as marked in circles in Fig.5.5), which also results in the inferior thermochromic performance. (Table 5.2) Although all of the four samples have a relatively higher T_{lum} at around 50%, the solar modulation all shows the minus value, which has no actual thermochromic performance.

Figure 5.5. Transmittance spectra of fabricated VO₂ films with short duration hydrothermal synthesis VO₂ powder samples. The circles in the figure indicate the appearance of the crosspoints.

Table 5.2. Thermochromic performance (T_{lum} and ΔT_{sol}) of high-crystallinity VO₂ NPs.

Temp.(°C)	Duration	T_{lum}		ΔT_{sol}		$\Delta T@2500\text{ nm}$	
		6 h	12 h	6 h	12 h	6 h	12 h
320		53.3%	45.6%	-1.04%	-1.05%	5.4%	10.8%
350		48.3%	54.5%	-0.82%	-0.91%	8.4%	3.1%

The blueshift of the crosspoint is caused by the different optical scattering properties between the room temperature VO₂(M) and high-temperature phase VO₂(R). The higher transmittance in the visible wavelength range is due to the less light scattered in the high-temperature VO₂(R). The relationship between the thermochromic performance and the crosspoints appearance is thoroughly discussed recently by Li *et al.*^[19] They observed that when the size of VO₂ NPs is larger than 63 nm, the crosspoints appear, and consequently, the thermochromic performance decreases. While the crosspoints disappear when the size

decreases to 30/39 nm because of the weakened light scattering in the rather small NPs. As shown in Fig. 5.2(e-h), the size of the NPs synthesized in the high-temperature and short-duration hydrothermal conditions is more than 50 nm. Thus, the appearance of the crosspoint is inevitably in the transmittance curves. However, the reason for such a low infrared optical modulation of high crystallinity samples is still unclear. We speculate that the abnormal high intensity of the XRD peak at 26.8° can provide some clues for studying the hidden cause. Further calculations on what is the effect of preferential growth of some crystal faces on the optical property of VO_2 are necessary. In such conditions, we can understand that besides the high crystallinity (high latent heat) and size (crosspoints appearance) of the VO_2 NPs, other uncovered causes are still in existence. The controllable growth of specific crystal planes may also impact the optical property significantly.

5.3.3 Effect of the value of filling factor

In addition to hydrothermal temperature and time, filling factor (FF) is also a key parameter to determine hydrothermal products. Ji. *et al.* found that VO_2 (A) was preferred at the filling factor of 0.4 or lower while filling factor over 0.5 results in the formation of VO_2 (R) due to the small energy gap between these two phases.^[20] The hydrothermal temperature was set at 270°C with oxalic acid as the reducing agent and V_2O_5 as the vanadium source. Under our hydrothermal condition, the FF is studied by changing the total solvent volume in the liner from 0.2 to 0.6 while keeping other hydrothermal parameters the same as the above sample prepared at 320°C for 12 h which has the highest crystallinity. Fig. 5.6 shows the XRD patterns of the hydrothermal samples with different FF values. In which, Fig. 5.5a is the same XRD pattern as that shown in Fig. 5.1vi. When the FF increases to 0.4, the XRD pattern exhibits peaks in the low intensity (Fig. 5.6b). With the FF value further raised to 0.6, the mixture of VO_2 (M) and VO_2 (D) was synthesized. The two main characteristic peaks of VO_2 (D) were marked with a star as shown in Fig. 5.5c. As discussed in the experiment part, the FF value is controlled via modifying the additional amount of DI water and at the same time reducing the solid content of the raw material. Song et al. recently found that the low hydrothermal temperature around 200°C and the less solid content favored the VO_2 (B) phase, but when the temperature increased to 220°C , the less solid

content produced the $\text{VO}_2(\text{D})$ instead.^[21] They also discovered that the low solid content produced the nanoaggregation, causing the growth of NPs.

Figure 5.6. XRD patterns of the hydrothermal samples with different filling factors.

The morphology of the hydrothermal samples with different FF is shown in Fig. 5.7. As the FF changes from 0.2 to 0.4, the shape of the NPs remains, while the size decreased significantly from an average of 93.7 nm to 54.7 nm due to the high-pressure hydrothermal environment. The decreased size of the NPs also exhibits the decreased intensity of the XRD peaks (Fig. 5.6b). The size of the NPs, as well as the XRD pattern, is similar to the samples obtained at the hydrothermal temperature of 260 and 290 °C. It speculates that the increased FF may offset the effect of increased hydrothermal temperature. Furthermore, when the FF increased to 0.6, the final product is $\text{VO}_2(\text{D})$. As shown in Fig. 5.7c, the shape of the NPs changes from round to oval, and the size of the NPs doubled to the average size

of 117.6 nm. The change of the morphology also suggests the phase evolution of the obtained VO₂ phase, which is in agreement with the XRD result shown in Fig.5.6.

Figure 5.7. SEM images of the hydrothermal samples with different filling factors with size distribution results attached below.

5.4 Conclusion

In summary, VO₂(M) NPs prepared by one-step hydrothermal synthesis within a short duration and a high temperature is developed. The pure phase VO₂(M) was successfully obtained at the short duration of 12 h at 290 °C or 6 h at 320 °C. The obtained VO₂(M) powder shows uniform morphology with high crystallinity and good dispersion. However, the thermochromic property for the short duration samples is rather inferior, which indicates the optical performance is not only related to the crystallinity and size of the NPs, but also connected to some uncovered factors such as the preferred crystal orientation. Furthermore, the filling factor was studied at the high-temperature hydrothermal synthesis, the low FF value was favored for VO₂(M), while a high FF value results in a larger size of VO₂(D).

