



NANYANG
TECHNOLOGICAL
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**NANOSTRUCTURED VANADIUM DIOXIDE WITH METAL TO
INSULATOR TRANSITION: PREPARATION AND
THERMOCHROMIC PROPERTIES**

WANG NING

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

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

2016

Statement of Originality

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

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Abstract

Vanadium dioxide (VO_2) is an interesting phase transition material, and has promising potential applications in smart window/sensors, field-emission transistor and memory devices. However, the application of this material in thermochromic smart windows is facing several critical limitations, namely the low visible transmission ($T_{\text{lum}} < 50\%$) and low solar modulating ability ($\Delta T_{\text{sol}} < 10\%$) as well as the relatively high phase transition temperature ($\tau_c \approx 68^\circ\text{C}$).

To address these few issues, three approaches including, doped thin films, biomimetic nanostructuring and nanobeam structures have been investigated. The rare earth (Eu^{3+} , La^{3+} , Tb^{3+}) doping could enhance both T_{lum} and ΔT_{sol} , and can reduce the τ_c to below 50°C at low doping levels but increase the τ_c at high doping levels, owing to the competition between the strain and the hole carriers. To further reduce τ_c , Mg/W-codoping in the VO_2 lattice could help to get the τ_c as low as 35°C and increase the T_{lum} as high as 81.3%. The counteraction between the electron and hole carriers results in a slight increase of τ_c along with the codoping.

Moth-eye mimic VO_2 surface for the first time have been fabricated via top-down and bottom-up methods. Due to the antireflection effect of such structure with gradient refractive index along the height, it could increase T_{lum} , and meanwhile the ΔT_{sol} can be simultaneously enhanced due to the higher surface area of VO_2 to provide solar modulation.

The pristine and doped VO_2 nanostructures could be synthesized under normal hydrothermal approaches, and it is of great interests that VO_2 nanobeams exhibit the dual surface plasmon resonance (SPR), which was firstly reported and such beam structure is also promising for electronic device.

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Figure 5.15 Recorded %T spectra in the wavelength range of 250 to 2500 nm at 20 and 90°C (a) and the %T hysteresis loop at 2500 nm at a temperature range of 20 to 100 °C (b) for the VO₂(M) thin films grown on fused silica substrates under different annealing temperatures from 550 to 750 °C.

Figure 5.16 Recorded %T spectra in the wavelength range 250 to 2500 nm at 20 and 90 °C(a) and the %T hysteresis loop at 2500 nm at the temperature range 20 to 100 °C(b) for the VO₂(M) thin film grown on soda glass with ITO buffer layer with the annealing temperature 550 °C. The inset in a) is the corresponding FESEM image, and the inset in b) is the first-order derivate of the %T.

Figure 6.1 (a) XRD patterns of the hydrothermal products under different amounts of N₂H₄·H₂O addition. (b) Corresponding FESEM images for the hydrothermal products. The N₂H₄·H₂O content is: b, 25 µL; c, 30 µL; d, 35 µL; e, 50 µL; f, 100 µL. In (b) and (c), the phase for nanowires is V₆O₁₃, and the phase for nanobeams is VO₂. The scale bar in b-f is 500 nm in length.

Figure 6.2 FESEM images for the W-doped VO₂ products under the doping level 1 at.% (a) and 1.5 at.% (b).

Figure 6.3 a) Bright-field TEM image of a layered V₂O₅-H₂O₂ precursor, with SAED and XRD patterns inset. b) Bright-field TEM image of a V₆O₁₃ tube and wires, with SAED patterns inset. c) Schematic diagram describing the formation of vanadium oxide nanostructures by a rolling mechanism.

Figure 6.4 FESEM images for the top view (a) and side view (b) of the V_2O_5 - H_2O_2 precursor film with layered structure.

Figure 6.5 High resolution XPS scan of (a) O1s and V2p and (b) V3p and W4f. (c) DSC curve for the 2.45 at.% W doped VO_2 nanobeams. (d) EDX spectrum recorded from a W-doped VO_2 (R) nanobeam.

Figure 6.6 DSC curves of the 1 at.% W doped (a) and 1.5 at.% W doped VO_2 products.

Figure 6.7 (a) SAED pattern recorded for a selected W-doped VO_2 nanobeam. The black and red indices correspond to the VO_2 (R) and VO_2 (M) phases, respectively. (b) BF-TEM and (c-d) DF-TEM images for the corresponding W-doped VO_2 nanobeam in (a). The DF-TEM images are recorded along [001] (c) and [010] (d) directions. The outer contour of the DF (001) TEM image is reproduced using dashed lines in (d). The dash circles in (a) indicate the positions of the objective aperture used to record images (c-d). The scale bars for the DF-TEM images are given in (b).

Figure 6.8 (a) Low magnification HAADF STEM image for a selected W-doped VO_2 nanobeam. (b) High resolution HAADF STEM image of a selected area on the edge of the nanobeam. Black arrows indicate atomic columns with higher contrast. (c-e) Simultaneously recorded HAADF STEM image (c) and EDX mapping of V (d), W (e) and O (f) across the nanobeam.

Figure 6.9 (a) UV-Vis-NIR %T spectra recorded in the temperature range 10 to 40 °C. (b) Base line subtracted SPR valleys of the %T spectra at 20 °C (blue line) with Gauss fitting (black and red lines). (c) %T contrast ($\%T_{\tau=10^\circ\text{C}} - \%T_{\tau>10^\circ\text{C}}$) at 2500 nm at different temperatures. (d) Temperature-dependent %T hysteresis loop recorded at a fixed wavelength of 2500 nm. The solid line represents the best least-square fitting result.

Figure 6.10 Doping level dependent %T spectra of VO_2 products at the temperature $>\tau_c$

and their SPR valleys.

Figure 6.11 (a) Temperature dependent thermochromic properties (T_{lum} , ΔT_{sol}) and (b) IR modulating ability (ΔT_{IR}) for a thin film deposited on a glass substrate with 2 at.% W-doped VO₂ nanobeams at the temperature from 13 to 40 °C. $\Delta T_{\text{sol/IR}}$ was calculated as $\Delta T_{\text{sol/IR}}(T) = T_{\text{sol/IR}}(10\text{ °C}) - T_{\text{sol/IR}}(T)$.

Figure 6.12 (a) FESEM image of the W-doped VO₂ nanoparticles after adding additional 30 µL NH₃·H₂O (30 wt.%) in the precursor. (b) UV-Vis-NIR %T spectra for the 200/70 nm-thick VO₂ thin film fabricated with the products in (a). The calculated T_{lum} and ΔT_{sol} are 31.2%, 6.4% for 200 nm-thick sample and 53.4%, 1.7% for 70 nm-thick sample.

Figure 6.13 (a) Resistance hysteresis loop of the film composed of W-doped VO₂ nanobeams. (b) Temperature-dependent I/V curve measured at a gate voltage of 2 V. (c) Temperature-dependent I/V_G curve measured at a drain voltage of 1 V. (d) Temperature-dependent drain current measured at a gate voltage of 2 V and a drain voltage of 1 V.

Figure 6.14 Side-view FESEM image for the FET device.

Figure A.1 Unit crystal structure for the VO₂ (M) (a) and the VO₂(R) (b).

Abbreviations

ATR	Attenuated Total Reflectance
BEI	Backscatter Electron Images
BSE	Backscattered Electron
BVS	Bond Valence Sum
EDS	Energy Dispersive X-ray Spectroscopy
UV-Vis-NIR	Ultraviolet-Visible- Near Infrared
HRTEM	High Resolution Transmission Electron Microscopy
PXRD	Powder X-ray Diffraction
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SEI	Secondary Electron Images
TEM	Transmission Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
HAADF	High-Angle Annular Dark Field
XRD	X-ray Diffraction
Z	Atomic Number

Chapter 1

Introduction

A hypothesis based on the basic background and the challenges for practical application of VO_2 , including the doping with cations, patterning of VO_2 on substrate as well as the hydrothermal synthesis of free standing VO_2 nanobeams was proposed to improve the thermochromic performance for VO_2 nanomaterials. The objective of this thesis will be investigating the doping mechanisms, top-down and bottom-up fabricating the patterned VO_2 thin films and synthesizing free standing VO_2 nanobeams. The scope will include the investigation on rare earth- and Mg/W-codoped VO_2 thin films, the fabrication of patterned VO_2 thin films with top-down etching and bottom-up annealing approaches and the systematically assembly of free standing VO_2 nanostructures. At last, the dissertation of the thesis will be overviewed and the major findings/outcomes will also be illustrated.

1.1 Hypothesis

Vanadium dioxide (VO_2) is an interesting correlated-electron material,^[1, 2] exhibiting a metal-insulator transition (MIT) with a sharp change in resistivity of several orders of magnitude that can be induced thermally at $\sim 68^\circ\text{C}$,^[3] or electrically^[4]/optically^[5]. During the MIT, it also undergoes a crystal structure transition from insulating M1 state (monoclinic $P2_1/c$) to metallic R state (rutile, $P4_2/mnm$).^[6, 7] As shown in Figure 1.1,^[8] for the $\text{VO}_2(\text{M})$, the V-V pairs show zigzag chains along the c -axis with two different V-V distances (0.262 and 0.316 nm) in the dimers, where $d_{\text{V-V}}=0.316\text{ nm}$ has surpassed the critical V-V interaction distance of 0.294 nm, giving rise to the localization of d -orbital electrons within the dimers, thus resulting in the insulating behavior with large resistivity in the order of $0.1\ \Omega\ \text{m}$.^[9] In contrast, for the $\text{VO}_2(\text{R})$, the V-V pairs exhibit uniform linear chains along the c -axis with single V-V distance of 0.288 nm within the pair, below the critical value of 0.294 nm, leading to the sharing of d -orbital electrons in the V-V chains, and giving rise to the metallic behavior with low resistivity in the order of $10^{-6}\ \Omega\ \text{m}$.^[10]

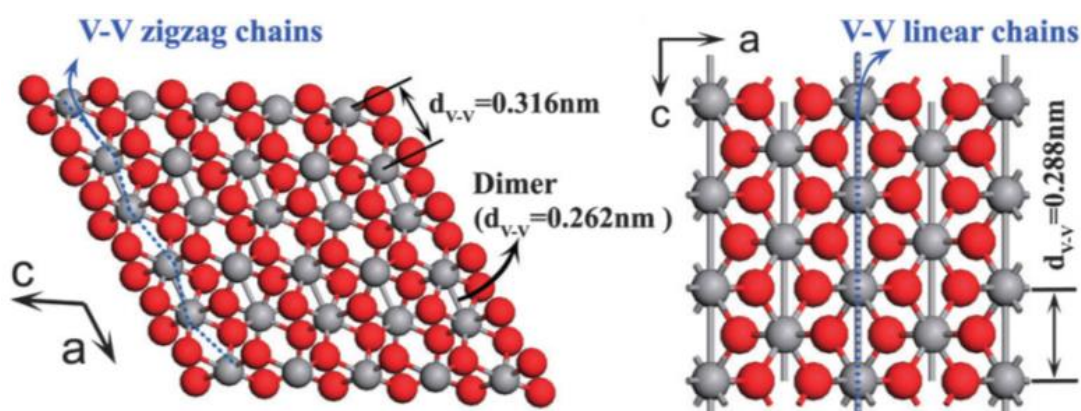
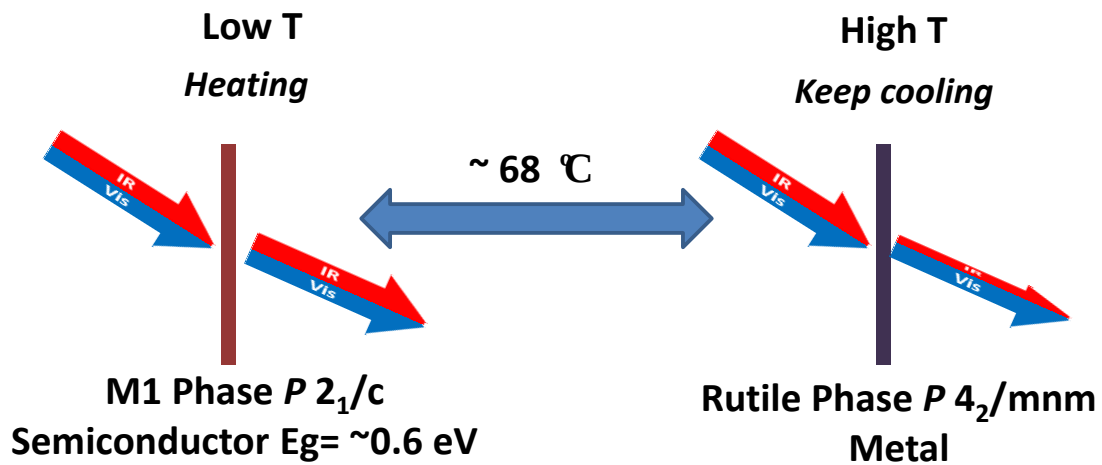


Figure 1.1 Atomic crystal structure of VO_2 : (a) View of the zigzag-type vanadium atom chains projected along the b -axis of the monoclinic cell for $\text{VO}_2(\text{M})$; (b) View of the infinite linear V-V chains projected along b -axis of the rutile cell for $\text{VO}_2(\text{R})$. Reprinted with permission from C. Wu et al., *Chem. Soc. Rev.* 42, 5157 (2013). Copyright 2013, RSC.

With respect to the optical properties, during the MIT, the VO_2 materials exhibit an obvious transmittance contrast in the IR region, i.e. the monoclinic state shows high transmission, while the rutile metallic state shows low transmission due to strong reflection and absorption. The IR modulation ability makes VO_2 a promising candidate for thermochromic smart window applications, which may keep the indoor temperature comfortable by transmitting/reflecting the IR light in winter/summer (Scheme 1.1).



Scheme 1.1 Schematic description of the solar modulating abilities of VO_2 materials, where the indoor temperature is kept comfortable by transmitting/reflecting the IR light at low T/High T.

However, the application of VO_2 in smart window still faces several challenges, e.g. a) the phase transition temperature (τ_c) is still far away from room temperature; b) the visible transmittance (T_{lum}) is still too low ($\sim 30\text{-}40\%$); c) the solar modulating ability (ΔT_{sol}) is still lack of efficiency ($\sim 2\text{-}8\%$); d) easy to be oxidized or etched in the air after a long term usage.

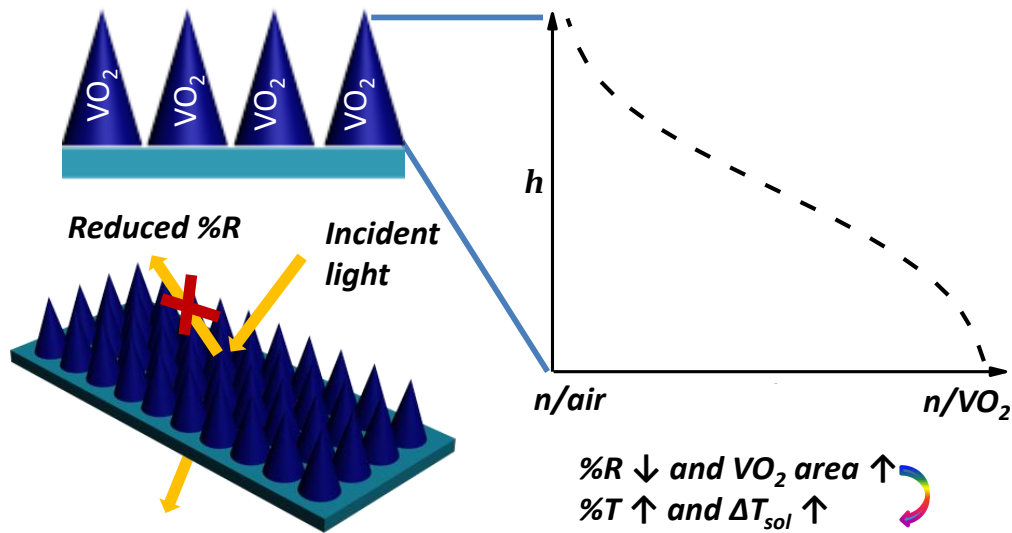
Patterning of VO_2 on the substrates is an effective way to tune the thermochromic properties. As is well known in the nature, the moth eye or cicada wing exhibits intriguing physical properties, such as the wide-angle & broadband antireflection, polarization insensitivity and the super-hydrophobicity. These amazing functions have been proved to be related with the densely packed, tapered cones morphology on the

surface, which has inspired scientists to fabricate biomimetic functional patterns on the material surfaces for particular applications.

For the moth eye structure, the surface consists of a hexagonal pattern of bumps, each roughly 200 nm high and spaced on 300 nm centers. The sub-wavelength nanostructures provide a continuous refractive index gradient between the air and the medium, decreasing the reflections effectively by reducing the refractive index gap on the air-medium interface. The refractive index gradient follows a specific fifth-order-polynomial dependence on depth:

$$n = n_s - (n_s - 1)(10u^3 - 15u^4 + 6u^5) \quad (1.1)$$

where $0 \leq u \leq 1$, representing the normalized optical thickness (0, on the medium surface; 1 in the air); n_s is the refractive index of the medium (substrate), n is the gradient refractive index. The grating criterion for the efficient antireflection is $p < \lambda/n_s$ and $h > \lambda/2$, where p is the pitch size, λ is the wavelength of the incident light.^[11] Therefore, the antireflection or enhancement of T_{lum} could be rationally expected for such biomimetic patterning VO_2 nanostructures and the enlarged solar modulating abilities (ΔT_{sol}) could also be expected since the VO_2 total area on the substrate is simultaneously increased (Scheme 1.2).



Scheme 1.2 Schematic description of the gradient refractive index, n , along the height, h , (top) and the antireflection effect of the Moth-eye biomimetic VO₂ pattern on the substrate (bottom).

Doping of ions into the VO₂ lattice is an alternative method to adjust the thermochromic properties.

Doping is an efficient approach to reduce the τ_c , optimize the combination of T_{lum} and ΔT_{sol} as well as tuning the film color. The V⁴⁺ in the VO₂ has ‘+4’ valence state and 0.058 Å ionic radius. The substitution of V⁴⁺ by other metal cations through doping could result in extra tensile/compressive stress and free electron/hole (e^-/h^+) carriers, which influenced the structure stability and the equilibrium carrier density^[12], and thus modulating the thermochromic performances of VO₂ nanomaterials (Scheme 1.3). As to the defects reaction replacing the V⁴⁺ by Mⁿ⁺, it could be described as:

$$M_V^x = M_V + 2e' \quad (n=6) \quad (1.2)$$

$$M_V^x = M_V'' + 2h \cdot \quad (n=2) \quad (1.3)$$

With regards to the stain effect, the τ_c can be adjusted by the uniaxial stress σ according to the Clausius-Clapeyron equation:

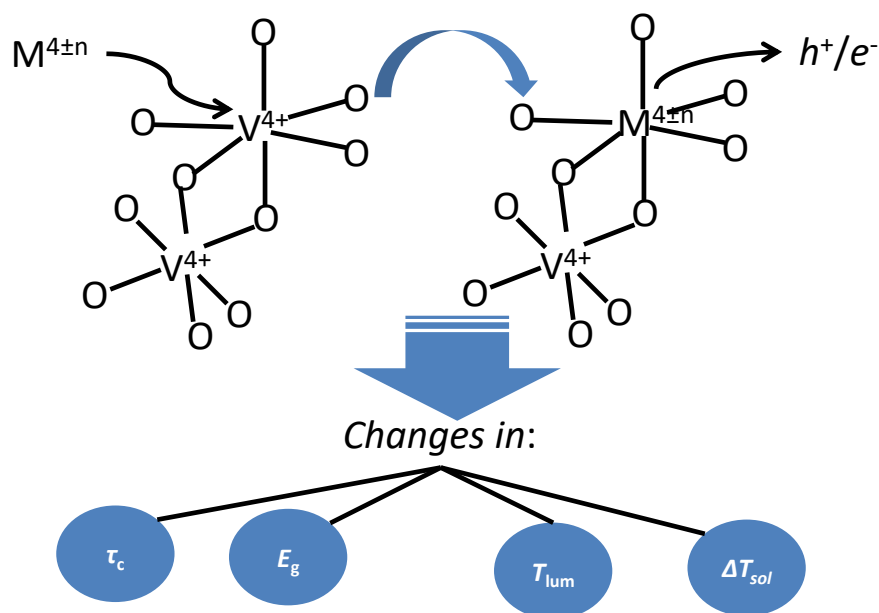
$$\frac{d\tau_c}{d\sigma} = (\varepsilon_0 \tau_c^0) / \Delta H \quad (1.4)$$

Where ΔH is the latent heat of transition, ε_0 is the initial strain and τ_c^0 is the initial phase transition temperature.^[13]

Rare earth cations have the much larger ionic radius than the V⁴⁺ cation, which should be expected to reduce the τ_c effectively, while the free electron carriers generated by the W⁶⁺ doping should make it exhibit higher τ_c reducing rate. Therefore, it could be proposed that the Mg/W-codoping with charge carrier counteraction and the RE doping with the

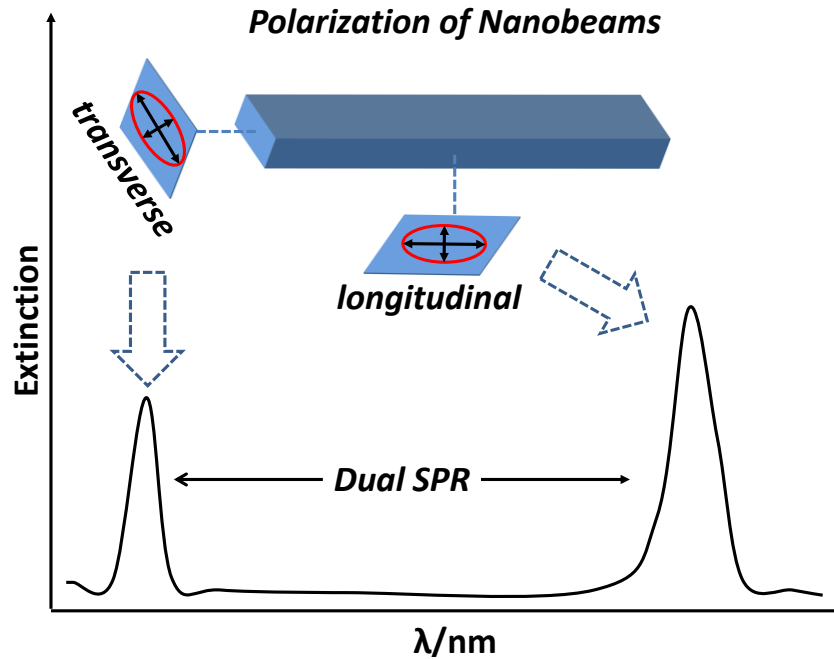
competition between the extra strain and the hole carriers as well as the patterned VO₂ surface may be applicable to enhance the thermochromic properties of VO₂.