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Chapter 6

Self-Assembled VO₂ Mesh Film-Based Resistance Switches with High Transparency and Abrupt ON/OFF Ratio

Vanadium dioxide (VO₂), a well-known phase transition material with abrupt resistance change during its transition temperature, is herein used to fabricate the transparent mesh film onto a glass slide through self-assembly mesh printing. A record high on/off ratio up to 10⁴ is achieved together with high visible transmittance of 86% compared to the normal glass slide with visible transmittance at 88%. The high transparent properties make the resistive switches be for next-generation electronics, such as see-through computing devices and beyond. Simple and scalable mesh printing approach integrated phase change material may provide a promising way to fabricate transparent resistance switches for the next-generation electronics.

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6.1 Introduction

Resistive switching behavior has been reported among conductive organic materials like poly-N-vinylcarbazole,^[1] perovskite oxide like SrTiO₃,^[2] as well as common binary transition metal oxide (TMO), such as ZnO,^[3-4] TiO₂,^[5] Nb₂O₅,^[6] and VO₂.^[3] Among all these materials, organic resistance switches suffer from high operating voltage, while most TMO switches such as ZnO, TiO₂, and Nb₂O₅ are facing the problem of low ON/OFF ratio. Vanadium dioxide (VO₂) is a compound that undergoes a metal-to-insulator transition (MIT) at a temperature of ~68 °C,^[7] which gives high resistance change^[8] and makes it one of the most potential materials for the resistive switching application.^[9] Besides, the near room temperature MIT and abrupt change of infrared transmission make VO₂ a potential candidate for some novel applications, such as thermochromic smart windows,^[10-13] camouflage,^[14] and thermal-actuator.^[15-16]

The resistive switches of VO₂ have been classified into nonvolatile and volatile types. Nonvolatile resistive switches can be integrated into memristors,^[17] while the volatile one can be assembled as selectors in memristors or transistors or can be coupled with capacitors or resistors into oscillators, which shows potential applications in artificial neural networks (ANN) and associative neuromorphic computing.^[18] However, their resistive switching behavior in VO₂ device has not been fully exploited, as up to 10⁴ resistance contrast has been observed across the MIT.⁹ The earlier VO₂ resistance switch was constructed on Si/SiO₂ substrate through chemical vapor deposition (CVD) and the MIT occurred at around 2 V, and the ON/OFF resistance ratio was less than one order of magnitude.^[19] The recent works on VO₂ resistance switches, such as VO₂ electrodeposition on Pt substrate^[20] and VO₂ RF sputtering on SiO_x/Si substrate^[21] or c-sapphire,^[22-23] improved the ON/OFF ratio within a certain degree. However, several challenges still need to be tackled for the next generation of electronic devices, such as high transparency as a component for transparent circuits, high ON/OFF ratio and low operation voltage.^[24] Moreover, most of the current works for VO₂ resistive switches focused on non-volatile random-access memory.^[25] With the development of artificial intelligence and the internet of thing,

volatile threshold switches, which could be applied in artificial neural networks and associative, are also highly in demand.

In this study, an easy-handling and inexpensive method-mesh printing is introduced to fabricate VO₂ film on the most widely used glass substrate,^[26] which gives the largest ON/OFF ratio, high transparency, and low operation voltage in the application of volatile resistive switches compared with the best-reported results.^[27]

6.2 Experimental Methods

Materials. Vanadium dioxide nanoparticles (VO₂, NPs weight-average molecular weight (Mw) = 82.94), purchased from Wenzhou Jingcheng Chemicals and DisperBYK 348 without further purification. Deionized water (18.2 MΩ) was used throughout the experiments.

Fabrication of transparent VO₂ mesh film. The schematic procedures of fabricating the transparent VO₂ self-assembly mesh film onto a glass slide are shown in Scheme 6.1. The glass slide with the thickness of about 1 mm is as-purchased from Sail Brand 7107 Microscope Slides with further ultrasonic cleaning by DI water and ethanol. The screen-printing mesh (Ponger 2000, Israel) was mounted directly above the clean glass slide. By using a 100 μL pipette, a certain amount of VO₂ dispersion was dropped onto the glass slide substrate through the mesh. The VO₂ dispersion was made through 10-min sonication of a certain weight percentage of VO₂ NPs, DI water and surfactant BYK 348. A sonicator (Elmasonic S60H, Elma Ultrasonic) with the ultrasonic frequency of 37 kHz with 550 W power consumption was used. When the NPs dispersion was dropped onto the top of the mesh, upon contact, the liquid immediately wetted the mesh walls and space between the mesh and glass slide, and then, with the evaporation of the DI water, the VO₂ NPs self-assembled towards the edge of the mesh walls due to the caterpillar force. Upon removing the mesh, the VO₂ mesh film was heated at 60 °C for 2 h in vacuum for water evaporation. At last, the final transparent VO₂ mesh film was obtained.

Scheme 6.1 Schematic diagram for the fabrication of self-assembly transparent VO₂ mesh film.

Fabrication of VO₂ resistance switches. As-fabricated transparent VO₂ mesh film on the glass substrate was spin-coated (Headway Research Spin Coater) with a layer of photoresist at the 3000 rpm for 30 s (AZ5214E, photoresist image reversal, MicroChemicals GmbH), and then pre-baked at 105 °C. The alignment was adjusted by microscopy to make sure that VO₂ NPs branches were located between the source and drain. The electrode patterns were subsequently transferred from the photolithography template to the VO₂ mesh film by exposing to UV light for 4 s at $\sim 44 \text{ mW cm}^{-2}$ (SUSS MicroTec, MJB4) and developed for 30 s (AZ Developer: DI H₂O = 1:1, AZ Electronic Materials GmbH). Then, Ti/Au (30/150 nm) films were deposited by electron beam evaporation (Edwards Auto 306). The microelectrodes were finally formed by a lift-off process.

Materials and Device Characterization. Structural analysis of as-purchased and as-fabricated VO₂ NPs and VO₂ mesh film were determined by Shimadzu X-ray diffractometer with Cu K α radiation ($\lambda = 0.1541 \text{ nm}$). The morphology of VO₂ NPs, as well as the SAED (selected area electron diffraction), were characterized using a transmission electron microscope (JEM-2010, JEOL, Japan) with an accelerating voltage of 200 kV. The microstructures of VO₂ mesh film were observed by the optical microscopy and the field emission scanning electron microscope (JEM-7600F, JEOL, Japan). The

element analysis mapping of VO₂ mesh was also characterized by Energy-dispersive X-ray spectroscopy (EDX) attached with JEM-7600F. The visible transmittance of transparent resistance switches and the infrared transmittance for VO₂ (M) confirmation were carried out using Agilent Cary 5000 UV-Vis-NIR spectrometer. A heating stage (PE120, Linkam, UK) was employed to control the temperature of the samples mounted on the spectrophotometer. The performance of the VO₂ mesh resistive switch was conducted under room temperature and atmospheric pressure. The I-V characteristics of the device were measured by Agilent B1500A digital source meter connected with triaxial cables to the probe station.

6.3 Results and Discussions

6.3.1 Transparent VO₂ mesh film fabrication and characterization

Figure 6.1a shows the photograph of the as-fabricated VO₂ mesh film on a glass slide, which displays the high optical transparency of the mesh film. The detailed morphology of the VO₂ mesh film was observed through SEM, as shown in Figure 6.1b. The uniform mesh structure formed by VO₂ NPs can be observed. Figure 6.1c is the visible transmittance spectrum range from 400 to 750 nm. From which, one can see that the continuous and uniform VO₂ mesh film exhibits 86 % of visible transmittance at 550 nm, which is comparable with that of a pure glass slide (around 88 %). The transparent result of the new VO₂ mesh structure is also much higher than our previous mesh work^[26] because the new mesh film fabrication method was used, which caused the narrower of the mesh lines and almost no residual NPs between the mesh lines.

Figure 6.1 Characterization of transparent VO₂ mesh film. a) photography of VO₂ mesh sample within the blue circle. b) SEM image of the VO₂ mesh film; c) Visible transmittance spectrum of VO₂ mesh film and a bare glass slide.

Figure 6.2 demonstrates the SEM results of VO₂ mesh film and the enlarged image of one knot overlapping with corresponding EDX mapping of the vanadium element, which exhibits uniform and continuous distribution of VO₂ NPs within the VO₂ mesh film.

Figure 6.2 EDX mapping result of the distributed vanadium (red) overlapping with the SEM picture of (a) the frame and (b) the specific knot of VO₂ mesh.

Figure 6.3 is the height profile of the VO₂ mesh film structure, measured by ZEISS Smartproof 5 widefield confocal microscope. Based on the results, the height of the mesh lines is around 50-100 nm.

Figure 6.3 Surface profiler characterizations of VO₂ mesh (550 X 550 μm), below with the roughness of indicated line in surface.

Figure 6.4a shows the TEM image of VO₂ NPs as well as the SAED results, which illustrates the polycrystalline characteristic of the VO₂ NPs with the average size of 50 nm. As shown in Figure 6.4b, the XRD result of the as-fabricated transparent VO₂ mesh film is consistent with the starting VO₂ NPs, and both match well with the standard card of VO₂ (PDF card No. 43-1051). This implies that the main functional material of VO₂ remains unchanged during the fabrication process for transparent VO₂ mesh film. In Figure 6.4c, Raman peaks at 191 cm⁻¹ and 223 cm⁻¹ indicate the V-V bond while 619 cm⁻¹ peak matches well with the V-O bond of VO₂ M phase, as well as the less intense peaks at 260, 308, 392 and 509 cm⁻¹ are known to be Raman modes of M phase VO₂.^[28] Infrared transmittance results of the transparent VO₂ mesh film are collected at the wavelength between 1000 and 2500 nm before (20 °C) and after (90 °C) the MIT. Figure 6.4d shows up to a 2% decrease of transmittance at high temperature, which proves the MIT of VO₂ occurs. However, the transmittance difference is smaller than the typical VO₂ film,^[29] which is mainly due to the limited amount of VO₂ NPs and the testing area.