In addition, the free standing VO₂ nanostructures assembled though normal hydrothermal method may exhibit interesting electrical and optical properties.



Scheme 1.3 Schematic description of the doping effects on the properties of VO₂ materials.

Since VO₂ exhibits the metallic conduction at the hot state, the surface plasmon resonance (SPR) should be expected for the VO₂(R). As illustrated in Scheme 1.4, the metal nanobeams should show the dual SPR extinction peaks due to the polarization along the transverse and the longitudinal axis. Therefore, the VO₂ nanobeams at the metallic state should be expected to exhibit the dual SPR %T valleys, which should be helpful to enhance the %T contrast at selected wavelength between the hot and cold state, and thus be meaningful for improving the solar modulating abilities.



Scheme 1.4 Illustration of the dual SPR peaks for the metal nanobeams arising from the transverse and longitudinal polarization.

1.2 Objectives and Scope

The main objectives of this thesis are:

- a) To investigate the doping mechanisms for τ_c modulation and thermochromic performance enhancement;
- b) To fabricate biomimetic moth eye patterned VO₂ surfaces via top down and bottom up methods as well as the mechanism of how such structure is relating with the thermochromic properties;
- c) To study the electrical and optical properties of free-standing VO₂ nanostructures, including nanoparticles and nanobeams.

Therefore, the scope of this thesis has been proposed accordingly.

The doping effect of crystalline RE-doped and Mg/W-codoped VO₂ thin films were investigated systematically via controlling the annealing process, e.g. annealing temperature, dwelling time, gas flow rate/vacuum level. Moreover, it has been reported that the VO₂ nanostructures on the substrate with proper patterns, e.g. nanogrid,^[14] nipple-arrays^[15] could be expected to show high visible transmission as well as large solar modulating abilities. Therefore, patterning of VO₂ on the substrate via top-down or bottom-up methods have been designed to tailor the thermochromic performance of VO₂. In the hydrothermal synthesis, the process condition such as reaction temperature, pH, and molar ratio of starting chemicals is critical for the assembly of various nanostructures. Therefore, different VO₂ nanostructures can be fabricated with systematically change of hydrothermal process.

1.3 Dissertation Overview

The thesis investigated various VO₂ nanostructures (continuous/patterned thin films, nanopowders, nanobeams) and doping efforts as well as their thermochromic properties.

Chapter 1 provides a rationale for the research and outlines the goals and scope.

Chapter 2 reviews the literature concerning crystal structure, MIT, synthesis methods and thermochromic properties of VO₂ nanomaterials.

Chapter 3 discusses the principles underlying the synthesis/characterization techniques employed and the methods of data analysis, including errors. All of the approaches have been fully discussed in this chapter.

Chapter 4 elaborates the fabrication and thermochromic properties of RE-doped and Mg/W-codoped VO₂ thin films.

Chapter 5 elaborates the patterned VO₂ nanostructures on substrate and its structure/property relationship.

Chapter 6 elaborates the structure evolution of hydrothermal synthesis of different VO₂ nanostructures. Their optical and electrical response has been investigated.

Chapter 7 summarizes the outcomes of the thesis, explains the contribution to the field of smart window application and discusses the future work in the thermochromic applications.

1.4 Findings and Outcomes

For the first time, this research reported the rare earth doping, moth eye structure and nanobeam structure with dual SPR effect. The RE doping can enhance both T_{lum} and ΔT_{sol} simultaneously but less intend to reduce the τ_c . The Mg/W-codoping is found to be effective to address the high τ_c issue. The non-cross-linked nanograin array of the morphology benefits with the enhanced T_{lum} and ΔT_{sol} .

The moth eye structured VO₂ surfaces have been fabricated via both bottom up and top down method. Such structure can increase both T_{lum} and ΔT_{sol} due to the antireflection effect from such moth eye structure and enlarged surface area of VO₂. The free standing W-doped VO₂ single crystal nanobeams with intriguing dual SPR has been first reported. The mechanisms of the structure evolution from nanowire-nanobeam-nanoparticle have been proposed.

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Chapter 2

Literature Review

As a phase transition material, VO_2 exhibits the interesting solar modulating abilities, which make it applicable in smart window industry. However, several challenges for VO_2 in smart window applications as illustrated in the literatures, including the high phase transition temperature, low visible transmission and the unacceptable solar modulating abilities cannot be solved till now. Therefore, the scope of this thesis is to reduce the phase transition temperature by doping with metal cations, and to improve both the visible transmission and the solar modulating abilities through surface patterning as well as efficient doping. The work that will be done in this thesis should be meaningful for the investigation of doping mechanisms and the practical application in thermochromic smart windows.

2.1 Overview

2.1.1 Crystal Structure and Metal to Insulator Transition of VO_2

In the vanadium oxide (VO_x) species, vanadium has various valence states as depicted in the V_2O_3 - V_2O_5 phase diagram (Figure 2-1). Amongst them, VO_2 that crystallized in monoclinic with space group $P 2_1/c$ shows an interesting metal-insulator transition (MIT) near the room temperature ($\tau_c=68^\circ\text{C}$), i.e. the insulating $\text{VO}_2(\text{M})$ is transformed into $\text{VO}_2(\text{R})$ above τ_c .

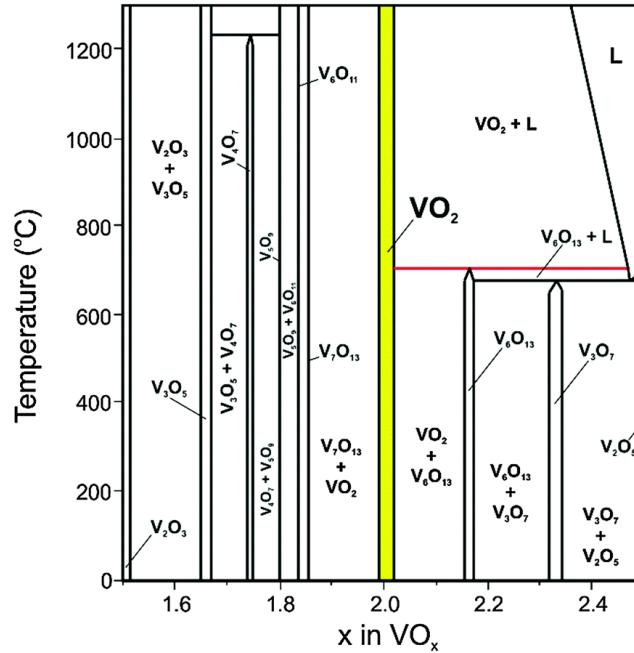


Figure 2.1 The V_2O_3 - V_2O_5 phase diagram.^[1]

In the year 1962, *Heckingbottom* and *Linnett*^[2] firstly reported that VO_2 should have a monoclinic crystal structure, and the crystal structure was exactly determined by J. C. *Rakotoniaina* et al.^[3] in the year 1993. As shown in Figure 2-2, the V-O distance varies from 1.762 to 2.051 Å in the $\text{VO}_2(\text{M})$ phase, whereas it slightly changes from 1.910 to 1.963 Å (Figure 2-2a, b). The crystal structure of $\text{VO}_2(\text{M})$ can be seemed as a monoclinic distortion of the tetragonal structure of $\text{VO}_2(\text{R})$, where the V atom locates in the center of VO_6 octahedron for $\text{VO}_2(\text{R})$,

but shifts toward to a triangular face of the VO_6 octahedron for $\text{VO}_2(\text{M})$.^[4]

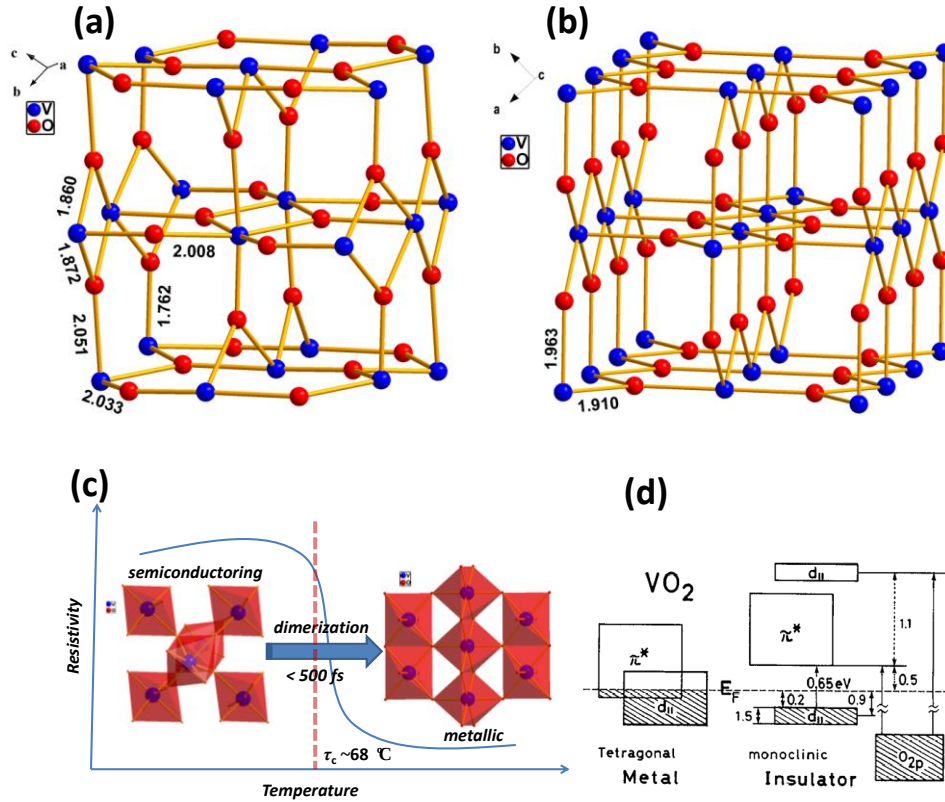


Figure 2.2 Crystal structure of VO_2 , (a) $\text{VO}_2(\text{M})$: Monoclinic, $P2_1/c$ ($\tau < \tau_c$), (b) $\text{VO}_2(\text{R})$: Tetragonal, $P4_2/mnm$ ($\tau > \tau_c$), reproduced from the data in the literature^[3]. (c) Schematic resistivity v.s. Temperature curve of VO_2 . (d) Diagram of band gap for VO_2 under metallic and insulating states.^[4]

With respect to the metal to insulator transition (MIT), VO_2 shows an abrupt resistance change by up to four orders of magnitude within 500 fs (10^{-15} s) around τ_c (Figure 2-2c)^[5] while a band gap ~ 0.6 eV between π^* and d_{11} orbitals is formed at the insulating state (Figure 2-2d). The nature of the MIT in VO_2 has been intensively investigated in terms of calculation and experimental studies. Goodenough (1971)^[6] investigated the transition temperatures τ_c and τ_c' for the mechanisms antiferroelectric-to-ferroelectric transition and homopolar-to-metallic V-V bonding transition, respectively. In $\text{VO}_2(\text{M})$, the shortest V-O distance $R_{\text{VO}} = 1.76$ Å is perpendicular to the c_R axis. The two bridging O atoms between paired V atoms have $R_{\text{VO}} = 1.86/1.87$ Å. The other three R_{VO} distances are

2.01/2.03/2.05 Å, revealing an antiferroelectric distortion, which is different from the ferroelectric distortion in VO₂(R) phase, where the V atoms locate in the center of the VO₆ octahedrons. He concluded that the driving force for MIT in VO₂ is the antiferroelectric distortion and the rule $\tau_c' \leq \tau_c$ should be obeyed for the pristine or doped VO₂ under low doping levels. He also pointed out that the τ_c should be controlled by the entropy of lattice vibration, rather than the thermal excitation of electrons. Gray et al. (2016) proposed a correlation-driven mechanism for the MIT of VO₂.^[7] They proposed that the temperature driven MIT at T_{MIT} (τ_c) of VO₂ is possibly driven by a purely electronic correlation transition at T_{Corr} ($T_{MIT} = T_{Corr} + 5$ K). As shown in Figure 2.3(a), above the T_{MIT} , VO₂(R) exhibits a metallic phase with a space group $P4_2/mnm$, where the V atoms occupy the sixfold oxygen-coordinated sites (Figure 2.3a-a1). At this state, the near-Fermi-level states π^* (twofold-degenerate e_g^π , d_{xz} , d_{yz}) and $d_{||}$ (single a_{1g} , $d_{x^2-y^2}$, parallel to c_R) orbitals, separated from the t_{2g} orbitals by the orthorhombic component of the crystal field, overlap in energy (Figure 2.3a-a2), and the generating nonzero density of states at the Fermi level attributes to the metallic behavior of the rutile phase.^[6, 8] Below the T_{MIT} , the crystal structure of VO₂ is changed to low-symmetry monoclinic system with $P2_1/c$ space group via dimerization of the adjacent V atoms along the c_R axis and tilting along $[110]_R$ and $[1\bar{1}0]_R$ directions (Figure 2.3a-a3). At this state, each V-V dimer shares a singlet electronic state ($d_{||}$) occupied by two strongly correlated V 3d¹ electrons (shown in blue). The dimerization splits the $d_{||}$ orbitals into bonding and antibonding states, and the tilting of the dimers moves the π^* orbital to higher energies owing to the p-d orbital overlap (Figure 2.3a-a4). Both of them results in a band gap of 0.6 eV, which accounts for the insulating behavior of VO₂(M). As shown in the plots of temperature dependent $d_{||}$ V-V singlet peak intensity (Figure 2.3b-b1), the T_{Corr} is different from the T_{MIT} ($T_{MIT} = T_{Corr} + 5$ K), and Figure 2.3b-b2 to b4 shows the correlation transition during the phase change from monoclinic to rutile phase, where (b2) the strongly correlated singlet electronic state is confined on the antiferroelectric distorted V-V dimer at $T \ll T_{MIT}$; (b3) The strong Coulomb correlations within the dimers soften at $T = T_{Corr}$, giving rise to a new monoclinic phase; (b4) The e-e

correlations are totally diminished above $T \gg T_{\text{MIT}}$, resulting in the phase transition to rutile metallic phase. *Budai et al.* (2014) first examined the lattice vibration during the MIT of VO_2 by measuring the temperature-dependent phonon density of states (PDOS).^[9] Based on the PDOS measurement results, they concluded that the entropy driving the MIT of VO_2 is dominated by strongly anharmonic phonons (accounts for $\sim 2/3$ of the total increase in entropy at the MIT) rather than electronic contributions, different from the electron-lattice Peierls MIT and strong e-e correlation Mott MIT models.^[10-12] Based on their lattice vibration model, the increased occupation of vanadium $d_{\parallel}$ orbitals triggers the Peierls instability, lowering the energy and opening the insulating bandgap, and the singlet $d_{\parallel}$ electrons are confined on the V-V dimers (Figure 2.3c-left). At the metallic state, the high phonon entropy is superior to the low electronic energy, resulting in large vibrational motions, which stabilizes the tetragonal phase and free up conduction electrons (Figure 2.3c-right). *Qazilbash et al.* (2007) analyzed the MIT of VO_2 using the infrared spectroscopy and nano-imaging, which revealed the Mott transition during cooling and heating processes.^[13] As shown in Figure 2.3d, the amplitude-contrast near-field images show the electronic insulator-to-metal transition in progress. At 341K, slightly below the τ_c , only the uniform maps of low scattering (dark blue) can be found. With further heating, the nanoclusters of $\text{VO}_2(\text{R})$ colored in green/red begin to appear steadily, and the MIT is finally completed above the temperature of 343.6 K.

Overall, the mechanism for the MIT of VO_2 can be demonstrated by the electron-lattice Peierls transition, strong electron-electron correlation Mott transition and the lattice vibration transition models in different aspects. However, a rational model that can be used to explain the MIT of VO_2 in all aspects is still hard to establish till now.

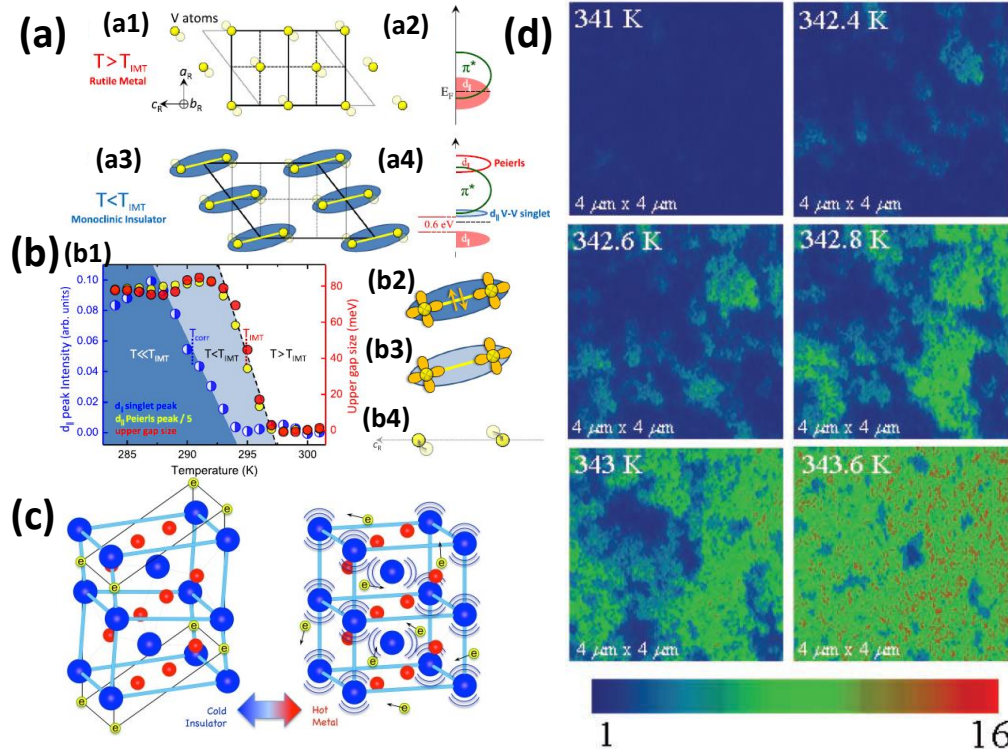


Figure 2.3 Correlation-driven mechanism for MIT (a, b)^[7]: (a1) Rutile lattice structure of VO_2 (R). (a2) Band gap of VO_2 (R).^[6, 8] (a3) Monoclinic lattice structure of VO_2 (M).^[8] (a4) Band gap of VO_2 (M).^[6, 8, 14-16] (b1) Temperature-dependent evolution of the $d_{||}$ V-V singlet peak intensity (blue and white symbols) as well as the structural transition (yellow solid symbols) in VO_2 . (b2-b4) Schematic representation of the three phases of VO_2 . Large phonon entropy-driven mechanism for MIT (c)^[9]: Schematic view of the lattice vibration induced MIT in VO_2 . Mott transition mechanism for MIT revealed by nano-imaging^[13] (d): Nearfield scattering amplitude images in the s-SNIM operating area ($4 \times 4 \mu\text{m}^2$) at the infrared frequency $\omega = 930 \text{ cm}^{-1}$. Metallic regions are highlighted in light blue, green, and red colours. Dark blue colour is the insulating phase.

2.1.2 Synthesis Methods of VO_2 Nanomaterials

As described above, amounts of valence state of vanadium exist in the VO_x compounds, which make it not easy to get specific vanadium oxides. Therefore, it should be very careful to control the synthesis conditions for the VO_2 nanomaterials.

a) Sol-gel methods

Sol-gel technique is a facile, cost-effective method to prepare VO₂ nanomaterials. In a typical sol-gel process for VO₂ preparation as shown in Figure 2.4, a V⁵⁺ or V⁴⁺ precursor is firstly prepared, and then the precursor is transferred onto a hydrophilic substrate through dip/spin coating with a following drying process. Finally, the VO₂ phase is formed by a high temperature annealing process under inert atmosphere, e.g. vacuum, N₂/Ar/CO₂.