Figure 6.4 (a) TEM and SAED results of VO₂ NPs (b) XRD results of VO₂ NPs and VO₂ mesh c) Raman result of VO₂ mesh film d) Infrared transmittance results of wavelength between 1000 - 2500 nm at 20 °C (blue) and 90 °C (red).

6.3.2 Affecting factors on VO₂ mesh film fabrication

During the fabrication of the transparent VO₂ mesh film, several factors could be tuned to control the continuous and transparency of the mesh film, such as the concentration of VO₂ NPs dispersion and the usage of the surfactant. First, the effect of surfactant is studied. It is found that the usage of a small amount of surfactant could dramatically decrease the surface tension of the VO₂ solution, which will be easier to wet the glass slide through the stainless-steel mesh. As shown in Figure 6.5a, the surface tension data of BYK 348 with a different concentration in DI water are collected. The pure DI water has a surface tension up to 70.74 mN/m, which was decreased to around 22.31, 21.48 and 20.52 mN/m with the concentration of BYK increased from 0.01, 0.05, to 0.5 vol.%, respectively. Similar trends were also observed in different concentration of VO₂ NPs (Figure 6.5b). Due to the similar surface tension results with 0.01 - 0.5 vol. % surfactant, the smallest weight percentage of 0.01 vol.% BYK was selected to mix with VO₂ dispersion to obtain the high-quality VO₂ mesh film. The dispersion with the surfactant amount below 0.01 vol. % has a similar surface tension as DI water. Furthermore, the effect of different concentration of the VO₂ dispersion is studied. To avoid the precipitation of VO₂ NPs, up to the weight percentage of 3 wt.% VO₂ NPs were dispersed into the DI water. Surface tension results of different concentrations of VO₂ solution with and without 0.01% BYK surfactant are also shown in Figure 6.5b.

Figure 6.5 Surface tension vs. (a) surfactant concentration and (b) VO₂ NPs concentration.

Figures 6.6a, b, c shows the corresponding VO₂ mesh films on a glass substrate with different concentrations of VO₂ NPs and the same amount of wetting dispersant (0.01 vol.% BYK). With the lower loading amount of VO₂, large numbers of voids due to lack of NPs can be observed, and the average distances of broken lines are 32.5 (Figure 6.6a) and 15.1 μm (Figure 6.6b) approximately. With the increment of VO₂ loading, such voids diminished as shown in Figure 6.6c, d. It is illustrated that enough NPs need to be provided to form a complete mesh film. On the other hand, at the same concentration of VO₂ NPs (3 wt.%), certain defects of blank and extra lines can always be observed in the mesh structure around the knot without using surfactant (Figure 6.6d), which is due to the relatively higher surface tension of the solution. Therefore, 3 wt.% VO₂ concentration with 0.01 vol.% BYK surfactant gives the most uniform and continuous VO₂ mesh film. (Figure 6.6c).

Figure 6.6 Optical microscope images for VO₂ mesh with different mixture percentage, inset with enlarged mesh structure (a) 1 wt. % VO₂, 0.01 vol. % BYK; (b) 2 wt. % VO₂, 0.01 vol. % BYK; (c) 3 wt. % VO₂, 0.01 vol. % BYK; (d) 3 wt. % VO₂, no BYK.

6.3.3 Performance of Transparent VO₂ mesh resistance switches

Figure 6.7a shows the schematic of the transparent VO₂ mesh resistance switch (fabrication details are shown in Section 6.2). The Au/Ti electrodes are aligned with the VO₂ mesh line for the resistance switching (RS) measurement. For comparison, the Au/Ti electrode deposited on a bare glass substrate with the same pattern is shown in Figure 6.7b.

Figure 6.7 Characterization of VO₂ mesh resistance switch. Optical images of Au/Ti electrode deposited on the (a) VO₂ mesh, (b) bare glass substrate.

To study the RS behavior of the VO₂ mesh resistance switch, we tested the I-V curves under the voltage sweeping mode, as shown in Figure 6.8a. The device with an initial high resistance state (HRS) changes to a low resistance state (LRS) when applying the voltage at the threshold voltage (V_{th}). This model correlated the coupling effect mechanism of electrical and joule heating when applying voltage on the two-terminal RS device. It is worth noting that the V_{th} for this VO₂ mesh RS is around 1.5 V, which is lower than the previously reported value of around 6 V at room temperature.^[30]

Figure 6.8 I-V characteristic of the VO₂ mesh resistive switch and bare glass slide.

The switching time for VO₂ mesh switches is less than 50 μ s (Figure 6.9) due to the machine testing limitation, which is much less than some reported VO₂ optical switches (around micrometers range).^[8,31] However, none of the reported VO₂ switches are transparent.

Figure 6.9 Current vs Time curve of VO₂ mesh switches during the I-V characterization.

As illustrated in Figure 6.10, a durability test up to 50 cycles was applied onto the VO₂ mesh RS. Within the testing period, the ratio of high and low resistance state roughly maintained around 10^4 .

Figure 6.10 the retention result of the VO₂ resistive switch.

However, the switching ratio for VO₂ mesh switches starts to drop after about 40 cycles and the XRD examination (Figure 6.11) shows that the peak intensity of VO₂ is diminished after 50 cycles. This could be due to the long-standing durability issue of the VO₂ which is currently involving intensive research and is out of the scope of this current research.^[32-33] More future work could be conducted by the encapsulation of this RS to solve this issue.