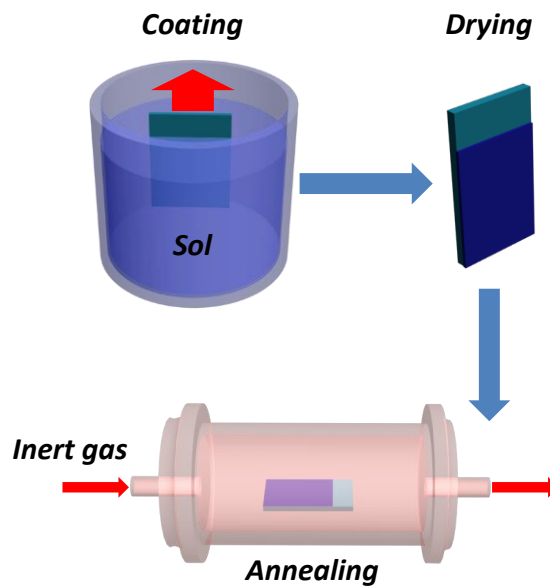


Figure 2.4 A typical Sol-gel process for the synthesis of VO₂ nanomaterials.

With respect to the precursor for VO₂ synthesis, *Pan et al.* (2004) utilized the vanadium oxyacetylacetonate [VO(acac)₂], dissolved in methanol as a precursor solution for the synthesis of pristine and doped VO₂ thin films.^[17] *Yuan et al.* (2002) used the inorganic precursor attained by quenching melted V₂O₅ with deionized water for fabrication of high-quality polycrystalline VO₂ thin films.^[18] *Partlow et al.* (1991) reported the production of VO₂ thin films with vanadium oxide isopropoxide [VO(OC₃H₇)₃] as organic sol-gel precursor.^[19] *Takahashi et al.* (2001) investigated the fabrication of doped VO₂ thin films using the V₂O₅-H₂O₂ inorganic precursor.^[20] *Kang et al.* (2010) illustrated the deposition of VO₂ thin

films utilizing the VOCl_2 solution precursor.^[21] Amongst those sol-gel precursors, the $\text{VO}(\text{acac})_2$ or inorganic precursors ($\text{V}_2\text{O}_5\text{-H}_2\text{O}$, $\text{V}_2\text{O}_5\text{-H}_2\text{O}_2$, VOCl_2) have obvious advantages in low-cost and low-toxicity, which is critical for practical applications.

For the annealing temperatures and inert atmospheres, the flowing N_2 atmosphere and the annealing temperature above $500\text{ }^\circ\text{C}$ were adopted as conditions for the synthesis of VO_2 thin films in the research performed by M. Pan et al.,^[17] I. Takahashi et al.,^[20] and L.T. Kang et al.^[21] The vacuum atmosphere and the annealing temperature $480\text{ }^\circ\text{C}$ were used by N.Y. Yuan et al. to synthesize $\text{VO}_2(\text{M})$ phase, however there still co-existed V_6O_{11} impurity phase in the final products.^[18] In addition, the mixture gas flow ($50\%\text{ CO}/50\%\text{ CO}_2$) and the annealing temperature above $400\text{ }^\circ\text{C}$ were also utilized by D.P. Partlow et al. to attain the $\text{VO}_2(\text{M})$ phase.^[19] All in all, the pure $\text{VO}_2(\text{M})$ phase under inert atmosphere could be formed above $500\text{ }^\circ\text{C}$ with normal annealing process.

b) Hydrothermal approaches

Hydrothermal method is an economical and powerful approach for versatile VO_2 nanomaterials. In the hydrothermal process, the supercritical solvent could lower the formation temperature of $\text{VO}_2(\text{M})$ from above $500\text{ }^\circ\text{C}$ normally needed in sol-gel process down to below $300\text{ }^\circ\text{C}$, which is critical and meaningful for the energy-saving requirements. In a typical hydrothermal process for obtaining VO_2 nanomaterials (Figure 2.5), the V^{4+} precursor is firstly prepared in a beaker, and then the precursor is transferred into a liner [PTFE (Polytetrafluoroethylene) /PPL (Polypropylene)], which is sealed in an autoclave for the following hydrothermal reaction. After hydrothermal reaction, the VO_2 nanomaterials are isolated through centrifuging for several times. Sometimes, an additional annealing process is needed for purifying the phase or increasing the crystallinity.

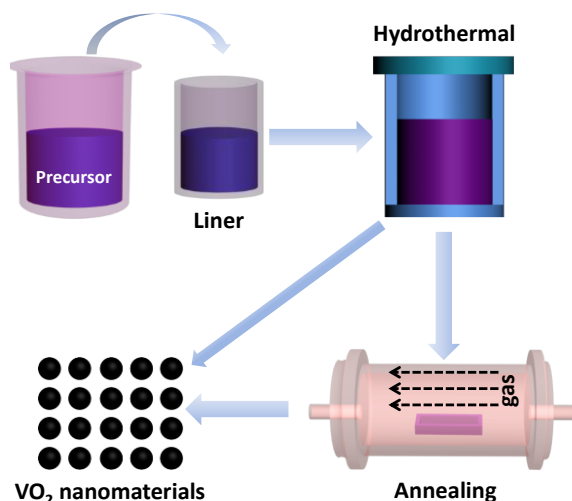


Figure 2.5 A typical hydrothermal process for the synthesis of VO₂ nanomaterials.

In practical cases, *Cao et al.* (2008) used V₂O₅ as vanadium source, oxalic acid as reducing reagent (molar ratio ~1:6) and DI water as solvent to synthesize a mixture of VO₂ nanorod and snowflake powders at the temperature of 240 °C.^[22] A further investigation revealed that sulfuric acid (H₂SO₄) can be used to modulate the morphology of the VO₂ products with increasing the zeta potential (more H⁺ in the solution) and reducing the growth rate (VO₂ has high solubility in strong acid), thereby resulting in the uniform VO₂ nanorod products.^[23] *Wu et al.* (2011) used a V(OH)₂NH₂ precursor to get VO₂ single domain nanorods with hydrothermal treatment at 200 °C for 36 h.^[24] *Huang et al.* (2013) used a two-step process to obtain VO₂(M) nanomaterials, where VO₂(B) nanoparticles were firstly got by a hydrothermal reaction between V₂O₅ and propylene glycol at the temperature 160-180 °C, and then an additional annealing process under N₂ atmosphere at 550 °C for 0.5-2h was performed to get a pure VO₂(M) phase. This two-step process is especially applicable for VO₂@SiO₂ core-shell nanostructures.^[25] *Powell et al.* (2015) reported a continuous hydrothermal process for synthesis of VO₂ nanoparticles with NH₄VO₃ and oxalic acid at the temperature 335-357 °C.^[26] *Ji et al.* (2011)^[27] reported a hydrothermal synthesis of single phase VO₂(M) nanoparticles with a reduced V₂O₅ gel by N₂H₄ at a temperature 260 °C for 24 h. The parameters and the product morphology

recorded in the literatures for the hydrothermal synthesis of VO₂ nanomaterials have been tabulated in Table 2.1. It is clear to see that the VO₂ nanomaterials can be obtained under hydrothermal conditions above the temperature 200 °C with proper starting materials, including the V^{5+/4+} source and/or reducing reagents.

Table 2.1 Parameters for the hydrothermal synthesis of VO₂ nanomaterials and the morphology of the products.

Precursor	T/°C	Process	Morphology	Ref.
V ₂ O ₅ -Oxalic acid	240	one-step	nanorod & snowflake	[22]
V(OH) ₂ NH ₂	200	one-step	nanorod	[24]
V ₂ O ₅ - propylene glycol	1 st 160-180, 2 ^{ed} 550	two-step	nanoparticles	[25]
NH ₄ VO ₃ -Oxalic acid	335-357	one-step	nanoparticles	[26]
V ₂ O ₅ -N ₂ H ₄	260	one-step	nanoparticles	[27]

c) APCVD

Atmospheric pressure chemical vapor deposition (APCVD), is an efficient technique to fabricate VO₂ thin films in a large scale or with a high throughput on glass substrates, although it has the disadvantages in controlling the film thickness and/or potential chemical contaminations.^[4] Figure 2.6 shows the diagram for a representative APCVD reactor. In a typical APCVD deposition process, the strategies will follow:^[28] i) The active gaseous reactants are created; ii) The reactants are transported into the reaction chamber by carrier gas; iii) Intermediate species are formed by the gaseous reaction between the reactants; iv) The gaseous reactants are absorbed onto the heated substrates, and the film as well as by-product species are formed after heterogeneous reactions; v) The nucleation and island growth of the film are continuously carried out by the diffusion of deposits along the heated substrates; vi) Volatile reaction products are desorbed from the surface of the substrate and the mass transport is stopped.

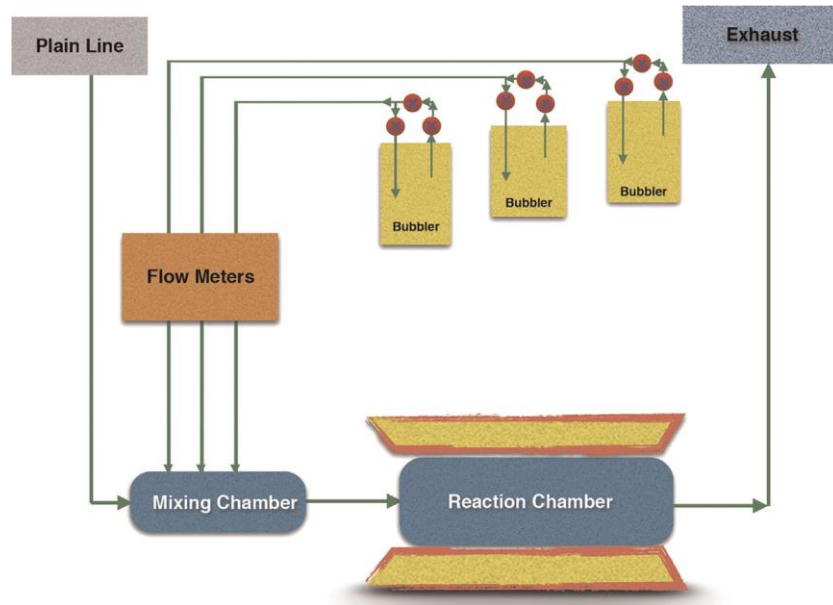


Figure 2.6 Schematic diagram of an APCVD reactor.^[28]

For the fabrication of VO_2 through APCVD, *Manning et al.* (2005) fabricated the solid solutions $\text{V}_{1-x}\text{M}_x\text{O}_2$ ($\text{M}=\text{Mo}, \text{Nb}$; $x=0.003-0.01$) on glass substrates from the reaction of VOCl_3 , H_2O and MCl_5 with the N_2 system gas flow at the temperature 650°C .^[29] *Blackman et al.* (2009) reported the deposition of W-doped VO_2 thin films on float glass with SiO_2 buffer layer through APCVD method, where the gaseous reactants contained VCl_4 , WCl_6 and water, the reaction temperature was 550°C and the system gas was N_2 (99.999%).^[30] *Vernardou et al.* (2014) fabricated the amorphous VO_2 thin films on SnO_2 pre-coated glass substrates by APCVD method using vanadyl(V) triisopropoxide ($\text{VO}(\text{OC}_3\text{H}_7)_3$) as single precursor, where the temperature was set at 450°C and the system gas was N_2 (96%).^[31] *Powell et al.* (2016) reported the APCVD coating of VO_2 thin films on SiO_2 pre-coated glass substrates using VCl_4 and ethyl acetate ($\text{C}_4\text{H}_8\text{O}_4$) as vanadium and oxygen sources, respectively, where the reactor temperature was set at 550°C and the system gas was N_2 (99.9%).^[32]

The precursor and parameters for synthesizing VO_2 thin films using APCVD method have been concluded in Table 2.2, which suggests that the precursor containing vanadium and oxygen sources, the N_2 system gas as well as the reactor

temperature above 550 °C are necessary for obtaining crystalline VO₂ thin films.

Table 2.2 Precursors and parameters for APCVD synthesis of VO₂ thin films.

Precursor	T/°C	System Gas	Crystallinity	Ref.
VOCl ₃ , H ₂ O	650	N ₂	crystalline	[29]
VCl ₄ , H ₂ O	550	N ₂	crystalline	[30]
VO(OC ₃ H ₇) ₃	450	N ₂	amorphous	[31]
VCl ₄ , C ₄ H ₈ O ₄	550	N ₂	crystalline	[32]

d) Solution combustion

An alternative approach for the VO₂ synthesis is the solution combustion method. In a typical solution combustion process, the V⁵⁺ precursor is firstly mixed with organic solvents in a beaker, and then the mixture is ignited or heated in a furnace to ignition point. Finally, the VO₂ product can be collected on the inner wall surface of the beaker. Compared with the methods mentioned above, the solution combustion is a facile and time-saving approach for the synthesis of VO₂ nanostructures.

Wang et al. (2010) reported the first case for solution combustion synthesis of VO₂ nanomaterials.^[33] In their experiment, VO(acac)₂ (acac-acetylacetonate) was dissolved by absolute ethanol in a beaker, which was then ignited for reaction (30 min). As shown in Figure 2.7, the temperature distribution in the beaker was real-time monitored during the reaction of combustion, where the VO₂ phase was formed due to the reducing/inert reaction atmosphere as well as the high temperature in the center which provided sufficient thermal energy to overcome the phase formation energy barrier.^[33]

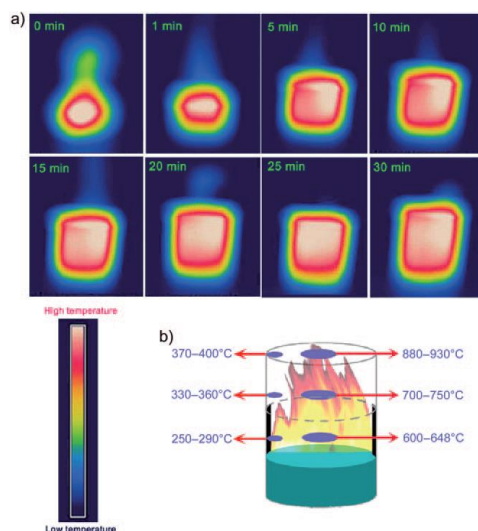


Figure 2.7 a) Spatial-temperature-distribution evolution in the confined space of the beaker, varying with the reaction time and captured by a thermal infrared camera from the side. b) Schematic illustration for the distribution of temperature within the inner wall surface and at the centre of the beaker, monitored by the thermocouple. ^[33]

G. P. Nagabhushana and G. T. Chandrappa developed the solution combustion method in 2013. The precursor they used was changed to aqueous solution of NH_4VO_3 (ammonium metavanadate) and DL-malic acid ($\text{C}_4\text{H}_6\text{O}_5$). Instead of directly igniting, the beaker containing the mixture was placed in a furnace with the temperature 470°C . After 5 min for smouldering combustion, the beaker was moved out for continuous combustion at room temperature. Finally, the VO_2 nanorods were collected on the inner wall surface of the beaker (Figure 2.8).^[34] Obviously, the developed combustion method takes shorter time and is more cost-effective due to the replacement of $\text{VO}(\text{acac})_2$ by NH_4VO_3 . However, due to the intrinsic defects of this design, e.g. low concentration of the precursor, hard to control of the flame, it is hard for this method for large scale production of VO_2 nanomaterials.

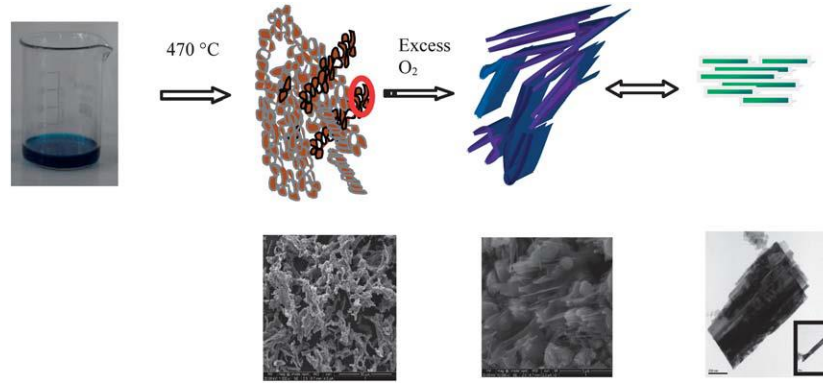


Figure 2.8 Schematic illustration of a VO₂ nanorods array evolution during the solution combustion process. ^[34]

2.1.3 Thermochromic properties of VO₂ Nanomaterials

VO₂ is widely investigated as thermochromic materials in terms of its solar modulating abilities, i.e. transparent at cold insulating state (VO₂(M)) and highly absorptive/reflective at hot metallic state (VO₂(R)). The solar modulating ability of VO₂ should be due to the change of optical constants along with the phase transition from VO₂(M) to VO₂(R) at $T_c=68\text{ }^{\circ}\text{C}$. As shown in Figure 2.9-b and c, in the NIR range ($1000\text{ nm} < \lambda < 2500\text{ nm}$), the extinction coefficient (k) at the hot state is much larger than that at cold state and the contrast of k reaches the maximum at $\lambda = 2500\text{ nm}$, where the refractive index (n) at the hot state is also bigger than those at the cold state. Based on the Fresnel reflection equation $R = 1 - \frac{4n}{(n+1)^2 + k^2}$, and the absorption coefficient expression $\alpha = \frac{4\pi k}{\lambda}$, the n and k contrast gives rise to the higher reflection (R) and larger absorption (A) at the hot state, respectively than that at the cold state in the NIR range, which results in a large transmission contrast ($\Delta T = T_{\text{cold}} - T_{\text{hot}}$). However, at the visible range ($380\text{ nm} < \lambda < 780\text{ nm}$), the hot state exhibits a lower n and higher k , giving rise to an unchanged visible transmission, which is meaningful for thermochromic smart window applications.

As for the thermochromic performance of VO₂ thin films, the FDTD (Finite Difference Time Domain) simulations have been performed by *Taylor et al.*

(2013)^[35] based on the optical constants in Figure 2.9-b, c. As shown in Figure 2.9-a, there is a trade-off between the T_{lum} and ΔT_{sol} , i.e. the large ΔT_{sol} is based on the sacrifice of T_{lum} . On the other hand, the bronze color of the VO₂ thin film is not comfortable for the eye, which will restrict its practical applications.

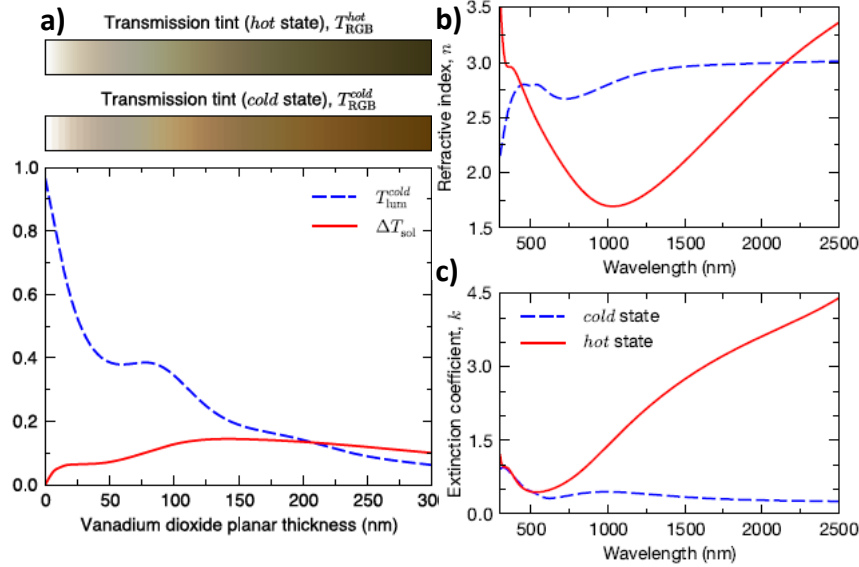


Figure 2.9 a) FDTD simulations of the corresponding T_{lum}^{cold} and ΔT_{sol} changes for planar VO₂ thin films with different thicknesses. The upper bars show the transmittance colour for both the hot and cold VO₂ phases. b) and c) Optical constants (n , k) of VO₂ in the hot (solid line) and cold states (dash line).^[35]

2.2 Methods to Improve the Thermochromic Performance of VO₂

In light of the intrinsic drawbacks of the VO₂ nanomaterials as described above, researchers over the world have proposed several approaches to improve the thermochromic performance of VO₂, e.g. ARC (antireflection coating) multilayer, biomimetic design, nanothermochromism, periodic patterning as well as porous structure as shown in Figure 2.10.

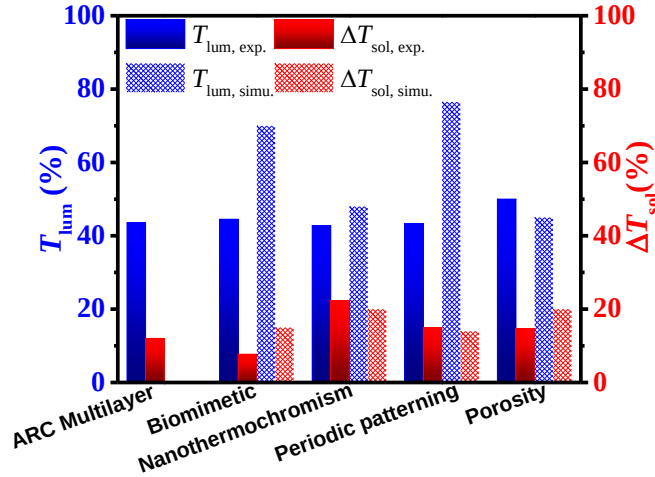


Figure 2.10 Methods proposed for enhancing the thermochromic performance of VO₂ nanomaterials.^[36]

2.2.1 ARC multilayer

On the surface of VO₂ thin film, there is a big refractive index (n) gap between the air ($n=1$) and the VO₂ ($n \approx 3$ at 1500 nm), which blocks the light transmission via strong reflection and absorption. The ARC multilayer structure has the ability to reduce the surface reflection/absorption and hence enhancing the transmission.

Mlyuka et al. (2009) reported multilayer structures (TiO₂/VO₂/TiO₂, TiO₂/VO₂/TiO₂/VO₂/TiO₂) for improving thermochromic performance of VO₂ thin films.^[37] As shown in Figure 2.11, the multilayer structure TiO₂/VO₂/TiO₂ (Figure 2.11-a) and TiO₂/VO₂/TiO₂/VO₂/TiO₂ (Figure 2.11-b) show higher T_{lum} compared with the single-layer VO₂ counterparts due to the gradient refractive index [$n(\text{VO}_2) \approx 3$, $n(\text{TiO}_2) \approx 2.2$] in the multilayer structure. The calculated T_{lum} and ΔT_{sol} for TiO₂/VO₂/TiO₂ and TiO₂/VO₂/TiO₂/VO₂/TiO₂ are 60%, 6% and 44%, 12%, respectively, which show 50%, 70% and 10%, 80% relatively improvement compared with the corresponding single-layer VO₂ thin films.

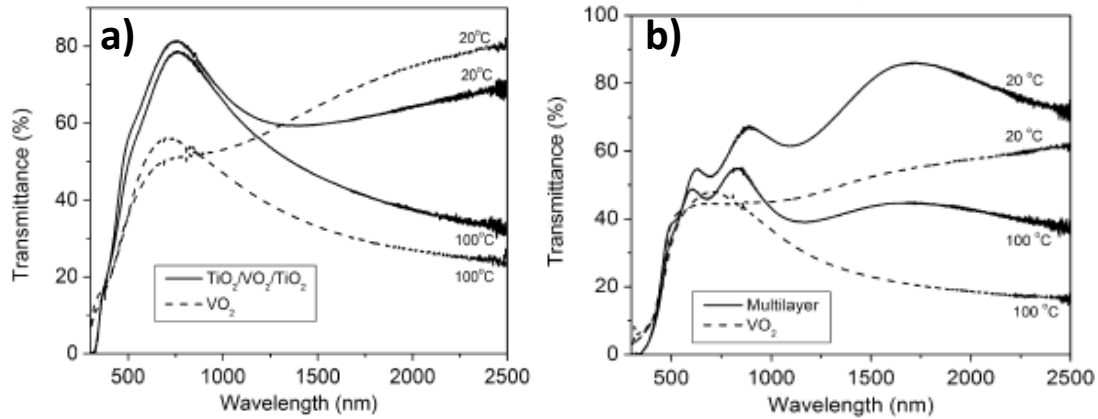


Figure 2.11 Spectral normal transmittance for three-layer $\text{TiO}_2/\text{VO}_2/\text{TiO}_2$ films (a) and five-layer $\text{TiO}_2/\text{VO}_2/\text{TiO}_2/\text{VO}_2/\text{TiO}_2$ films (b), compared with corresponding VO_2 films.

[37]

Sun et al. (2016) [38] reported a spinodally decomposed $\text{TiO}_2\text{-VO}_2$ multilayer structure with enhanced thermochromic properties. With the antireflection effect of the Ti-rich layer in the multilayer structure, the T_{lum} could be increased from 18.5% (M phase)/18.6% (R phase) to 22%(M phase)/20.9%(R phase), and the ΔT_{sol} could also be enhanced from 11.5% to 13.1%, compared with single component thin film of VO_2 .

Powell et al. (2016) [32] fabricated $\text{VO}_2\text{-SiO}_2\text{-TiO}_2$ multilayer structure for energy-saving window panels. As shown in Figure 2.12, a combination of $T_{\text{lum}}=43.04\%$ and $\Delta T_{\text{sol}}=7.2\%$ could be achieved in a multilayer structure $\text{VO}_2(50 \text{ nm})\text{-SiO}_2(1300 \text{ nm})\text{-TiO}_2(100 \text{ nm})$. The low value of ΔT_{sol} should be ascribed to the low density of the VO_2 thin film deposited by APCVD as described in the report.

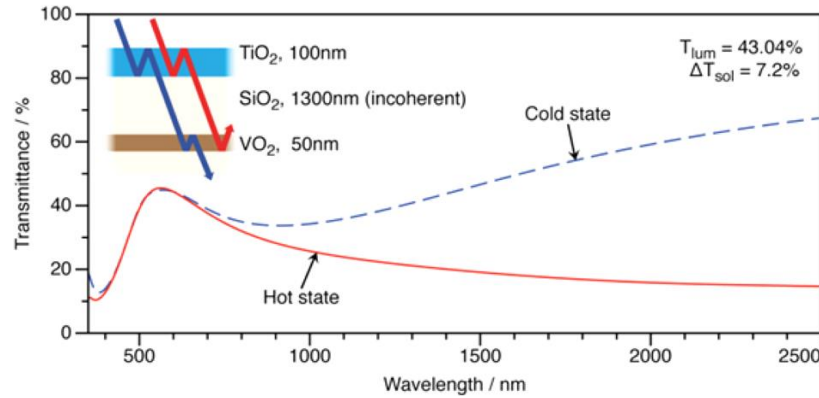


Figure 2.12 UV-Vis-NIR %T spectra at hot/cold state for $\text{TiO}_2/\text{SiO}_2/\text{VO}_2$ multilayer thin film.^[32]

Zheng et al. (2015) reported a $\text{TiO}_2(\text{A})\text{-VO}_2\text{-TiO}_2(\text{R})$ multilayer structure with enhanced thermochromic properties.^[39] As shown in Figure 2.13-a, the multilayer structure shows bronze color with an applicable luminous transmission ($T_{\text{lum}}=30\%$). Compared with the bilayer $\text{TiO}_2(\text{R})\text{-VO}_2$ structure, the $\text{TiO}_2(\text{A})\text{-VO}_2\text{-TiO}_2(\text{R})$ multilayer structure exhibits larger solar modulating ability ($\Delta T_{\text{sol}}=10.2\%$ v.s. $\Delta T_{\text{sol}}=8.6\%$) as well as similar visible transmittance ($T_{\text{lum}}=30.1\%$ v.s. $T_{\text{lum}}=32.4\%$).

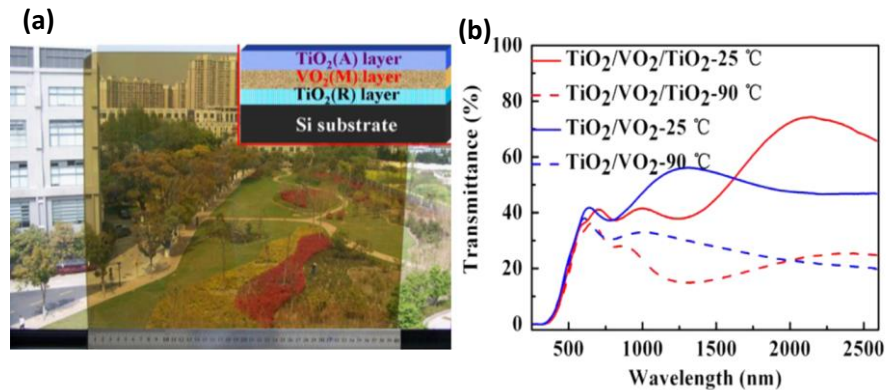


Figure 2.13 a) Photograph of large-scale ($400 \times 400 \text{ mm}^2$ area) multilayer film at room temperature (the inset is corresponding structure diagram of the multilayer film). b) Optical transmittance spectra of $\text{TiO}_2(\text{R})/\text{VO}_2(\text{M})/\text{TiO}_2(\text{A})$ multilayer film and $\text{TiO}_2(\text{R})/\text{VO}_2(\text{M})$ bilayer film at low and high temperature.^[39]

2.2.2 Biomimetic nanostructure

The biomimetic nanostructure, such as moth-eye nipple array is an alternative approach to reduce the refractive index gap on the air/VO₂/substrate interfaces to enhance the thermochromic performance of VO₂ nanomaterials.

Taylor et al. (2013)^[35] reported the FDTD (finite difference time domain) simulation of VO₂ coated silica nipple arrays on glass substrate (Figure 2.14). In this design, the silica nipple arrays were assigned as a local hexagonal arrangement. A rule of $W=P\sqrt{4/3}-2C$ could be used to achieve the highest VO₂ coating density that maintains the peak-to-trough height difference simultaneously, where W is the base-width, P is the pitch size and C is the VO₂ coating thickness. The P value was optimized to be ~ 130 nm, since 99.9%/99% of visible light up to angles of 25.9°/42.0° cannot resolve the structure under this pitch size. The H range should be 250 to 1200 nm, in order to make sure the antireflection efficient. A combination of $T_{lum}=57.5\%$, $\Delta T_{sol}=19.4\%$ could be reached with parameters $H=700$ nm, $W=134$ nm, $C=8$ nm and $P=130$ nm.

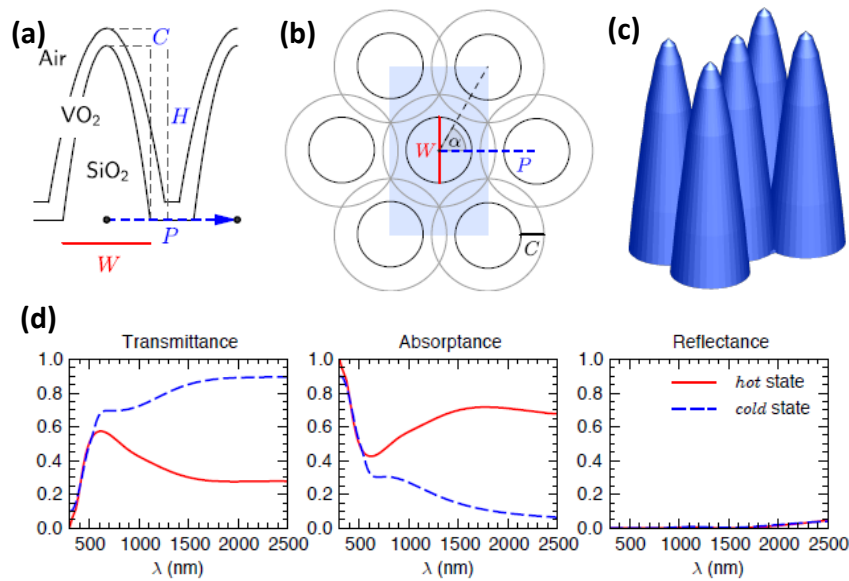


Figure 2.14 Elevations of a nanotextured surface on the side (a) and top (b) with circular paraboloid cones arranged hexagonally (c). P is the Pitch, W is base-width and C is the

VO₂ coating thickness. In (b), under $W=P(4/3)^{1/2}-2C$, both the height difference from peak to trough and the areal density at the air/VO₂ interface are maximized. (d) FDTD simulation of normal-incident transmittance, absorptance as well as reflectance spectra for a moth-eye smart-window with $H = 700$ nm, $P = 130$ nm, $C = 8$ nm and $W = 134$ nm.

The calculated $T_{\text{lum}}=57.5\%$, $\Delta T_{\text{sol}}=19.4\%$.^[35]

2.2.3 Nanothermochromism

In the nanothermochromic design, the VO₂ nanomaterials are embedded into the dielectric matrix, e.g. silica, polymer, which show much increased luminous transmittance and enhanced solar modulating abilities, mainly ascribed to the best matches of optical parameters at the air/VO₂@matrix/glass interfaces.^[41]

Li et al. (2010) reported a calculation of the nanothermochromic model based on effective medium theory, which revealed the significant decrease of luminous absorption jointly with improved T_{lum} and ΔT_{sol} .^[41] As shown in Figure 2.15, four cases of models, including spherical (Figure 2.15-a), prolate spheroids oriented (Figure 2.15-b), oblate spheroids oriented (Figure 2.15-c) and prolate spheroids randomly oriented (Figure 2.15-d) VO₂ nanoparticle suspension in dielectric mediums were considered in the effective medium theory based calculations. The calculation results (Figure 2.15-e) uncovered that the best combination of T_{lum} and ΔT_{sol} could be obtained under the VO₂ shape of spheres for the randomly oriented suspension with a filling factor of 0.01.

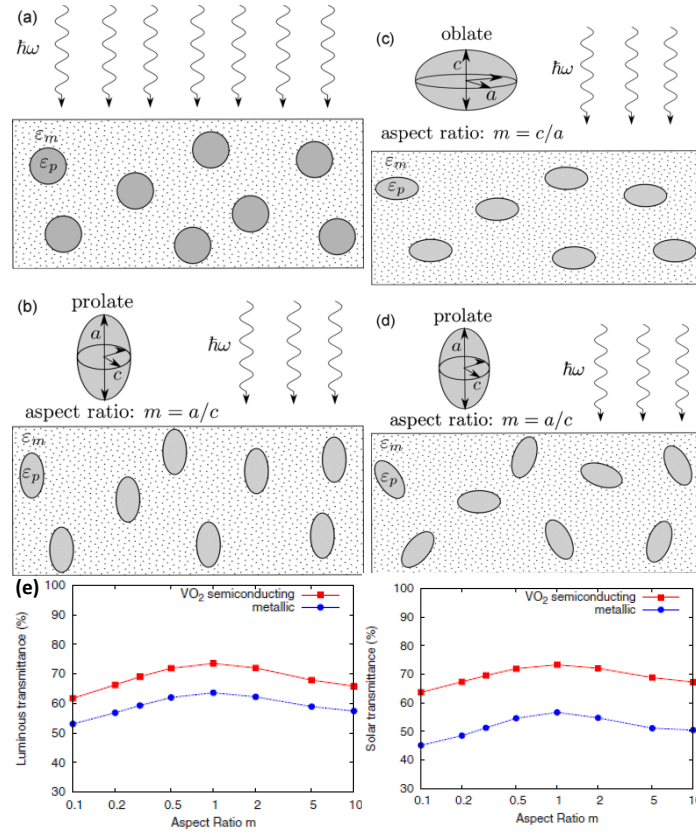


Figure 2.15 Structural models for composites of nanoparticles embedded in a medium, where the dielectric function for the particle and the medium is corresponding ϵ_p and ϵ_m . The nanoparticles are taken to be spherical (a), oriented prolate (b), oriented oblate (c), and random prolate (d) with major a and minor c axes. The m , aspect ratio, is defined for the oblate and PSs. The photon energy $\hbar\omega$ for the electromagnetic radiation has also been shown. (e) Integrated luminous and solar transmittance of VO_2 nanoparticles with aspect ratio m and a filling factor 0.01, which are dispersed in a dielectric medium. The VO_2 spheroids are oriented randomly.^[41]

Granqvist et al. (2011)^[42] simulated the optical properties of a core (medium) - shell (VO_2) nanothermochromic structure using the effective medium theory. As depicted in Figure 2.16, the dielectric medium core with the dielectric constant ϵ_c (n_c) and diameter x is coated with VO_2 shell with dielectric constant ϵ_s (n_s) and thickness t (Figure 2.16-d). The core-shell structures are suspended in a dielectric medium with the dielectric constant ϵ_m (n_m). The calculation reveals that the VO_2 hollow nanothermochromic structure (vacuum core with $n_c=1$) exhibits the best

thermochromic performance with the largest ΔT_{sol} (Figure 2.16-c) at the sacrifice of a somewhat lowered T_{lum} (Figure 2.16-a, b).

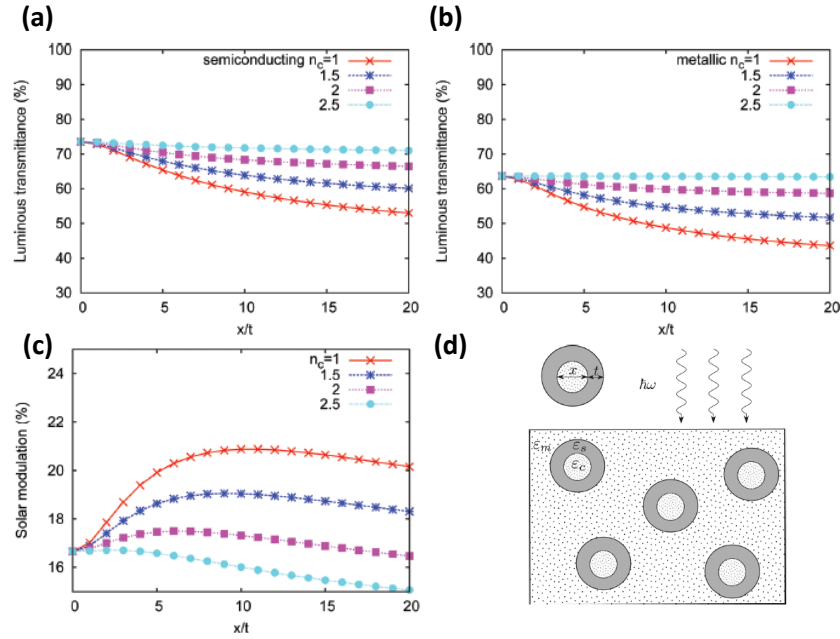


Figure 2.16 Luminous transmittance at semiconducting (a) and (b) metallic states as well as solar modulation (c) for spherical shells (thickness t) of VO_2 surrounding cores (diameter x) with the shown values of the dielectric constant n_c and embedded in a dielectric medium represented by $n_m=1.5$. Data are shown for $\tau < \tau_{\text{cr}}$ (semiconducting VO_2) and for $\tau > \tau_{\text{cr}}$ (metallic VO_2). The material was $5 \mu\text{m}$ thick and contained 1 vol. % of VO_2 . (d) Structural model representing core-shell nanoshells in a surrounding medium under irradiation of photons with energy $\hbar\omega$.^[42]

2.2.4 Periodic patterning

Periodic patterning is a method to fabricate periodically arranged VO_2 nanograins on to substrate to modulate the luminous transmission as well as the solar modulating abilities.

Liu et al. (2015)^[43] calculated the thermochromic performance of VO_2 thin films with periodic patterned nanoholes using FDTD method. The nanoholes with the dimension larger than visible length have the capability to largely enhance the

visible transmission whilst the VO₂ nanograins at the edge keep the ability to modulate the solar energy, which could totally improve the thermochromic performance of VO₂ thin films as the functional coating for smart window. As shown in Figure 2.17 (a-c), three kinds of nanoholes, i.e. square cells with square holes (a), square cells with circular holes (b), hexagonal cells with circular holes (c), were taken into account for the FDTD calculation. The calculation result revealed that the square cells with square holes ($p=180$ nm, $l=150$ nm) showed a performance with $T_{lum}(20^{\circ}\text{C} / 100^{\circ}\text{C})=57.6/63.4\%$, $\Delta T_{sol}=4.9\%$ (Figure 2.17-d); the square cells with circular holes ($p=180$ nm, $r=80$ nm) suggested a combination of $T_{lum}(20^{\circ}\text{C} / 100^{\circ}\text{C})=51.5/51.8\%$, $\Delta T_{sol}=10.7\%$ (Figure 2.18-e); the hexagonal cells with circular holes ($p=180$ nm, $r=80$ nm) exhibited a thermochromic property with $T_{lum}(20^{\circ}\text{C} / 100^{\circ}\text{C})=63.3/64.0\%$, $\Delta T_{sol}=9.2\%$ (Figure 2.17-f). Figure 2.17-g suggests that under the similar filling factor (~ 0.2), the square cells with square holes could give the best combination of $T_{lum}(20^{\circ}\text{C} / 100^{\circ}\text{C})=31.1/26.8\%$ and $\Delta T_{sol}=14.7\%$.

Lu et al. (2016)^[36] fabricated a real case of micropatterned VO₂ thin films, which showed the enhanced thermochromic properties. As shown in Figure 2.18 (a-f), the micropatterned VO₂ thin films with the mesh size 325/230/55 μm were produced on glass sides, which showed the applicable visible transmission. The UV-Vis-NIR test as shown in Figure 2.18 (g, h) revealed that a combination of average T_{lum} and ΔT_{sol} upto 43.3% and 14.9%, respectively could be reached at thickness=1000 μm and mesh size=55 μm .