Figure 6.11 XRD comparison data of VO₂ mesh switches before and after 50 cycles.

The visible transmission spectrum was measured through switching ON threshold voltage, which showed that the VO₂ resistance switches remain high transparent during the switching process as shown in Figure 6.12.

Figure 6.12 Visible transmission of the transparent VO₂ mesh resistance switches with voltage from 0-5 V applied.

As mentioned in the introduction, RS can be divided into two modes, nonvolatile memory switching, and volatile threshold switching.^[34-35] Here, the I-V characteristics clearly demonstrate that the RS behavior is independent of the voltage polarity and there is only one stable resistance state at zero voltage, which is corresponding to a typical unipolar volatile threshold switching characteristic. The ON/OFF ratio for HRS and LRS in the transparent VO₂ resistance is more than 10^4 , which is the highest result among the transparent resistance switching devices in recent years, as summarized in Figure 6.13. Resistance switches made from functional materials include ZnO,^[36] ZnSrO₃,^[37-38] SrTiO₃^[39] could exhibit around 80-90 % visible transmission. However, the ON/OFF ratio of those resistance switches is no more than 100. For the volatile threshold resistive switches applying in selectors, artificial neuron networks, and associative computing, a higher ON/OFF ratio is required. VO₂ resistive change could reach 10^4 due to its own intrinsic phase transition property. Above all, VO₂ mesh shows high potential for the transparent resistive switching application, for its high ON/OFF ratio and low-cost fabrication.

Figure 6.13 Comparison between the result of our work and recently reported resistance switches based on PVP,^[40] ZnSnO₃,^[37-38] WO_x,^[41] SnO₂/ZnO,^[36] SrTiO₃,^[39] TiO₂,^[42] BTCO,^[43] and Fe: SnO₂.^[27]

6.4 Conclusions

In this work, a simple and low-cost method to fabricate the transparent VO₂ resistance switch was reported. VO₂ NPs with an average diameter of less than 100 nm were screen printed onto a common glass slide by stainless steel mesh to fabricate the transparent resistance switch device through photolithography and e-beam evaporation process. A volatile resistance switch behavior, as well as the highest ON/OFF ratio up to 10000 with low operation voltage, was achieved in VO₂ mesh film on the normal glass slide with high visible transmission of around 86 %. The facile fabrication method and novel micro-patterned structures of transparent mesh VO₂ resistance switching devices give a new promising direction for the next-generation electronic devices.

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Chapter 7

Conclusions and Recommendations

In this thesis, the objective is to develop cost-effectively, facile one-step hydrothermal of pure phase monoclinic VO₂ nanomaterials with high crystallinity. The prepared samples can be further exploited in various applications such as optical and electrical devices. The approaches, including modifying the amount of the reduction reagent, the hydrothermal duration, the precursor concentration, as well as the concentration of the doping element, have been carefully studied. Further approaches such as hydrothermal temperature and filling factor were implemented based on the changes of the liner in the hydrothermal synthesis. The pure phase with high crystallinity VO₂ was successfully synthesized. The prepared VO₂ samples were fabricated into the thermochromic coating films as well as the electrical switching device. The comparable solar modulation performance was characterized, and an abrupt resistance change was observed during the switching device testing. It proves the potential of VO₂ in optical and electrical applications with high crystallinity.

7.1 Conclusions

7.1.1 Conclusions of one-step hydrothermal of VO₂ and its application in thermochromic coatings

The stimuli of the VO₂(M) phase change and the applications have attracted numerous researches and discussions. ^[1] To synthesize high crystallinity VO₂ nanoparticles (NPs) is the key segment for further development in the applications. Hydrothermal synthesis has been a long-time competitor for controlling the size, morphology, and phases of the VO₂ NPs compared with high-cost physical methods such as sputtering ^[2] and ALD and multi-steps chemical techniques like sol-gel, ^[3] electrochemical. ^[4] However, the synthesis of single-phase VO₂(M) NPs with uniform morphology has always been a challenge in the ongoing study. ^[5]

In the first result chapter, without the assistant of the doping and seed, the single-phase VO₂(M) NPs have been successfully obtained with hydrothermal duration at 24 h with the hydrothermal temperature set at 260 °C. The hydrothermal parameters, including the amount of the reducing reagent, hydrothermal duration, and precursor concentration, were carefully studied to obtain the uniform pure VO₂(M) with high crystallinity.

The amount of the reduction adjusted, starting from 30 µl and gradually up to 90 µl. At 30 µl volume, the obtained sample is the V₂O₅ nanowires. The sample phase is the same as the raw material, but the shape evolved from the sheet structure of the V₂O₅·H₂O₂ precursor. Because the aim product is V (+4), the amount continues to rise to 50 µl, the V₂O₅ reduced to V₆O₁₃ according to the XRD pattern, and the morphology is the microbelt structure. The V₆O₁₃ microbelts are formed due to the aggregation of the V₂O₅ nanowires, with the valence value of the V element decrease from V(+5). At the edge of the microbelts, the small amounts of NPs could be observed. With the N₂H₄·H₂O₂ slightly increased to 60 µl, the single-phase VO₂(M) NPs with uniform morphology are obtained. Based on such phase transformation, a hydrothermal synthesis mechanism could be speculated. With the high temperature and pressure, the sheet structure of the precursor turns into nanowires at the initial stage. The reduction process begins with an increased amount of N₂H₄·H₂O. The

nanowires grow together into the microwires via an oriented attachment mechanism, and then the NPs gradually appear at the edge of the microbelts and further detached from the main part. In addition, when the reducing agent was further raised to 70 μl , the phase of the obtained sample is still $\text{VO}_2(\text{M})$ with much lower crystallinity but larger particle size. When the $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ amount was at 80 and 90 μl , the reducing process continues, as the final product is V_6O_{11} and V_3O_5 separately, but the size of the obtained samples became bigger and bigger consistently from around 100 nm in an average size to the above 500 nm due to the excessive amount of the reducing agent. Thus, the amount for the $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ is fixed at 60 μl in further synthesis.