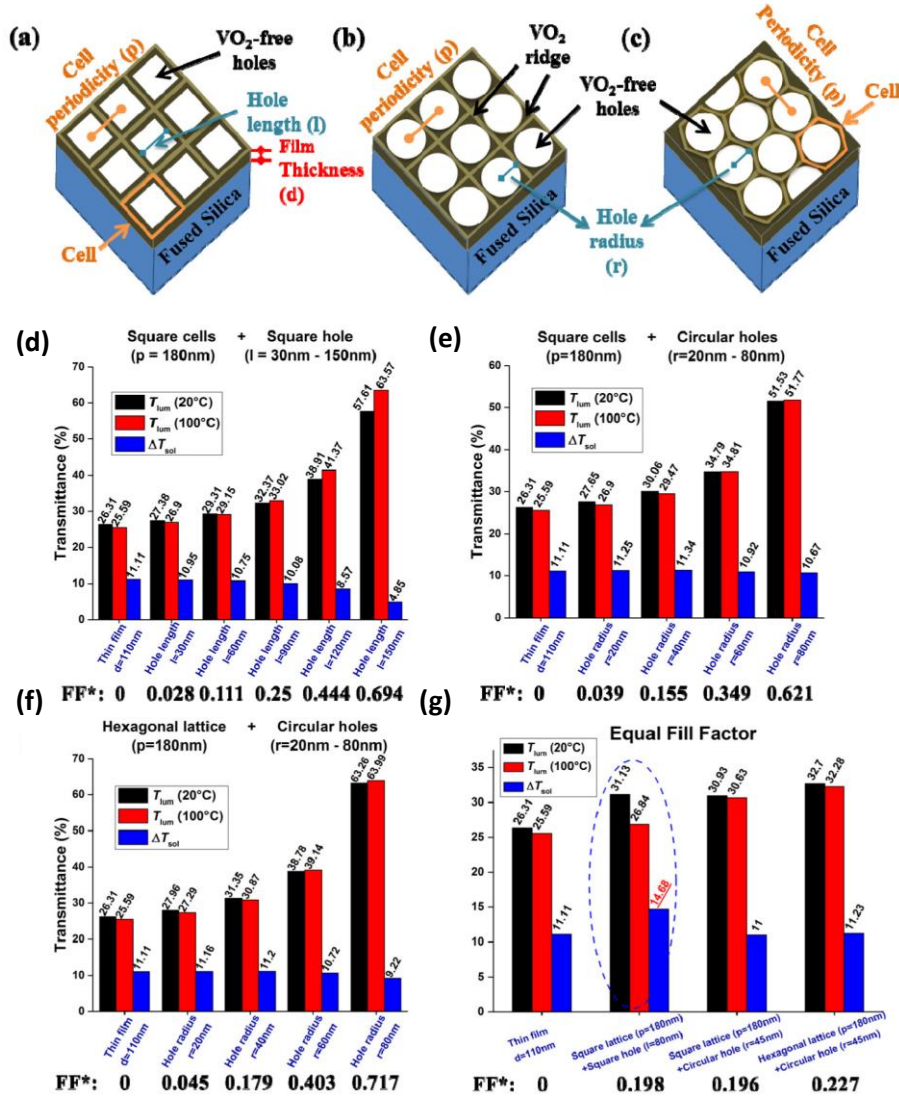


Figure 2.17 Three 3D models for perforated VO₂ thin films, (a) square lattices composed of square holes, (b) square lattices composed of circular holes and (c) hexagonal lattices composed of circular holes that are packed densely with defined holes and periodicity as labelled. Nanogrid parameters v.s. thermochromic properties (d-g). (d) Length varied from 30 nm to 150 nm (Square holes in square cells); (e) Radius varied from 20 nm to 80 nm (circular holes in square cells); (f) Radius varied from 20 nm to 80 nm (circular holes in hexagonal cells); (g) Four kinds of structural systems with similar filling factors. ^[43]

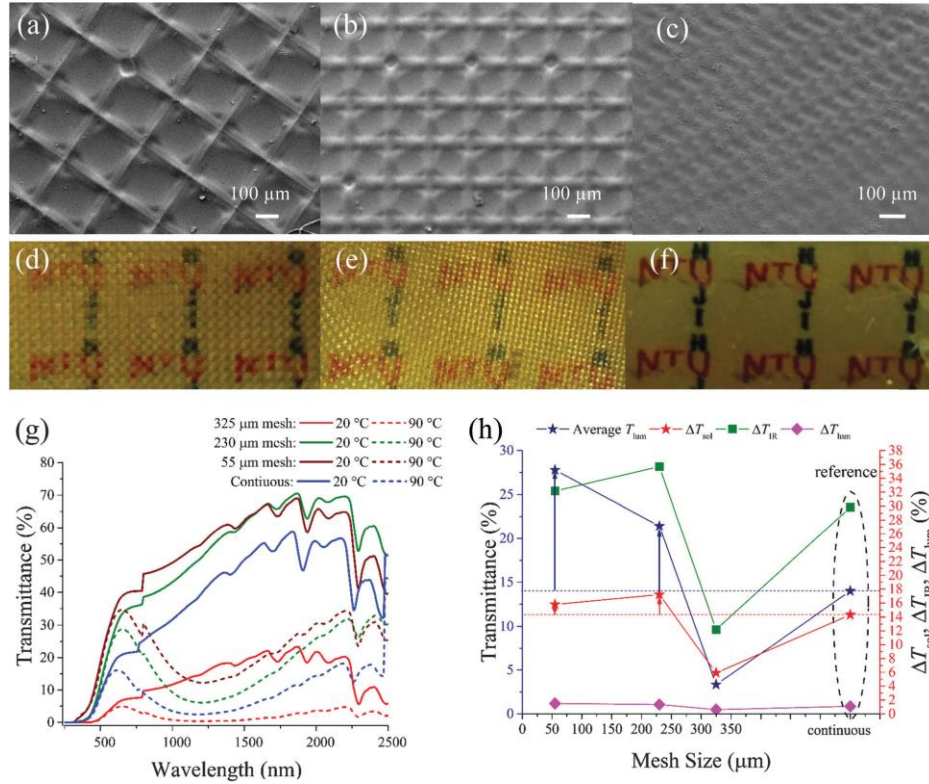


Figure 2.18 Effect of periodicity (the mesh opening size) on performance of the VO₂ thin film. SEM images for the VO₂ thin films with the mesh size (a) D= 325 μm, (b) D= 230 μm, and (c) D= 55 μm. Real VO₂ thin films as shown in (d) D= 325 μm, (e) D= 230 μm, and (f) D= 55 μm. (g) UV-Vis-NIR transmission spectra for thin films with D = 1000 μm with the VO₂ solid content 0.5 wt%; (h) mesh size dependent ΔT_{lum} , ΔT_{sol} and ΔT_{IR} .

[36]

2.2.5 Porosity

The nanoporous morphology of the VO₂ thin film could effectively reduce the refractive index and thus minimize the reflection as well as the absorption, which is critical for attaining high thermochromic performance.

As for the nanoporous formation in the VO₂ thin films, the application of polymer-assisted deposition (PAD) is an effective approach to increase the porosity. The precursor-polymer system for the PAD used for VO₂ porous thin films could be VOCl₂-PVP (Polyvinylpyrrolidone) reported by *Hu et al.* (2016,

Figure 2.19-a)^[44] and *Kang et al.* (2011, Figure 2.19-e)^[45] or V_2O_5 sol-CTAB (cetyltrimethyl ammonium bromide) reported by *Xu et al.* (2012, Figure 2.19-d)^[46]. An alternative approach for nanoporous fabrication is utilizing PS (polystyrene) sacrificing colloidal template to produce periodic nanoporosity. *Zhou et al.* (2013)^[47] reported the fabrication of periodic porous VO_2 thin film with enhanced maximum visible transmittance as high as 81.0%, where the dimension of the porous could be controlled by the precursor concentration (Figure 2.19-b). In addition, *Yang et al.* (2012)^[48] reported the synthesis of nanotubular/nanoporous VO_2 layers (Figure 2.19-c) with interesting supercooling effects. As calculated in Figure 2.19-f as plots of thickness, porosity versus T_{lum} , ΔT_{sol} , ΔT_{sol} could be increased without sacrificing T_{lum} by increasing the thin film porosity.^[45] And an optimized combination of $T_{lum}=45\%$, $\Delta T_{sol}=18\%$ could be attained under 40% porosity and 125 nm film thickness.

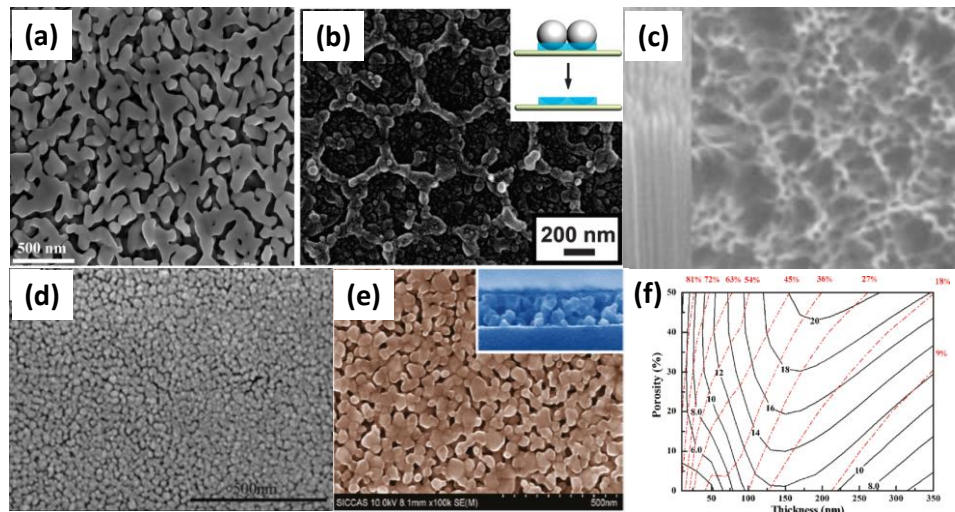


Figure 2.19 Nanoporous VO_2 thin films. (a) SEM image of porous VO_2 thin film prepared with $VOCl_2$ precursor solution.^[44] (b) SEM image of porous VO_2 thin film starting from sacrificing colloidal PS template.^[47] (c) SEM image of anodically grown nanotubular VO_2 thin film.^[48] (d) SEM image of nanoporous VO_2 thin film prepared with V_2O_5 sol.^[46] (e) SEM image of nanoporous VO_2 thin film prepared by a polymer-assisted deposition.^[45] (f) Computed luminous transmittance in an insulator state (T_{lum} , red dotted lines) and solar modulation between MIT (ΔT_{sol} , black solid lines) as a function of the thickness and porosity of the VO_2 films.^[45]

2.2.6 Doping

Vanadium dioxide exhibits a phase transition (MIT) across the critical temperature (τ_c) around 68 °C, where the sharp transition as well as the low τ_c determine how smart (quickly response to the environment) of the this material. The doping of metal cations in the VO₂ lattice is an efficient way to decrease the τ_c (Table 2.3).^[6] The cations with high valence state (W⁶⁺,^[49, 50] Mo⁶⁺,^[51] Nb⁵⁺,^[51] Ta⁵⁺^[52]) could result in extra free electrons (V³⁺ impurities), which can reduce the bandgap in insulating state, minimize the energy barrier of MIT, and thus decrease the τ_c accordingly. On the other hand, the cations with ionic radii larger than that of V⁴⁺ ($r=0.058$ nm), such as Mg²⁺ ($r=0.072$ nm)^[53] could lead to the extra strain, which can also reduce the τ_c effectively. On the contrary, the cations with low valence state and smaller/nearer ionic radii, e.g. Al³⁺ (0.0535 nm), Fe³⁺ (0.055 nm) and Cr³⁺ (0.0615 nm) could only give rise to the increase of τ_c .^[6]

Table 2.3 Doping effect of cations on modulating the thermochromic performance of VO₂.

Dopant	T_{lum}	ΔT_{sol}	τ_c	Mechanism	Ref.
W ⁶⁺	↓	↓	↓ (~20-26 °C/at.%)	e ⁻ ↑	[49, 50]
Nb ⁵⁺	↓	↓	↓ (~2 °C/at.%)	e ⁻ ↑	[51]
Mo ⁶⁺	↑	↓	↓ (~3 °C/at.%)	e ⁻ ↑	[51]
Ta ⁵⁺	—	—	↓	e ⁻ ↑	[52]
Mg ²⁺	↑	↑	↓ (~3 °C/at.%)	h ⁺ ↑	[53]
Cr ³⁺	↑	↓	↑	h ⁺ ↑	[6]
Al ³⁺	—	—	↓ (~2.7 °C/at.%)	h ⁺ ↑	[6]
Fe ³⁺	—	—	↓ (~6 °C/at.%)	h ⁺ ↑	[6]

As for thermochromic properties, many efforts have been carried out to enhance the thermochromic properties of VO₂ nanomaterials through doping approaches. Compared with VO₂ continuous thin films, VO₂ nanocomposite shows obvious advantages in solar modulating abilities.^[41] Gao et al. (2012)^[57] fabricated antimony (Sb³⁺) doped VO₂ nanocomposite foils with $T_{lum}=35\%$, $\Delta T_{IR, \lambda=2000\text{ nm}}=40.6\%$, and the τ_c could be tuned in the range of 55-68 °C (Figure 2.20-b). Shen et al. (2014)^[53] reported the Zr-doped and W–Zr-codoped VO₂ nanocomposite.

The Zr doping has the ability to decrease τ_c from 68.6 to 64.3 °C at 9.8 at.% doping level, increase T_{lum} up to 60.4%, improve ΔT_{sol} up to 14.1% and modify the color by lightening the yellowish color. The τ_c could be further reduced to 28.6 °C through W–Zr-codoping (Figure 2.20-c). Zhou et al. (2013)^[53] reported a composite foil fabricated from Mg doped VO₂ nanoparticles with T_{lum} =54.2% and ΔT_{sol} =10.6% (Figure 2.20-d).

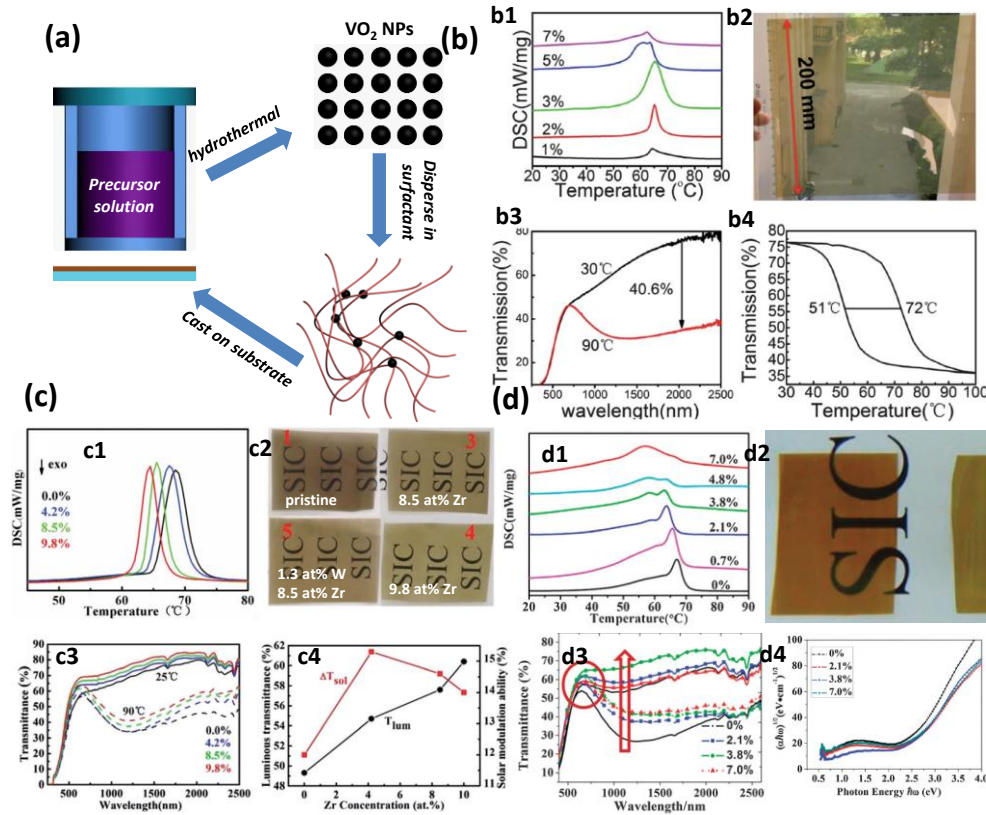


Figure 2.20 (a) Schematic illustration for fabrication of VO₂ nanocomposite foils. (b) DSC curves of VO₂ powders with different amounts of Sb³⁺ doping (b1), an image of the film on PET via casting (b2), the optical transmittance spectra (b3) and the %T hysteresis loop at the wavelength 2000 nm (b4).^[57] (c) DSC heat flow of the VO₂ nanoparticles doped with different quantities of Zr⁴⁺ (c1), the graphs of Zr-doped and W–Zr-codoped VO₂ foils (c2), the transmittance spectra at 25 °C and 90 °C (c3), the T_{lum} and ΔT_{sol} (c4) for the VO₂ foils doped with Zr under different atomic doping levels.^[53] (d) DSC heat flow of the VO₂ nanoparticles doped with Mg²⁺ (d1), VO₂ foil doped with 0.0 (left), 2.1 at% (right) Mg (d2), UV-Vis-NIR transmittance spectra of the Mg-doped VO₂ foils (d3), the relationship between $(a\hbar\omega)^{1/2}$ and $\hbar\omega$ for the VO₂ foils doped with Mg under various

atomic doping levels (d4).^[53]

2.3 PhD in context of literature

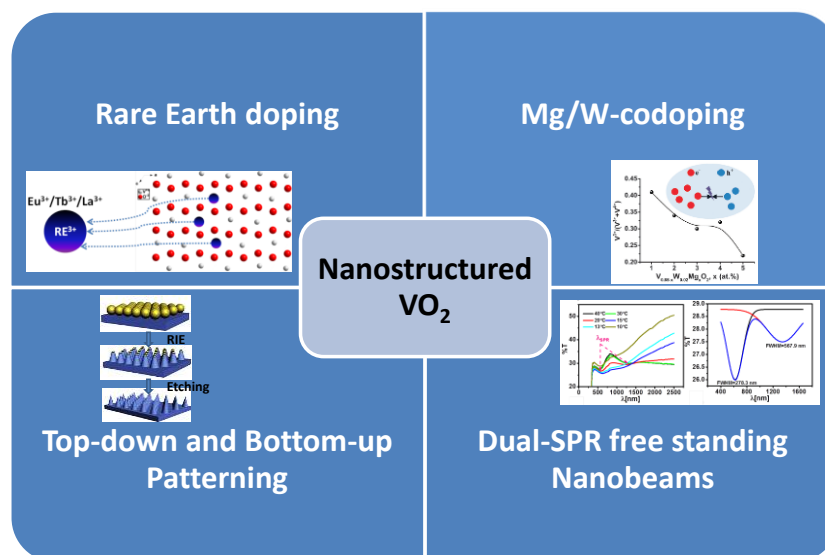
As demonstrated in the literatures, as a phase transition material, VO₂ has promising potential applications in thermochromic smart windows for energy saving. However, the practical application of this material can still not be expected due to the challenges in the following: a) τ_c is far away from the room temperature; b) Visible transmission is not adequate for the eye vision; c) Solar modulating ability cannot reach the requirement of energy saving; d) The fabrication of VO₂ products (thin films, pigments) is not cost-effective.

In this thesis, a systematical research in the following has been performed to enrich the comprehensive understanding of the MIT mechanism of VO₂ as well as the applicable approaches to promote the practical applications as smart windows.

- i) Rare Earth doping and Mg/W-codoping in VO₂;
- ii) Top-down and bottom-up patterned VO₂ surface;
- iii) Hydrothermal assembly of VO₂ free standing nanostructures and their thermochromic properties.

The contribution of this thesis to the development of VO₂ thermochromic materials is as the follows (scheme 2.1): a) systematically investigated the Rare Earth doping in VO₂ and proposed the RE doping mechanism in terms of competition between the extra strain and h^+ carriers; b) proposed the Mg/W-codoping mechanisms in terms of counteraction effect of free electron (e^-) and hole (h^+) carriers in the Mg/W-codoped VO₂ thin films; c) Established the top-down and bottom-up assembly methods for the patterned VO₂ surface with enhanced thermochromic properties; d) developed facile hydrothermal method for

the synthesis of free standing pristine and doped VO_2 nanostructures with intriguing properties.



Scheme 2.1 Illustration of our contribution to the VO_2 thermochromic materials.

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Chapter 3

Experimental Methodology

The techniques for synthesis, characterization of VO₂ nanomaterials shown in this thesis and the principles underlying the techniques will be discussed in detail. The techniques include the Sol-Gel, Hydrothermal reaction for synthesis; XRD, XPS, TEM, SEM, AFM for phase and morphology; TGA, DSC for thermal stability and phase transition; UV-Vis-NIR spectrometer equipped with heating/cooling stage for temperature dependent optical properties as well as Ellipsometry for optical parameters.

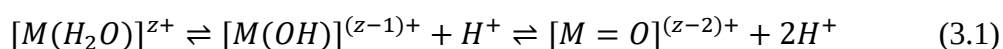
3.1 Rationale for selection

In this thesis, series of VO₂ thin films and nanostructures will be prepared for thermochromic applications. Due to the low-cost and easy-to-handle advantages, the sol-gel and hydrothermal methods are selected for preparation of thin films and nanostructures, respectively. For the determination of VO₂ phase in the product, XRD is selected to characterize the crystal lattice as the wavelength of X-ray (Cu-K α =1.5406 Å) is just similar to the lattice parameters and the scattering of X-ray in the technique is elastic; XPS is selected to confirm the stoichiometry due to the oxidation-state dependent binding energies. The diffraction function of TEM can also be used to analyze the phase information of VO₂. As for the morphologies, the size, shape and distribution of the grains could be monitored by the SEM, TEM and AFM, which could collect the secondary electron, transition electron and force signals, respectively. With respect to the thermal stability and phase transition, TGA and DSC are selected to monitor the weight loss and specific heat flow during heating to get the decomposition and phase transition temperatures. The UV-Vis-NIR spectrometer is selected to record the temperature dependent transmittance and reflectance owing to its wavelength range from 200 to 3000 nm. The ellipsometry is used to get the optical parameters of VO₂ thin films due to its advantages in investigating the dielectric properties of thin films, e.g. complex refractive index or dielectric function.