Next, the hydrothermal duration is studied from 12 h to 168 h. The 168 h, which is 7 days, is the longest duration of all the reported $\text{VO}_2(\text{M})$ hydrothermal synthesis. At the 12 h duration, a large amount of the hollow half-sphere shape NPs is observed, with the XRD pattern has a relatively low intensity. It suggests that the $\text{VO}_2(\text{M})$ NPs are not fully developed; hence the duration needs to be increased. When the duration is at 72 h and 168 h, the NPs size continues to grow larger from 60 nm at 24 h to nearly 90 nm at 168 h. Based on the DSC results, the crystallinity does improve as the latent heat is larger. However, the thermochromic results suggest another way. When the size of NPs is larger than 60 nm, the blueshift of the $\text{VO}_2(\text{R})$ transmittance curve emerges. It considerably deteriorates the solar modulation of the thermochromic performance; therefore, the standard hydrothermal duration is chosen at 24 h in the following synthesis.

Furthermore, the precursor concentration is the third parameter discussed in the thesis. To adjust the precursor concentration, the volume of the solvent, including H_2O_2 and DI water, was kept unchanged, while the amount of the raw material of V_2O_5 powder was tuning from 1 mmol up to 2 mmol accordingly. From the XRD results, from the 1 mmol to 1.5 mmol V_2O_5 amount, the valence value of V of the obtained sample was maintained at +4, with the phase transited gradually from $\text{VO}_2(\text{M})$ to $\text{VO}_2(\text{B})$ with an unknown intermediate phase under the same reducing agent amount. However, when the precursor amount increased to 2 mmol, the final product exhibits the V_6O_{13} with a small amount of the $\text{VO}_2(\text{M})$. It suggests that the reducing agent has a far more impact during the hydrothermal

process. The morphology changed from VO₂ NPs to ultralong nanowires and eventually to the microbelt, similar to the result with 50 μ l N₂H₄·H₂O.

As the results in the first result chapter, the single-phase VO₂(M) can be achieved with uniform morphology under the appropriate reduction amount and the precursor concentration. Although the crystallinity of obtained VO₂(M) with longer duration is drastically promoted, the size of the NPs is increased hugely as well, which in the end compromises the thermochromic performance. Therefore, in the second result chapter, the short duration 6 h and 12 h was applied throughout the hydrothermal study to investigate the suitable hydrothermal temperature that could deliver the VO₂(M). However, in the typical hydrothermal synthesis, the liner is generally made of polytetrafluoroethylene (PTFE), of which the melting temperature is around 327 °C, so the hydrothermal temperature is typically set below 300 °C, which also caused the longer duration for the synthesis of VO₂(M). To increase the hydrothermal temperature beyond 300 °C, the liner was changed to quartz liner, which has a melting temperature up to 1670 °C that provides the possibility for the high-temperature hydrothermal synthesis of VO₂(M). Thus, in the following hydrothermal synthesis, the temperature can be set above 300 °C.

The hydrothermal temperature was set from 260 °C according to the hydrothermal results up to 350 °C with an interval of 30 °C. The hydrothermal duration was kept within 6 h and 12 h. Based on the XRD results, when the hydrothermal temperature is below 300 °C, the VO₂(M) is not formed at 6 h duration. Until the duration increased to 12 h with 290 °C, the (011) characteristic peak of VO₂(M) has shown, but the intensity is relatively low. However, the particle size already grows to nearly 80 nm, larger than the 24 h in the 260 °C of which the average size is around 60 nm. When the hydrothermal temperature increased above 300 °C, the single-phase VO₂(M) with high peak intensity was obtained at 6 h duration. However, the particle size is nearly 100 nm, larger than the 72 h and 168 h samples. With the temperature further increased to 350 °C, the size of the NPs slightly decreased. With the duration increased from 6 h to 12 h at the same hydrothermal temperature, the NPs size is also slightly decreased. According to the size distribution results, the abnormal phenomenon is primarily due to the more uniform size distribution at

a higher temperature and longer duration when the temperature is beyond 300 °C, as the standard deviation (SD) decreased. Based on the SEM results of the hydrothermal samples from 260 to 350 °C, the NPs growth process can be divided into two parts. The first stage is before the formation of VO₂(M). The particle size grows apparently from 55.1 nm to above 90 nm within the hydrothermal duration at 6 h, and 12 h with the temperature increased from 260 to 320 °C. While the second phase is from 320 to 350 °C, as the VO₂(M) already formed, however, the longer duration and higher temperature, the size of the obtained NPs gets slightly smaller while still above 90 nm.