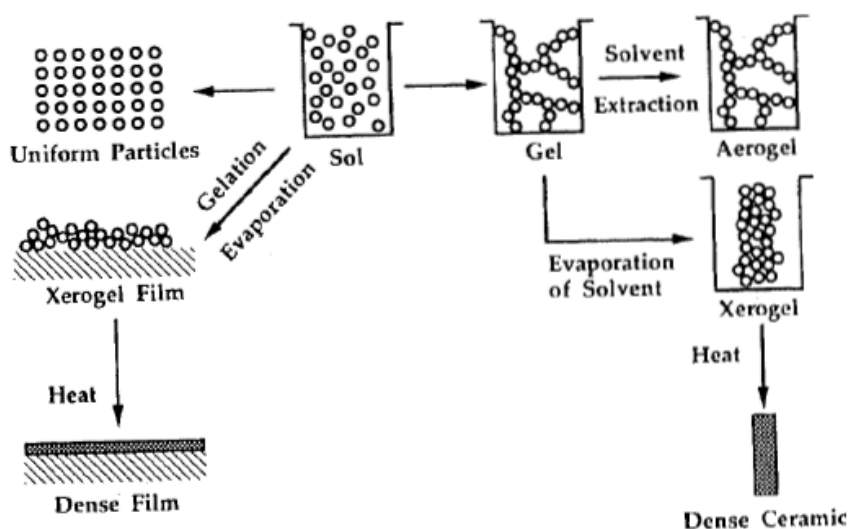
3.2 Technologies for synthesis

3.2.1 Sol-gel technique^[1]

In a normal inorganic sol-gel process (scheme 3.1), a sol or colloidal suspension of starting compounds in water is firstly prepared through hydrolysis (Equation 3.1).



The formula of the sol can be written as $[\text{MO}_N\text{H}_{2N-h}]^{(z-h)+}$, where N is the number of water molecules coordinated to the M centers and h is termed as the molar ratio of hydrolysis. Especially, the $[\text{MO}_N\text{H}_{2N}]^{(z)+}$ ($h=0$) and $[\text{MO}_N]^{(z-2N)+}$ ($h=2N$) are regarded as aquo-ion and oxo-ion sol, respectively. Moreover, the sol will be oxo-hydroxo ($[\text{MO}_x(\text{OH})_{N-x}]^{(N+x-z)-}$, $h>N$), hydroxo-aquo ($[\text{M}(\text{OH})_x(\text{H}_2\text{O})_{N-x}]^{(z-x)+}$, $h<N$), and hydroxo complex ($[\text{M}(\text{OH})_N]^{(N-z)-}$, $h=N$) in special conditions.



Scheme 3.1 Schematic illustration of a sol-gel process from a colloidal suspension to final uniform particles, dense films, and dense ceramics.^[1]

The precise nature of the sol depends on the charge (z), coordination number (N) and the electronegativity of the central metal as well as the pH of the aqueous solution.^[2] The effect of z and the pH on the chemical state of the sol has been summarized by Kepert (1963)^[3] as illustrated in Figure 3.1. As depicted in Figure 3.1, the metal center with $z \leq 4$ in the sol is mostly coordinated with the water (aquo sol) or OH^- (hydroxo sol) in the whole pH range (0-14). As for the metal center with $z \geq 5$, the sol is in the state hydroxo or oxo in the whole pH range. It should be noticed that the sol with the high valence state metal center ($z \geq 7$), O^{2-} is the only ligand contributing to the coordination environment of the metal center.

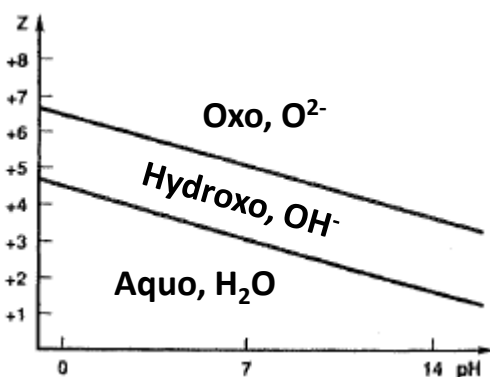
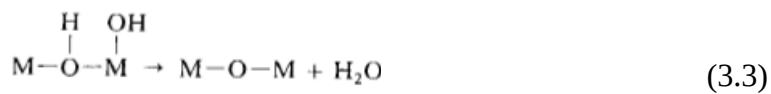
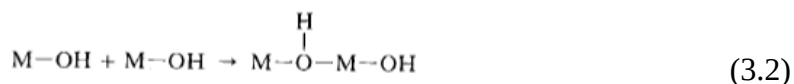


Figure 3.1 Diagram of charge v.s. pH, indicating the ‘aquo’, ‘hydroxo’ and ‘oxo’ domains.^[3]

In the next step, the sol is coated onto the substrate to form xerogel film through gelation and evaporation (Equation 3.2, 3.3).^[1]



Finally, the metal oxide thin films are obtained through further annealing in air or under inert atmospheres.

3.2.2 Hydrothermal technique^[4]

Hydrothermal is a term, which is originated from Geology, describing the formation of rocks and minerals in the earth’s crust under supercritical water with elevated temperature and pressure.^[4]

As for the water used as the solvent in hydrothermal reactions, it exhibits a slow increase of saturation vapor pressure below 200 °C, but then undergoes a sharp increase of pressure with further heating (Figure 3.2), which benefits the dissolving of minerals that is insoluble at normal conditions, and therefore help to recrystallize or generate new crystalline products via nucleation and crystal growth under the supercritical conditions.

In a normal hydrothermal apparatus, an aqueous suspension or solution of reagents transferred into a Teflon liner is sealed in a stainless steel autoclave (Figure 3.2) for autogenous pressure reaction at the temperature around 200 °C.

Considering a hydrothermal system, where n_A mol of solid A is partially dissolved (n_{1A} mol) in n_B mol of solvent B, ^[4] the free energy (G) will be Equation 3.4:

$$G = n_A \mu_A + n_{1A} \mu_{1A} + n_B \mu_B \quad (3.4)$$

where μ is the corresponding chemical potential. For the continuous dissolution of the solid A in solvent B, the change in G under constant pressure and temperature should be:

$$dG/dn = \mu_{1A} - \mu_A \quad (3.5)$$

When $\mu_{1A} < \mu_A$, the process can occur on its own owing to the negative ΔG . If $\mu_{1A} > \mu_A$, the substance from solution B will participate in the crystallization, and when $\mu_{1A} = \mu_A$, an equilibrium is reached.^[4]

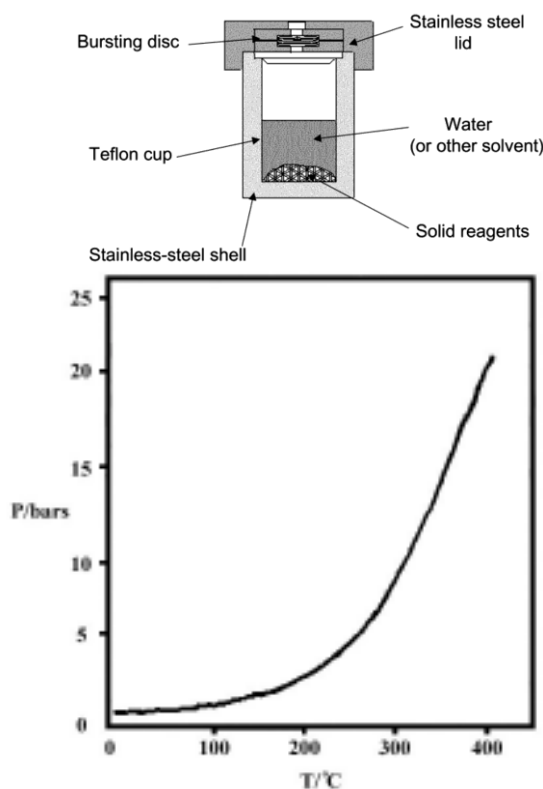


Figure 3.2 Hydrothermal autoclave from KPRBLOG (up) and temperature dependence of saturation vapor pressure of water (down)^[4].

In the standard hydrothermal designs, the reactions are carried out under isothermal and isobar conditions without stirring (Figure 3.3a).^[5] As shown in Figure 3.3a, to begin with, the hydrothermal fluid contains only water and precursor materials (point I) and it becomes more and more concentrated with time. At point II, it reaches the supersaturation state, where the precursor materials can still be dissolved even the concentration has been above the solubility limit. At point III, a certain level of supersaturation, the spontaneous crystallization finally takes place, resulting in the decrease of concentration of the fluid.^[5] Actually, both of the nucleation and crystal growth occur in the supersaturation region, and the rates of the nucleation as well as crystal growth are strongly correlated with the supersaturation level as illustrated in Figure 3.3b. It can be clearly observed that the rate of nucleation will be larger than that of crystal growth at high supersaturation level, where nanomaterials can be expected in the products.^[5]

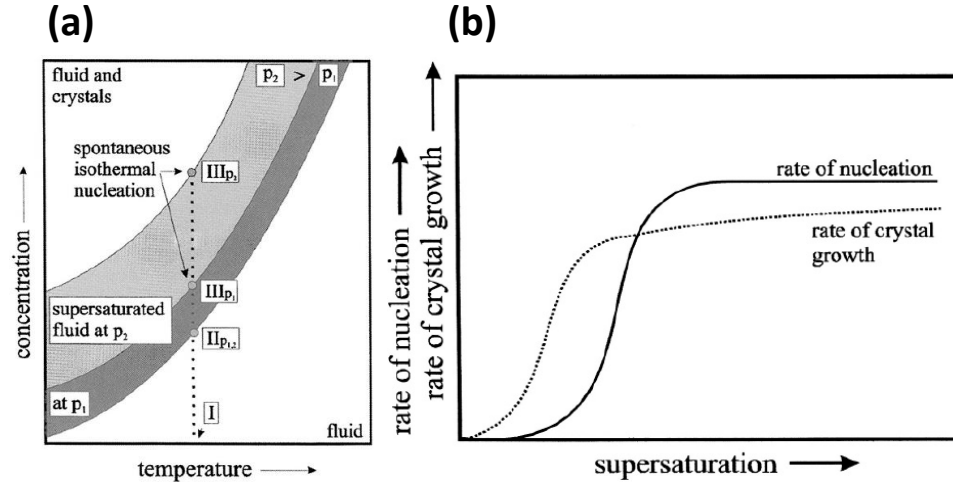


Figure 3.3 (a) Isothermal-isobar hydrothermal processing: At I) only water and precursor are present. Between the point I) and III): time-dependent precursor materials dissolution. (b) Supersaturation dependent isothermal rate of nucleation and crystal growth.^[5]

3.3 Technologies for Characterization

3.3.1 X-ray diffraction

X-ray is a form of electromagnetic radiation with the wavelength 0.01-10 nm and photon energy 10-100 KeV. Those X-rays with the wavelength below 0.1 nm and photon energy above 10 KeV are called hard X-rays,^[6] which can be used to determine the crystal structures by X-ray crystallography owing to the atomic scale wavelength and the technique is called X-ray diffraction (XRD).

In the determination of crystal structures, XRD works based on Bragg's diffraction law:^[7]

The constructive interference only occurs when the path difference between two X-rays ($AB+BC=2d_{hkl}\sin\theta$) equals to multiples of wavelength ($2d_{hkl}\sin\theta=\lambda$, Figure 3.4).

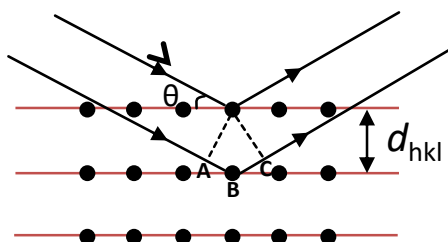


Figure 3.4 Diffraction of X-rays by the (h, k, l) face of a crystal.

Figure 3.5 shows an illustration of normal XRD diffractometer. In the diffractometer, there are mainly five functional parts: X-ray source (A), primary optics (B), sample holder (C), secondary optics (D) and the detector (E).

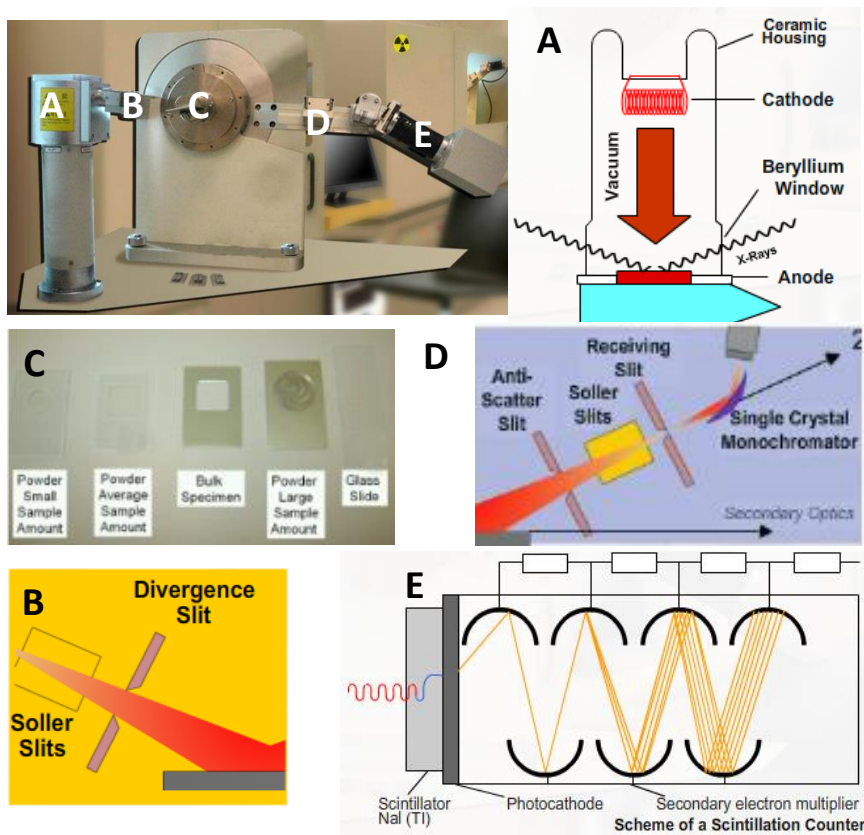


Figure 3.5 XRD diffractometer and its functional parts. Copy right 2007-2008, School of Materials Science & Engineering, NTU & Roots Excellence.

X-ray source. The source of the diffractometer is an X-ray tube, which is composed of ceramic housing, cathode, beryllium window and an Anode. The cathode is a tungsten

filament and the anode is normally a copper target. The X-rays are generated by shooting the anode with the electrons emitted from the cathode and accelerated by a potential of several tens of thousands volts. In the shooting process, the nuclear cores decelerate the electrons quickly and the passing through generates the white radiation, then the hitting of inner shell electrons gives rise to the transition of higher level electrons to the lower level positions, leading to characteristic radiations. The most intense characteristic radiations are $K\alpha_1$, $K\alpha_2$ and $K\beta$. $K\alpha_1$ and $K\alpha_2$ are usually utilized in the XRD characterizations.

Primary optics. The primary optics contains soller slits and divergence slits, sometimes also includes a monochromator. The soller slits are used to reduce the axial divergence of the incident X-ray beam to below 6° ; benefiting a better peak symmetry. The divergence slits are used to reduce the height divergence, which narrows the peaks and increases the resolution. The optional monochromator is used as a filter to absorb most of the $K\beta$ lines and the white radiation to further increase the resolution.

Secondary optics. The secondary optics includes the anti-scatter slits, soller slits, receiving slits and a secondary monochromator. The anti-scatter and receiving slits are used to reduce the height divergence and remove the diffusely scattered X-rays from the amorphous and air scattering. The secondary monochromator is used to suppress the white radiation and $K\beta$ lines, and is also utilized to remove the fluorescent radiation originating from the sample.

Detector. The mostly used X-ray detector is the scintillation counter, which consists in a scintillator that emits visible light on exposure to X-rays.

After attaining a XRD pattern shown as plots of intensity v.s. 2θ , the data can be indexed with 'Match' software by comparing with the standard mineral patterns.

3.3.2 X-ray photoelectron spectroscopy

XPS (X-ray photoelectron spectroscopy) is a powerful method to characterize the surface chemical information, including the elemental composition, empirical formula, chemical state and electronic state of elements.

In a typical XPS spectrum (Figure 3.6), the number of electrons per unit time (counts) is recorded in a range of binding energy. Every element in the surface (7-11 nm) exhibits particular XPS peaks at its characteristic binding energy positions. Each peak corresponds to a special orbital (eg. 1s, 2p, 3d, 4f) of the electron in the element, and the number of counts at the peaks is directly related with the abundance of the elements in the surface.^[8]

After getting a XPS spectrum, the peaks are firstly calibrated with the standard C 1s binding energy (284.6 eV), then the back-ground base line is generated using the Shirley+Linear method and the peaks are fitted and/or split using the least-square approach. Finally, the concentration of the elements (x_i) is calculated using the equation^[9]:

$$x_i = \frac{I_{x,i}/\phi_i}{\sum_j I_{x,j}/\phi_j} \quad (3.6)$$

Where $I_{x,i}$ is the photon electron signal intensity (usually be replaced by the peak area) and the ϕ_i is the sensitivity factors for the elements.

The valence state of the cations for the elements could also be analyzed by fitting and splitting the particular wide peaks of the elements, which can be used for stoichiometry determination as well.^[10]

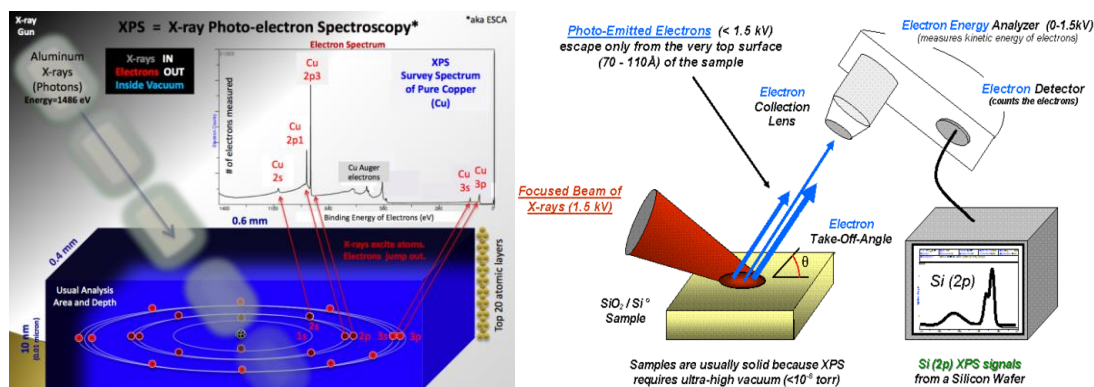


Figure 3.6 Illustration of photo-electric effect in XPS (left) and the high resolution XPS scan of the Si 2p for SiO₂/Si sample (right). Copy right from Bvcris.

3.3.3 Scanning electron microscopy

Scanning electron microscopy (SEM) is a technique to characterize the surface morphology by collecting and analyzing the secondary electron signals, and analyse the element composition by the additional EDX detectors. The resolution can be as high as 1.5 nm.

In a typical SEM instrument (Figure 3.7), there are mainly four parts: electron gun, electron column, specimen chamber and main control panel.

Electron gun. There are two types electron gun for the SEM, i.e. thermionic gun and field emission gun. Both are composed of three parts, including filament, wehnelt cap and anode. The thermoelectrons are generated by applying a high accelerating voltage between the filament and the anode, and thus resulting in an electron beams streaming down in the SEM column. The wehnelt cap/cylinder composed of thermionic devices is used to focus and control the electron beams.^[11]

Electron column. There is mainly a magnetic lens system (condenser lens, objective lens, scanning coils) in the electron column, which is used to focus and illuminate the specimen to get the image of surface topography. The condenser lens is used to

control the intensity of the irradiation electron beam and the objective lens is used to focus the scanning electron beams with small spot size onto the specimen surface.

Energy Dispersive X-ray (EDX). EDX detector on the SEM is used to characterize the element composition and/or the element distribution on the sample surface owing to its ability to collect the characteristic X-ray lines of different elements.

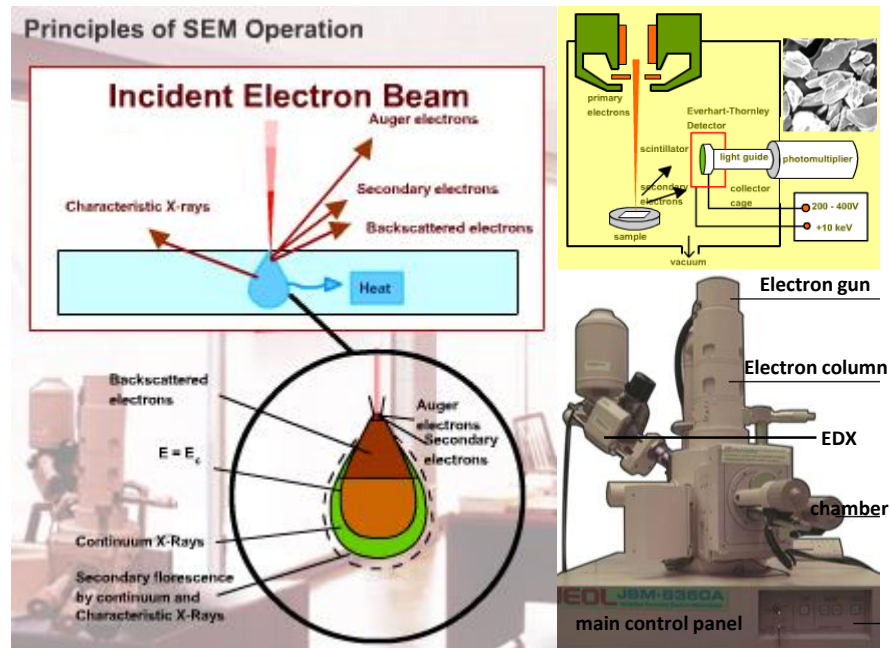


Figure 3.7 Principle of SEM operation (left), illumination for obtaining a secondary electron image in the electron column (right up) and view of a typical SEM instrument (right down).

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Field-emission SEM is a special SEM that equipped with field emission gun liberating electrons, which shows higher brightness, longer operating time, and could exhibit a better resolution.

3.3.4 Transmission electron microscopy

Transmission electron microscopy (TEM) has the advantage of super resolution (1.9 Å) in observing the morphology and lattice information of nanomaterials through high magnification as well as high resolution imaging system. Besides, the advance research on crystal structure, chemical composition and doping can also be performed with TEM via diffraction pattern, X-ray and electron-energy analysis.

In a typical TEM instrument, there are three main parts, including illuminating system, imaging system and a recording system (Figure 3.8). The illuminating system contains the electron gun, condenser lens system. The imaging system consists of objective lens, intermediate lens system as well as the projector lens and viewing chamber. The recording system is the Charge-Coupled Devices (CCD) system.

Operation principle. As shown in Figure 3.8, the electron beam generated from the electron gun is firstly transferred onto the specimen by the condenser lens system. The 1st condenser lens is used to focus the electron beam onto the optical axis and control the spot size. The 2nd condenser lens is used to control the brightness of the electron beams and align the beam passing through the optical axis. At the second step, the electron beam passes through the specimen, and is then focused by the objective lens system at various diameters. At the third step, the field strength is adjusted by the intermediate lens system, i.e. high strength for imaging and weak strength for diffraction. At the fourth step, the magnification is tuned by the projector lens system. The first projector lens is used to magnify the image and invert it for proper orientation. The second projector lens is used to focus the image onto the fluorescent screen for viewing.^[12]

Sample preparation. For the powder sample, it is firstly grinded to fine particles, and then dispersed in ethanol under ultrasonic and finally dropped onto copper grid with carbon supporting film. For the thin film sample, it is usually peeled off from the substrate and dispersed in ethanol and finally dropped onto copper grid with carbon supporting film. As for the cross-section thin film sample, it is always cut in

microscale and lifted out in a FIB system, and finally attached onto special copper grid.

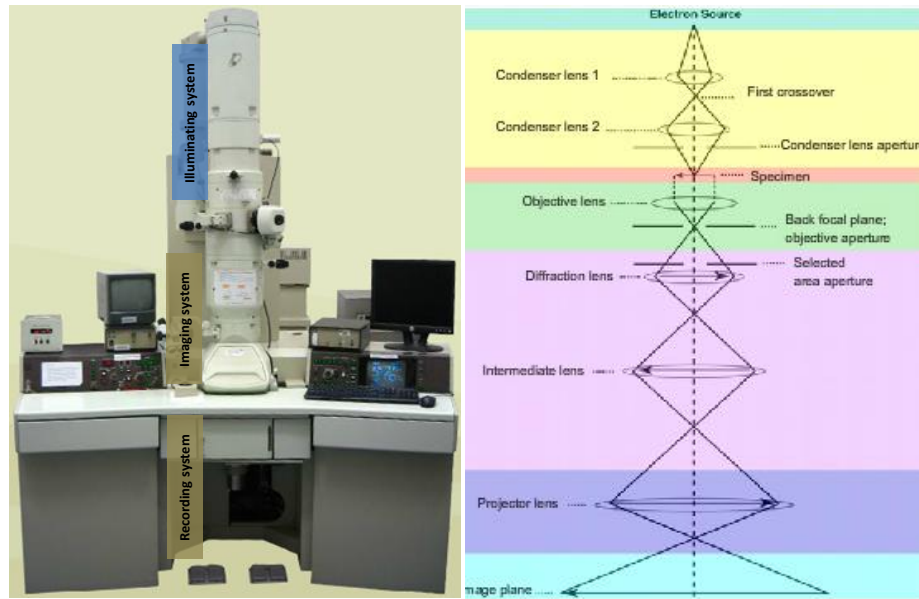


Figure 3.8 View of a typical TEM instrument (left) and principle of TEM operation (right).

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3.3.5 Atomic force microscopy

Atomic force microscopy (AFM) is a kind of scanning probe microscopy with a tip on a cantilever, which is used to characterize the topography by recording the interaction forces between the tip and the sample surface.

In a general AFM set-up, there are always a quadrant photodiode as position sensitive detector for laser beam control, a controller, a cantilever with a tip and a piezo ceramic height control motor for adjusting the distance between the sample surface and the tip (Figure 3.9a).

There are three main scanning modes for the AFM, i.e. contact mode, tapping mode and non-contact mode, which is clarified by the interaction forces used for the

detection, i.e. repulsive force for the contacting mode, attractive force for the non-contact mode, intermittent for the tapping mode (Figure 3.9b).^[13]

For the contact scanning mode, the tip is kept continuous contact with the sample surface during scanning, which results in a high resolution and is preferably utilized for sample with hard surface.

For the tapping scanning mode, the tip is attached to an oscillating cantilever, which enables the tip contact with the sample surface gently and frequently during scanning, and always shows a good resolution.

As for the non-contact mode, the tip is also attached to an oscillating cantilever, but it is kept a certain distance (5-15 nm) between the tip and the sample surface during the scanning. The restriction for this scanning mode is the vacuum atmosphere as well as the soft surface for the sample.

With regard to normal materials, the tapping mode is the most frequently used scanning method, which is adequate to give surface information for the sample, including the topography, surface roughness, grain size distribution and the nano-scale film thickness.^[14, 15]

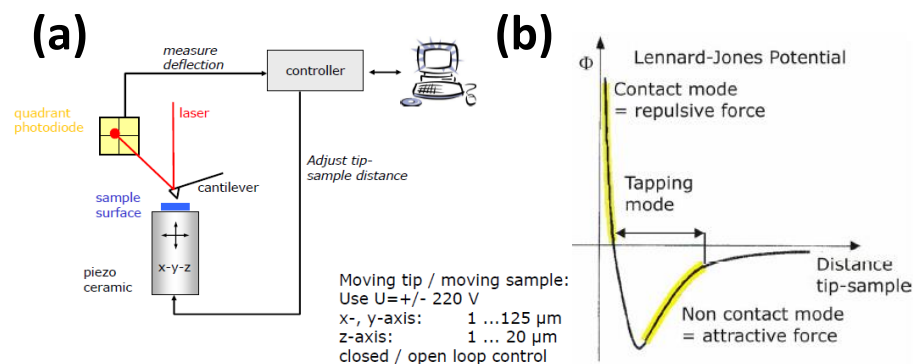


Figure 3.9 (a) General AFM set-up. (b) Interaction forces for AFM under different scanning mode. Copy right 2006 from Astrid Kronenberger.

3.3.6 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a method to characterize the thermal stability properties of materials by analyzing the weight loss during heating process in atmospheres. It can be applied in determining the lattice solvents, organic ligands as well as the thermal stability of the frameworks.

Figure 3.10 shows a typical TGA instrument, consisting of electronic weighing system and controlling system. The electronic weighing system contains the furnace, tare system, temperature programmer and the gas inlet/outlet systems, which enable them to make a micro-thermobalance measurement.

Through the micro-thermobalance measurements, it is able to analyze any changes of the mass owing to oxygen absorption, thermal degradation, oxidation and/or other heterogeneous reactions.^[16]

As for a normal heterogeneous reaction as shown in Equation 3.7, the release of $C(g)$ during heating corresponds to the weight loss in the TG curve, and the residue after thermal decomposition comes from the product $B(s)$.



In addition, the first derivative of the TG weight-loss curve can be used to analyze the starting and ending temperature of the decomposition from the peaks.

With respect to the kinetics for the reaction (Equation 3.7), the degree of reaction

$$\alpha = (m_0 - m)/(m_0 - m_f) \quad (3.8)$$

Where m is the concentration of reactants, m_0 and m_f are the initial and final concentration, respectively. For constant heating rate test, $v = dT/dt$,

$$\int_0^\alpha \frac{1}{g(\alpha)} d\alpha = \int_{T_0}^T \frac{A}{v} e^{\frac{-E}{RT}} dT = f(\alpha) \quad (3.9)$$

Where $f(\alpha)=kt$, $g(\alpha)=d(\alpha)/kdt$, k is the constant for reaction rate, v is the heating rate, A is the constant, R is the ideal gas constant, and E is the activation energy.^[16]

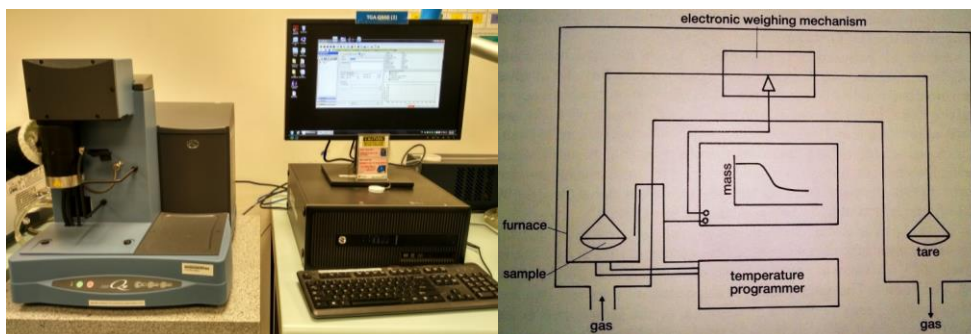


Figure 3.10 General TGA set-up (left) and electronic weighing mechanism in TGA (right).

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3.3.7 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a characterization method to measure the heat flow of a milligram-scale sample, which is applicable in determining the heat capacity, enthalpy of melting/fusion, enthalpy of reaction/thermal degradation, glass transition temperature as well as phase transition temperature.^[17]

As shown in Figure 3.11, a typical DSC instrument includes a heating unit with differential thermocouples and a controller, which also connects with a gas supplier as well as a cooling system. The system can work with a programmed heating/cooling sequence under an inert gas/air atmosphere.

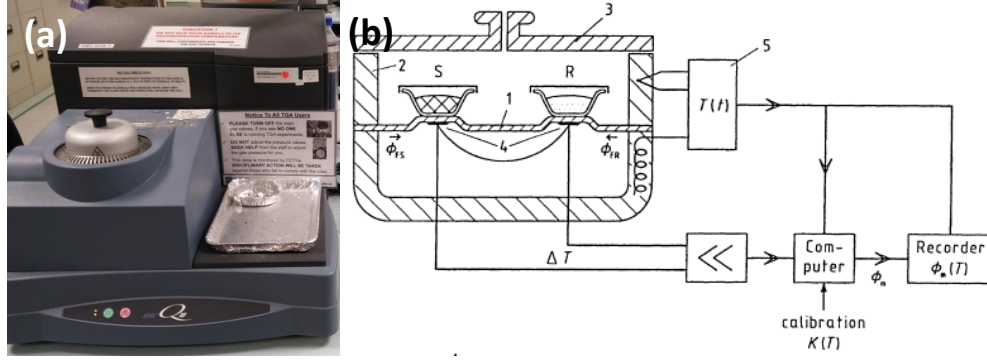


Figure 3.11 General DSC set-up (a) and heat flux DSC with disk-type measuring system (b).

1 disk, 2 furnace, 3 lid, 4 differential thermocouple(s), 5 programmer and controller, S crucible with sample substance, R crucible with reference sample substance, ϕ_{FS} heat flow rate from furnace to sample crucible, ϕ_{FR} heat flow rate from furnace to reference sample crucible, ϕ_m measured heat flow rate, K calibration factor.^[17] Copy right 2003 from Springer Press.

With respect to the principles of heat flux measurement in disk-type DSC instrument, as depicted in Figure 3.11b, a differential signal (ΔT) generated in the measurement is proportional to the difference between the heat flowrates to the sample and to the reference:

$$\phi_{FS} - \phi_{FR} \sim -\Delta T \text{ with } \Delta T = T_S - T_R \quad (3.10)$$

$$\text{And } \Delta T = R \frac{dT}{dt} (C_S - C_R) \quad (3.11)$$

Measurement of heat capacity. The basic equation for the heat capacity measurement (under steady state conditions) is

$$\Delta\phi_{SR} = \phi_S - \phi_R = C_S \frac{dT_S}{dt} - C_R \frac{dT_R}{dt} = (C_S - C_R)\beta \quad (3.12)$$

Where the $\Delta\phi_{SR}$ is the heat flow rate difference between the sample and the reference, C_S is the heat capacity of the sample, β is the heating rate.

The heat capacity can be determined by a “classical” three-step procedure, that is

- a) Zero-line $\phi_0(T)$ heating flow rate determination by using empty crucibles on both the sample and reference sites, which reflect the asymmetry of the DSC;
- b) Calibration by using a substance with known heat capacity (C_{Ref}) to replace the empty crucible on the sample site.

$$c_{Ref}m_{Ref}\beta = K_{\phi}(T)(\phi_{Ref} - \phi_0) \quad (3.13)$$

Where $K_{\phi}(T)$ is a temperature dependent calibration factor;

- c) At last, the calibration substance on the sample site is replaced by the sample, and it can be got:

$$c_Sm_S\beta = K_{\phi}(T)(\phi_S - \phi_0) \quad (3.14)$$

Then, c_S can be obtained by comparing the heat flow rates into the sample and into the calibration substance:

$$c_S = \frac{\phi_S - \phi_0}{\phi_{Ref} - \phi_0} \frac{m_{Ref}}{m_S} c_{Ref} \quad (3.15)$$

Phase transition temperature. For the phase transition materials, there will be endothermic/exothermic peaks at the phase transition temperature, which can be recorded to calculate the phase transition temperature. The peak width can also reveal the grain size of the materials, and the reversibility of the phase transition can be characterized by heating and cooling cycles.

Crystallinity degree of materials. For the determination of material's crystallinity, the DSC method can also supply a rational approach by comparing the latent heat at the phase transition temperature with the standard value of single crystalline sample.

$$w_c(T) = \frac{A_1(T) - A_2(T)}{\Delta_{fus}h(T)} \quad (3.16)$$

Where $w_c(T)$ is the degree of crystallinity, $\Delta_{fus}h(T)$ is the single/full crystalline sample's latent heat, $A_1(T)$ and $A_2(T)$ correspond to the peak area as indicated in Figure 3.12.

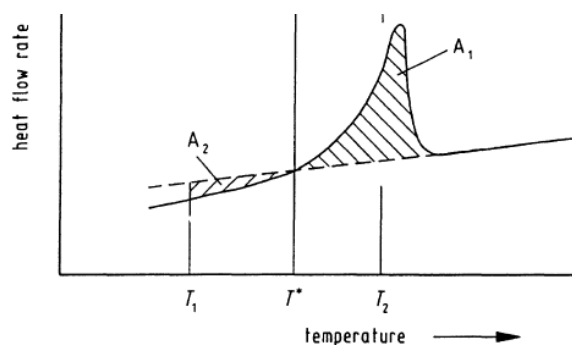
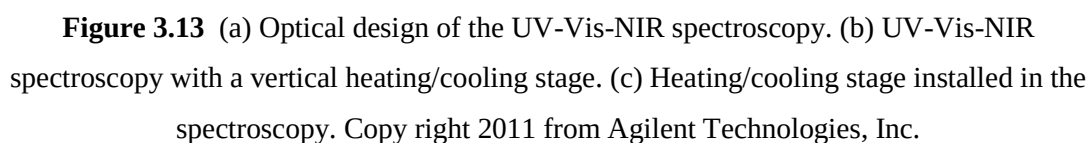


Figure 3.12 A crystallization peak of a sample for determination of crystallization degree.^[17]

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3.3.8 UV-Vis-NIR spectroscopy

UV-Vis-NIR spectroscopy is a technique to characterize the photometric properties (%T, %R, absorbance) of materials in a wavelength range 175-3300 nm, and the spectroscopy is composed of light source, lens, detector and some necessary accessories (Figure 3.13a)


$$A = \lg(I_0/I) \quad (3.17)$$

$$\%T=100 \cdot I/I_0 \quad (3.18)$$

$$\text{Thus, } A = \lg(100/\%T) \quad (3.19)$$

As for the thermochromic properties discussed in this thesis, a heating/cooling stage (Figure 3.13c) with 20 °C/min heating/cooling rate is used as an accessory to test the temperature-dependent integrated visible transmission (T_{lum}) and the solar transmission (T_{sol}):

$$T_{\text{lum/sol}} = \int \phi_{\text{lum/sol}}(\lambda) T(\lambda) d\lambda / \int \phi_{\text{lum/sol}}(\lambda) d\lambda \quad (3.20)$$

Where $T(\lambda)$ is the recorded transmittance, ϕ_{lum} is the standard visible efficiency function of the photopic vision for human eyes (figure 3.14 b)^[19] and ϕ_{sol} is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon, Figure 3.14a).^[20]

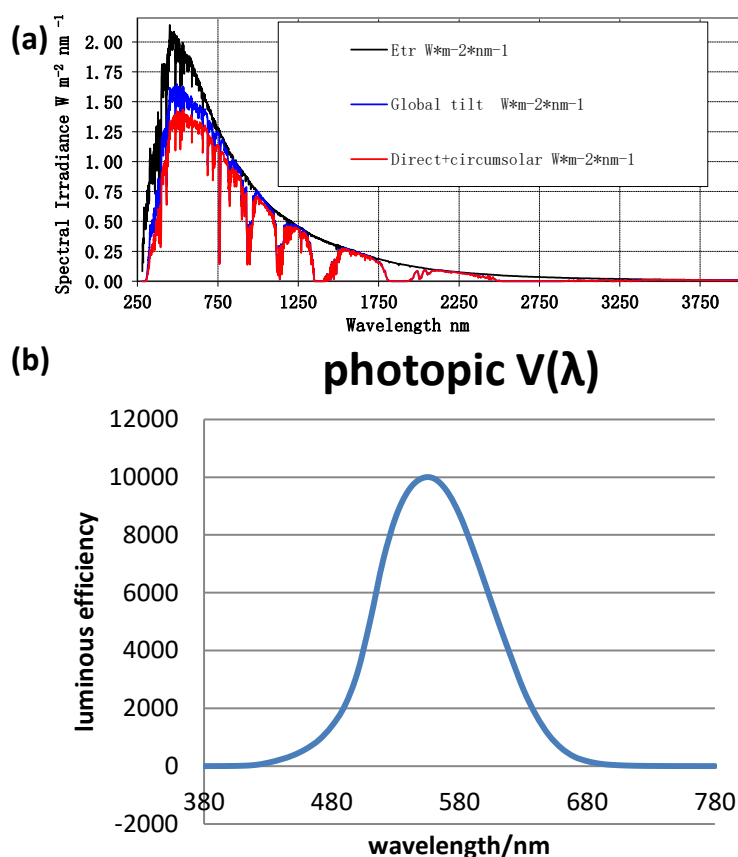


Figure 3.14 (a) ASTM G173-03 Reference Spectra.^[20] (b) Photopic spectra for the human eye.^[19]

With respect to the reflectance (%R) measurement, an integrated sphere is attached to the spectroscopy (Figure 3.15) for collecting the reflection signals precisely. This integrated sphere has inside coating of MgO or BaSO_4 , and is used to integrated the diffusely reflection from the sample and standard reference ($\%R \approx 100\%$), which is essential in the reflectance accessory.

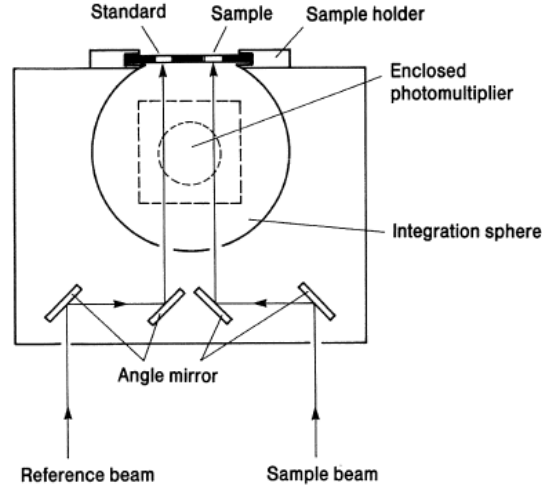


Figure 3.15 %R measurement system with an integrated sphere in a spectroscopy.^[18]

3.3.9 Ellipsometry

Ellipsometry is a method to measure the polarization change (Ψ and Δ) of the light reflected from the sample surface with the advantage of no-destruction. After fitting based on a proper mode, the refractive index (n), extinction coefficient (k), the thin film thickness as well as the surface roughness can be obtained.^[21]

As shown in Figure 3.16, the ellipsometer contains a light polarizer with an alignment detector, a detector with rotating analyzer as well as a solid state detector, a sample holder with vacuum adhesion system and a goniometer for automated incident angle control (Figure 3.16a). The recording signal of the ellipsometer is the polarization ψ (Ψ) and δ (Δ), which are correlated with a ratio of complex reflection in the parallel ($\tilde{R}_p$) and the perpendicular ($\tilde{R}_s$) direction. Based on Fresnel equation, the reflections can be expressed below:^[21]

$$\tilde{R}_p = \frac{\tilde{n}_1 \cos \phi_0 - \tilde{n}_0 \cos \tilde{\phi}_1}{\tilde{n}_1 \cos \phi_0 + \tilde{n}_0 \cos \tilde{\phi}_1} \quad (3.21)$$

$$\tilde{R}_s = \frac{\tilde{n}_0 \cos \phi_0 - \tilde{n}_1 \cos \tilde{\phi}_1}{\tilde{n}_0 \cos \phi_0 + \tilde{n}_1 \cos \tilde{\phi}_1} \quad (3.22)$$

The collected data (Ψ and Δ) are firstly simulated with rational layer-by-layer model (substrate, interlayer and thin film). After getting a minimum MSE (mean square error), the thin film thickness, optical constants (n , k) as well as surface roughness can be obtained accordingly.