Further DSC study was performed on the VO₂(M) samples to reveal the relationship among crystallinity, hydrothermal temperature, and duration. As the VO₂(M) is not formed until the hydrothermal is raised to 290 °C, the data is not applicable at 260 °C. At 290 °C, the value of ΔH is relatively small, which is corresponding to the weak (011) peak. As the VO₂(M) formed at 320 and 350 °C, the value of ΔH increased to 31.6 J/g and 38.4 J/g for the 6 h and 12 h duration hydrothermal at 320 °C, while to 20.2 J/g and 25.6 J/g at 350 °C. Thus, the highest crystallinity is obtained at 320 °C and 12 h duration, which is corresponding to the highest peak ratio between (110) and (011) peak of VO₂(M). However, the ΔH is lower than the 260 °C sample with a longer duration, as 168 h sample exhibits ΔH is at 49.4 J/g. Thus, with the larger NPs size up to around 90 – 100 nm and relatively low enthalpy, the thermochromic performance is expected to be inferior. The solar modulation based on the calculations of the transmittance spectra gives the minus value. The result is rather impaired. Besides the larger particle size and slightly lower enthalpy, the inferior thermochromic performance could be the faceted growth based on the abnormal high intensity of the 26.8° peak. However, the link between the faceted growth as well as the solar modulation is still unclear. Further supplementary calculations work needs to be done in the future.

Apart from the increment of the hydrothermal temperature, another main factor that was changed in the high-temperature hydrothermal study is the liner: the liner material changed from PTFE to quartz; the volume of the liner. Thus, the filling factor (FF) study is crucial as the ratio of the precursor volume to the liner volume. Since the liner volume is

unchangeable, to adjust FF is to modify the volume of the precursor. As to keep the other parameter fixed, the volume of the precursor is adjusted by the additional amount of the DI water. The FF value was chosen from 0.2 in the high-temperature hydrothermal, up to 0.6, to keep the pressure within the safer range. The hydrothermal temperature is set at 320 °C and 12 h duration, as the highest crystallinity is obtained at this condition. The above hydrothermal synthesis FF value is set as 0.2. When FF increased to 0.4, the XRD pattern exhibits peaks in the low intensity, and size decreased significantly from an average of 93.7 nm to 54.7 nm due to the high-pressure hydrothermal environment. With the FF value further raised to 0.6, the mixture of VO₂ (M) and VO₂ (D) was synthesized with low peak intensity for both phases. The shape of the obtained VO₂(D) is oval, with the average size doubled to 117.6 nm.

7.1.2 Fabrication of VO₂ mesh structure and its application in resistance switches

Besides the application in the smart window coatings based on the optical transmittance change between monoclinic and rutile phase, VO₂(M) NPs exhibit high resistance change up to the 10⁵ from room temperature semiconducting phase to the high-temperature metallic phase across the phase transition. As discussed in the literature review chapter, this exceptional property gives VO₂(M) the potential for kinds of electronic devices, including two/three-terminal switch, oscillator, memristor, and electro-optical/thermal devices. Thus, VO₂(M) NPs were developed into the transparent resistance switches in the third result chapter. Besides, next-generation electronics are emerging to be transparent, transient, and flexible. The high transparent electronic component is inevitable for the transparent circuits and further complex device fabrication.

In the fabrication of the transparent resistance switch, the self-assembly mesh-printing method and the caterpillar force in the “coffee ring effect” via solvent evaporation were applied. The obtained continuous and uniform VO₂ mesh film exhibits 86% of visible transmittance at 550 nm wavelength, as compared with the 88% transmittance of the pure glass slide. However, in the infrared wavelength, the transmittance difference is only up to 2% in the 1000 nm to 2500 nm range. The exhibited thermochromic property is much

smaller than the typical VO₂ (M) films with transparent transmittance normally below 50%, due to the very limited amount of the VO₂(M) NPs within the test area.

In addition, the factors that affect the VO₂(M) mesh film fabrication were carefully studied, including surfactant concentration and VO₂(M) NP concentration. The relationship between surfactant concentration versus surface tension was studied first, as the surface tension affects the moving speed of NPs during the solvent evaporation. The surface tension was dropped drastically from 70.7 mN/m to 22.3 mN/m with the surfactant concentration increased to 0.01 vol % from 0, but with the concentration further increased to 0.05 and 0.5 vol %, the value slightly decreased to 21.5 and 20.5 mN/m. Thus, to maintain a higher percentage of the VO₂(M) NPs and lower surface tension, the 0.01 vol % surfactant concentration was chosen. Secondly, the VO₂(M) concentration was adjusted from 1 wt.% to 3 wt.%. With the lower loading amount of VO₂, large numbers of voids due to lack of NPs can be observed, and the averaged distance of broken lines are 32.5 and 15.1 μ m at 1 wt.% and 2 wt. % separately. As the VO₂(M) concentration raised to 3 wt %, the continuous VO₂(M) mesh structure was formed.

Once the continuous VO₂ mesh film was obtained, the next procedure is to fabricate the transparent resistance switches. The aligned Au/Ti electrodes are deposited onto VO₂ mesh lines. The detailed fabrication process is in chapter 6. The resistance switching (RS) behavior is studied under voltage sweeping mode. The threshold voltage for the device changing from a high resistance state to a low resistance state is around 1.5 V at room temperature, which is lower than the reported VO₂ resistance switches. In addition, at the durability test of the VO₂ mesh switches, the switching ratio starts to drop after about 40 cycles. According to the XRD data of the VO₂ mesh film before and after the durability test, the peak intensity starts to decrease. This is due to the long-standing durability issue of the VO₂, which has currently drawn intensive work and still needs to be tackled. However, although the durability problem, based on the high transparency result and high ON/OFF ratio based on the VO₂ phase change as well as the low-cost self-assembly method, the fabricated transparent VO₂ mesh shows high potential for the transparent resistance switching applications.

7.2 Recommendations

7.2.1 Improvements on the VO₂ smart window application

7.2.1.1 Enhance thermochromic performance

As discussed in Chapters 4 and 5, the thermochromic performance of the prepared VO₂ smart window coating is in general assessed by two primary data, ΔT_{sol} and T_{lum} . Based on the different duration hydrothermal samples in chapter 4, the larger of the obtained VO₂ NPs will exhibit the blueshift of the crosspoint of the transmittance spectra and decrease ΔT_{sol} . Thus, the main object of the VO₂ NPs synthesis is to obtain a smaller particle size but high crystallinity. However, it is still a challenging objective, as the high hydrothermal temperature or high annealing temperature required to synthesize the VO₂ NPs. Moreover, based on the calculations study, for the VO₂-based films, the limitation of the T_{lum} is around 40%, while the modulation ability is no more than 10%.^[6] Thus, it is crucial to fabricate VO₂ composite or multilayers to promote thermochromic performance. In the preparation of the VO₂ coatings in this thesis, the prepared Si-Al gel was added to reduce the scattering of the VO₂ NPs. In addition, more possible materials are being investigated to improve thermochromic performance and, furthermore, convert the VO₂ smart windows into multifunctional devices.

7.2.1.2 Improve the stability of the VO₂

As discussed in the literature review, VO_x has multiphases and valence combinations, including, Wadsley (V_nO_{2n+1}) and Magneli (V₂O_{2n-1}) phases. The monoclinic phase prepared by the hydrothermal synthesis in this thesis is not the most stable phase, as the V(+4) can be easily oxidized to V(+5) or the hydroxides, especially when the environmental humidity is high. The stability of the VO₂ has been a long-standing problem in practical applications.

In order to separate the VO₂ NPs from the oxygen and moisture, one possible solution has been proposed to coat the VO₂ NPs with the extra layer, forming the “core-shell” structure, as shown in Fig. 7.1a. The possible materials for the “shell” structure, including SiO₂, ZnO have been studied, while the VO₂ NPs sit in the “core” position to be protected from deterioration.^[7] However, due to the different lattice structures of the VO₂(M) and VO₂(R), the volume change of the NPs cannot be neglected, which will cause the fracture of the shell structure to some extent, and this may weaken the separation purpose from the shell. Fig. 7.1b exhibits the VO₂ film is protected by the extra upper layer as the “shell.” To maintain the transmittance of the VO₂ film, the protective layer needs to high transparency and maintain stability in the oxygen and humidity environment. The possible materials, including Al₂O₃ and SiN_x, have been coated onto the VO₂ film.

Figure 7.1 (a) Schematic diagram of the core-shell structure to improve the stability (b) Extra upper protective layer for the separation of the VO₂ film. Reproduced with permission from the Royal Society of Chemistry.^[7]

7.2.2 Flexible VO₂ electronic devices

In chapter 6, the transparent resistance switches were fabricated based on the VO₂ mesh structure as the next generation electronics component. Besides the transparent property, the flexible and transient are the other emerging requirements for next-generation electronics. Thus, to fabricate the flexible VO₂ electronic devices is going to be the upcoming demand. The VO₂ thin film (TF) and VO₂ nanobeams (NBs) based flexible

devices have been studied in recent years, such as the flexible actuators composed of VO₂ and carbon nanotube (CNT) films, [8] and VO₂ NB based flexible strain sensors. [9]

However, to fabricate the flexible devices based on the VO₂ NPs is tough work. The room temperature phase of VO₂ is semiconducting and unstable in the oxygen and humidity environment. At the same time, the current NP-based flexible devices are fabricated by the metal NPs such as Au, Pt, and Pd, or metal alloys with diameters from 10 to 100 nm with high conductivity. [10] However, the hydrothermal prepared VO₂ NPs are generally within the range of 30-100 nm and transit the metallic phase above the critical temperature with a high conductivity change. VO₂ NPs have a high potential for flexible devices, especially for the sensors. Fig. 7.2 exhibits the three typical categories that the flexible strain made of NPs. The first approach is to sense the deformation by measuring the conductivity change via the distance among particles or the surface coverage change. The second is to alter the sensitivity of the sensors by deformation via the resistance changes. And the last one is the stable sensitivity performance with deformation.

Figure 7.2 Different types of NP-based flexible sensors. (a) NP-based strain gauge for sensing deformation via the change of NPs distance. (b) NP-based strain gauge via the tuning of the surface coverage. (c) NP-based flexible sensors for ambient conditions such as temperature or relative humidity (RH) (d) different sensitivity was achieved by the different load applied. (e) Flexible

sensor not affected by the deformation. (f) high durability of the NP-based flexible sensor with continuous deformation. Reproduced with permission, ^[10] American Chemistry Society.

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