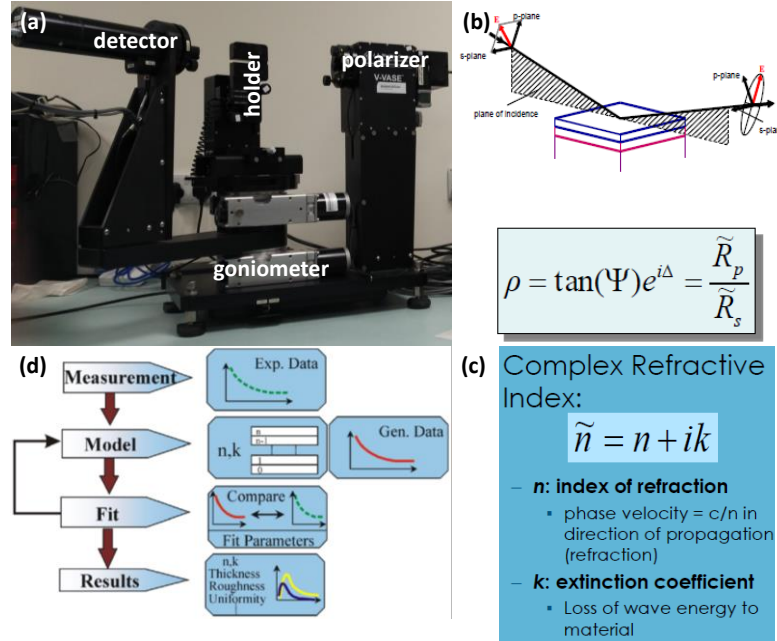


Figure 3.16 (a) Ellipsometry setup for Woollam VASE[®] ellipsometer. (b) Detected Ψ and Δ by the ellipsometer for optical analysis, where ρ is the ratio of Fresnel reflection coefficients $\tilde{R}_p$ and $\tilde{R}_s$ for parallel (p-) and perpendicular (s-) polarized light, respectively. (c) Complex refractive index composed of refractive index (n) and extinction coefficient (k) that can be obtained by the analysis. (d) Standard operation and analysis procedure for the ellipsometry.

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Especially, the VO₂ mode used in this thesis can be established as Table 3.1 based on the optical constants reported by Mlyuka et al. (2009).^[22]

Table 3.1 VO₂ ellipsometry mode based on (n, k).

VO ₂ ellipsometry mode based on (n, k) ^[22]								
wavelength/nm	n	k	wavelength/nm	n	k	wavelength/nm	n	k
305	1.73894	1.15753	510	2.80459	0.43706	715	2.7279	0.3602
315	1.80551	1.14001	520	2.81818	0.41387	725	2.72409	0.36721
325	1.88823	1.12249	530	2.83166	0.39963	735	2.72081	0.37422
335	1.96493	1.10442	540	2.84513	0.3854	745	2.71753	0.38123
345	2.05674	1.07133	550	2.85415	0.37116	755	2.71424	0.38526
355	2.16405	1.03824	560	2.86166	0.35938	765	2.713	0.38915
365	2.24852	1.01065	570	2.86917	0.34995	775	2.71183	0.39305
375	2.31509	0.98437	580	2.87313	0.34051	785	2.71066	0.39694
385	2.38272	0.94815	590	2.86812	0.33356	795	2.71043	0.40122
395	2.46157	0.89387	600	2.86311	0.33259	805	2.71293	0.40589
405	2.52461	0.85633	610	2.85811	0.33162	815	2.71543	0.41056
420	2.60345	0.78704	625	2.8412	0.33015	830	2.71919	0.41749
430	2.65601	0.74546	635	2.82907	0.3303	840	2.72169	0.42187
440	2.68041	0.71042	645	2.81655	0.33264	850	2.72524	0.42625
450	2.70111	0.66978	655	2.80049	0.33497	860	2.72962	0.43063
460	2.72116	0.62259	665	2.78443	0.33731	870	2.734	0.43465
470	2.73785	0.58505	675	2.76913	0.34093	880	2.73838	0.43794
480	2.75453	0.54536	685	2.75882	0.34531	890	2.74276	0.44122
490	2.77122	0.50281	695	2.74851	0.34968	900	2.74714	0.4445
500	2.7879	0.46821	705	2.73821	0.35406	910	2.75176	0.44796
920	2.75654	0.45171	1125	2.86327	0.45327	1330	2.93952	0.42468
930	2.76132	0.45547	1135	2.86886	0.45121	1340	2.9414	0.42051
940	2.76609	0.45923	1145	2.87387	0.45185	1350	2.94328	0.41634
950	2.77087	0.45958	1155	2.87888	0.45294	1360	2.94515	0.41216
960	2.77565	0.45958	1165	2.88388	0.45403	1370	2.94703	0.40799
970	2.78043	0.45958	1175	2.88889	0.45513	1380	2.94939	0.40382
980	2.78521	0.45958	1185	2.8939	0.4521	1390	2.95263	0.40322
990	2.78963	0.46019	1195	2.8989	0.4486	1400	2.95588	0.40322
1000	2.79361	0.46154	1205	2.90216	0.4451	1410	2.95912	0.40322
1010	2.79759	0.46289	1215	2.90455	0.44188	1420	2.96237	0.40023
1020	2.80157	0.46368	1225	2.90694	0.43994	1430	2.96561	0.39556
1030	2.80555	0.46265	1235	2.90933	0.43799	1440	2.96886	0.39089
1040	2.80955	0.46162	1245	2.91172	0.43604	1450	2.97161	0.38621
1050	2.81573	0.46058	1255	2.91446	0.4341	1460	2.97411	0.38384
1060	2.82192	0.45958	1265	2.91844	0.43187	1470	2.97661	0.38165
1070	2.8281	0.45958	1275	2.92242	0.42953	1480	2.97912	0.37946
1080	2.83428	0.45958	1285	2.9264	0.42719	1490	2.98162	0.37727
1090	2.84068	0.45958	1295	2.93038	0.4249	1500	2.98294	0.37626
1100	2.84714	0.45842	1305	2.93436	0.4249	1510	2.98294	0.37529

3.4 Overview of Methodologies

In summary, the VO₂ thin films will be fabricated with sol-gel methods and the VO₂ nanostructures will be produced using the hydrothermal technique. With respect to the morphologies, the FESEM, AFM and TEM will be used to characterize the grain size, grain shape and the size distribution. Regarding to the elemental analysis, the XPS, EDX point/line or mapping methods will be utilized to determine the elemental composition and distribution in the VO₂ product. As for the thermal stabilities and the phase transition, the TGA and DSC will be applied to determine the decomposition and phase transition temperatures. The crystalline phase and the lattice information will be tested with the XRD and the SAED/HRTEM techniques. With regard to the optical properties, the UV-Vis-NIR spectroscopy will be used to characterize the temperature dependent %T/%R spectra and the ellipsometry will be utilized to get the optical constants of the VO₂ thin films.

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Chapter 4*

Rare Earth doping and Mg/W-codoping in VO₂

The rare earth-doped and Mg/W-codoped VO₂ thin films were fabricated through sol-gel techniques, and the doping mechanisms for RE- and Mg/W-codoping were illustrated and summarized. The RE (Eu, Tb, La) doped VO₂ thin films were found to exhibit enhanced visible transmission and enlarged solar modulating abilities as well as the reduced phase transition temperature. Especially, the La-doped VO₂ thin films showed the best performance for continuous VO₂ thin films. The competition between the extra strain and the hole carriers in RE-doping was found to control the τ_c modulation. Mg/W-codoped VO₂ thin films showed the widened optical band gap, enhanced visible transmission and the near ambient phase transition temperature. The charge carrier counteraction arising from the Mg²⁺ and W⁶⁺ doping gave rise to a slight increase of τ_c in Mg/W-codoped VO₂ thin films.

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4.1 Introduction

Vanadium dioxide (VO₂) is an intriguing correlated electron material with a first-order phase transition at around 341 K, accompanying by a metal-to-insulator transition (MIT) and a IR modulation,^[1] which has been widely investigated in the fields of sensors,^[2, 3] magnetic refrigeration,^[4] memory devices,^[5-8] light modulators^[9, 10] and smart windows^[11, 12]. Especially for the thermochromic smart window applications, VO₂ is well known by its large IR modulation under thermal impulse due to the change of optical parameters.^[13]

In the fabrication of VO₂ thin films, sol-gel is a cost-effective and facile method owing to the inorganic precursor sol/solution as well as the simple set up for the experiment.^[14, 15] In the sol-gel process, the previous precursor for VO₂ synthesis is always the organic (VO(acac)₂^[16], VO(OC₃H₇)₃^[17]) or unstable V₂O₅-H₂O inorganic system^[18], which has the limit in safety and stability. The atmosphere used in the followed annealing process is usually Ar, N₂ and/or vacuum, and the annealing temperature is around 550 °C.^[18-20]

With regard to the doping effect, it has been of intense interest for researchers owing to its efficiency in modulating the phase transition temperature (τ_c) and its ability to modify the thermochromic performance in terms of better combination of visible transmission (T_{lum}) and solar modulating abilities (ΔT_{sol}). The replacement of vanadium by metal cations with high valence state (Mo⁶⁺,^[21] W⁶⁺,^[22, 23] Nb⁵⁺,^[21] Ta⁵⁺^[24]) in the VO₂ lattice can result in extra free electrons, which is able to accelerate the MIT, and decrease the τ_c accordingly. In addition, the substitution of vanadium by metal cations with larger ionic radii compared with V⁴⁺ (r=0.058 nm), such as Mg²⁺ (r=0.072 nm),^[25] Eu³⁺ (r=0.0947 nm)^[26] and Tb³⁺ (r=0.0923 nm),^[27] can lead to the extra strain, which can also reduce the τ_c due to the decline of MIT energy barrier. The relationship between the generated strain and the τ_c can be expressed by the Clausius-Clapeyron equation.

$$d\tau_c / d\sigma = (\varepsilon_0 \tau_c^0) / \Delta H \quad (4.1)$$

Where, ΔH is the latent heat of MIT transition, σ is the strain, ε_0 is the initial strain and τ_c^0 is the initial phase transition temperature.^[28]

Whereas, doping with metal cations at low valence state and smaller/nearer ionic radii, e.g. Al³⁺ (0.0535 nm), Ga³⁺ (0.062 nm), Fe³⁺ (0.055 nm), Cr³⁺ (0.0615 nm) could give rise to the increase of τ_c , mainly owing to the generation of extra hole carriers and the relax of lattice.^[1] For improving the thermochromic properties, the dopants Tb³⁺, Eu³⁺, Zr⁴⁺ and Mg²⁺ (Table 4.1) have been found to be effective in enhancing the T_{lum} and ΔT_{sol} simultaneously.

Table 4.1 Doping effect of metal cations on VO₂ thermochromic properties.

Dopant	T_{lum}	ΔT_{sol}	τ_c	Mechanism	Ref.
W ⁶⁺	↓	↓	↓(~20-26 °C/at.%)	e ⁻ ↑	[29, 30]
Ti ⁴⁺	↑	↑	↑	smaller radius	[31, 32]
Co ²⁺	—	—	↓	larger radius	[24]
Nb ⁵⁺	↓	↓	↓(~2 °C/at.%)	e ⁻ ↑	[21]
Mo ⁶⁺	↑	↓	↓(~3 °C/at.%)	e ⁻ ↑	[21]
Ta ⁵⁺	—	—	↓	e ⁻ ↑	[24]
Mg ²⁺	↑	↑	↓(~3 °C/at.%)	h ⁺ ↑	[33, 34]
Zr ⁴⁺	↑	↑	↓(~0.4 °C/at.%)	larger radius	[25]
Cr ³⁺	↑	↓	↑	h ⁺ ↑	[35]
Sn ⁴⁺	—	—	↑(~1 °C/at.%)	smaller radius	[36]
Al ³⁺	—	—	↓(~2.7 °C/at.%)	h ⁺ ↑	[37]
Fe ³⁺	—	—	↓(~6 °C/at.%)	h ⁺ ↑	[38]
Eu ³⁺	↑	↑	↓(~5 °C/at.%)	larger radius	[26]
Ce ³⁺	—	—	↓(~4.5 °C/at.%)	larger radius	[39]
La ³⁺	↑	↑	↓(~1.1 °C/at.%)	larger radius	[40]
Tb ³⁺	↑	↑	↓(~1.5 °C/at.%)	larger radius	[27]

In this chapter, a facile sol-gel technique with V₂O₅-H₂O₂ or V₂O₅-ox precursor followed by an one-step annealing in inert atmosphere was presented for synthesis of RE-doped and Mg/W-codoped VO₂ continuous thin films with modulated thermochromic properties.

4.2 Materials and methods

In this chapter, all materials V₂O₅ (99.6%, Alfa Aesar), vanadium powder (99.9%, Alfa Aesar), H₂O₂ (30 wt.%, Sigma-Aldrich), polyvinylpyrrolidone (PVP40, Sigma-Aldrich), oxalic acid (99.9%, Alfa Aesar), Mg/W powders (99.9%, Alfa Aesar) and Eu₂O₃/La₂O₃/Tb₂O₃ powder (99%, Alfa Aesar) were used as received without any further purification.

Precursor preparation

V₂O₅-H₂O₂ precursor. 300 mg V₂O₅ powder was added into 30 mL 30 wt.% H₂O₂ with rigorous stirring for 40 min in ice bath and a clear yellow solution was formed. Then the clear solution was warmed at 50 °C with continuous stirring until the color was changed to dark red. Prior to use, the dark red sol was aged at room temperature for 2-3 days until a stable uniform dark red gel was formed.

Rare earth doped precursor. Weighed rare earth oxide (Eu₂O₃/La₂O₃/Tb₂O₃) powder and 182 mg V₂O₅ powder were added into 90 °C-preheated 15 mL 30 wt.% H₂O₂ with rigorous stirring in a 300 mL glass beaker. After a strong evaporation, the dark red precipitation was formed at the bottom of the beaker, and then it was re-dissolved by an additional 5 mL 30 wt.% H₂O₂ in ice bath to get a clear brownish solution. At last, 12 mg PVP was added into the clear solution under strong stirring, and the rare earth doped precursor was finally ready for use.

Mg/W-codoped precursor. Weighed Mg/W metallic powder was added into 90 °C-preheated 20 mL 30 wt.% H₂O₂ with rigorous stirring in a 300 mL glass beaker for 5 hours to form a clear solution. Then 182 mg V₂O₅ powder was added into the hot solution under stirring. After a violent evaporation, a clear brownish sol was obtained, and 400 mg oxalic acid as well as 12 mg PVP was added into the sol immediately to form the blue colored Mg/W-codoped precursor after stirring for 2 more hours at 90 °C.

VO₂ thin film preparation

The prepared precursors were transferred onto 15×15×0.5 mm³ fused silica substrates through spin coating or dip coating. The thin film thickness could be modified by tuning the coating rate. The dried gel was then annealed in a tube furnace under inert atmosphere (Ar/N₂/CO₂/vacuum) for 2 hours at a temperature 350/450/550/650/750 °C with a gas flow rate 200 mL/min or under a vacuum level 1.2 ×10⁻³ Pa.

Characterization

The crystalline phase of the vanadium dioxide thin films was characterized with Shimadzu XRD-6000 thin film X-Ray diffractometer (Cu-Kα, λ = 0.15406 nm) with a voltage 40 kV and a current 30 mA at an X-ray grazing angle of 0.3-1.0 ° under 2 theta continuous scanning mode. The surface topography was determined by the atomic force microscopy (AFM, DI-3100, Bruker, Germany) using tapping mode and/or a field emission scanning electron microscopy (FESEM, JSM 7600F, JEOL, Japan) with a voltage 5 kV and a probe current 7 μA. The morphology and crystalline structure were also characterized by a transition electron microscopy (TEM, JEM 2010, JEOL, Japan) with an accelerating voltage 200 kV. The chemical composition was characterized by an X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, USA) with 900 μm spot, 3 scans, 75 eV pass energy. The XPS data were collected in the V 2p, Mg 1s and W 4f binding energy regions, and analyzed with Advantage Data System software. The thickness of the VO₂ thin film was measured by Alpha-Step IQ Surface Profiler. The thermal gravimetric analysis of the precursors was performed with thermogravimetric analyzer (Hi-Res TGA, Q500, Research Instruments Pte Ltd, USA) with a heating rate 10 °C/min under N₂ atmosphere. The transmittance spectra in the range of 250-2500 nm were measured with a UV-Vis-NIR spectrophotometer (Cary 5000, Agilent Ltd, USA) equipped with a Linkam PE120 system Peltier simple heating & cooling stage. The integrated visible transmittance (T_{lum} , 380-780 nm) and solar transmittance (T_{sol} , 280-2500 nm) were calculated based on the recorded %T spectra using the Equation 3.20 and the ΔT_{sol} is obtained by $\Delta T_{sol} = T_{sol, \tau < \tau_c} - T_{sol, \tau > \tau_c}$. The hysteresis loop of %T at the wavelength of 2500 nm was measured at the temperature ranging from 10 to 90 °C. The phase transition temperature τ_c was calculated from the

temperature dependent heating and cooling %T data by fitting with a sigmoidal expression³⁹

$$f(\tau) = A2 + (A1 - A2)/[1 + \exp(\frac{\tau - \tau_0}{B})] \quad (4.2)$$

Where, A1, A2, τ_0 and B are fitting parameters. τ_0 gives the transition temperature in the heating and cooling process and $\tau_c = (\tau_{0,h} + \tau_{0,c})/2$, $\Delta\tau_c = \tau_{0,h} - \tau_{0,c}$.

4.3 Outcomes

4.3.1 Rare earth doped VO₂ thin Film

4.3.1.1 Eu doped VO₂ thin Film

Phase and morphology of Eu-doped VO₂ thin films. As illustrated in Figure 4.1, the XRD peaks of the Eu-doped vanadium dioxide thin films could be assigned to the (011), (200), (210) and (220) faces of the VO₂(M) phase with the space group $P2_1/c$ (JCPDS #82-661), revealing the successful formation of pure VO₂(M) phase for the Eu-doped thin films under the doping level 0-5 at.%. The broad diffraction peak around $2\theta=20^\circ$ should be ascribed to the background diffraction of the fused silica substrate, and the high background diffraction intensity at low 2θ angles should be owing to the fluorescence emitted from V atoms. The absence of europium compound (Eu₂O₃ and/or EuVO₄) XRD peaks indicated the successful replacement of V⁴⁺ by Eu³⁺ cations in the V_{1-x}Eu_xO₂ lattice, which belonged to a *P*-type semiconductor.

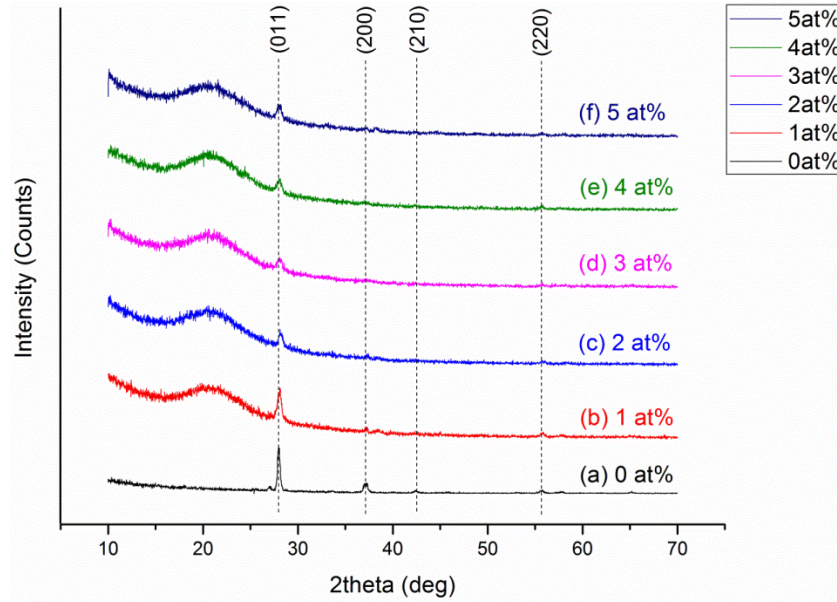


Figure 4.1 XRD patterns of the Eu-doped VO₂ films grown on fused silica substrate with the doping level 0-5 at.% (a-f).^[26]

The surface morphology of the Eu-doped VO₂ thin films was characterized with the FESEM. As shown in Figure 4.2a, the 1 at.% Eu-doped VO₂ thin film exhibited a porous morphology with elongated rod-like grains arranged randomly, which was similar to the undoped VO₂ thin films synthesized using sol-gel method with V₂O₅-H₂O₂ precursor^[66]. When the doping level of Eu³⁺ was above 3 at.%, the morphology was changed to continuous closely-packed nanograin array structures with the average grain size ~100 nm. (Figure 4.2b, c). This may be due to the increase of hole-carrier (h⁺) density arising from the Eu³⁺ doping ($M_V^{Eu} = M_V' + h\cdot$). More substitution of V⁴⁺ by Eu³⁺ occurs, more local free h⁺ charge carriers will be generated, which should be able to result in the attraction between the grains, and gave rise to the densely packed structure. On the other hand, it may also be induced by the lattice distortion from the larger radius of Eu³⁺ dopant compared with the V⁴⁺ (0.95 Å v.s. 0.58 Å), which should be able to increase the nucleation rate, and thus reduced the mean grain size with higher surface energy to form the densely packed nanostructure. With further increasing the doping level to 5 at.% (Figure 4.2d), the obtained VO₂ thin film began to be discontinuous and the grain size becomes smaller. This could be ascribed to the agglomeration of the VO₂ nanograins arising from the high surface tension of the nano-sized VO₂ grain.

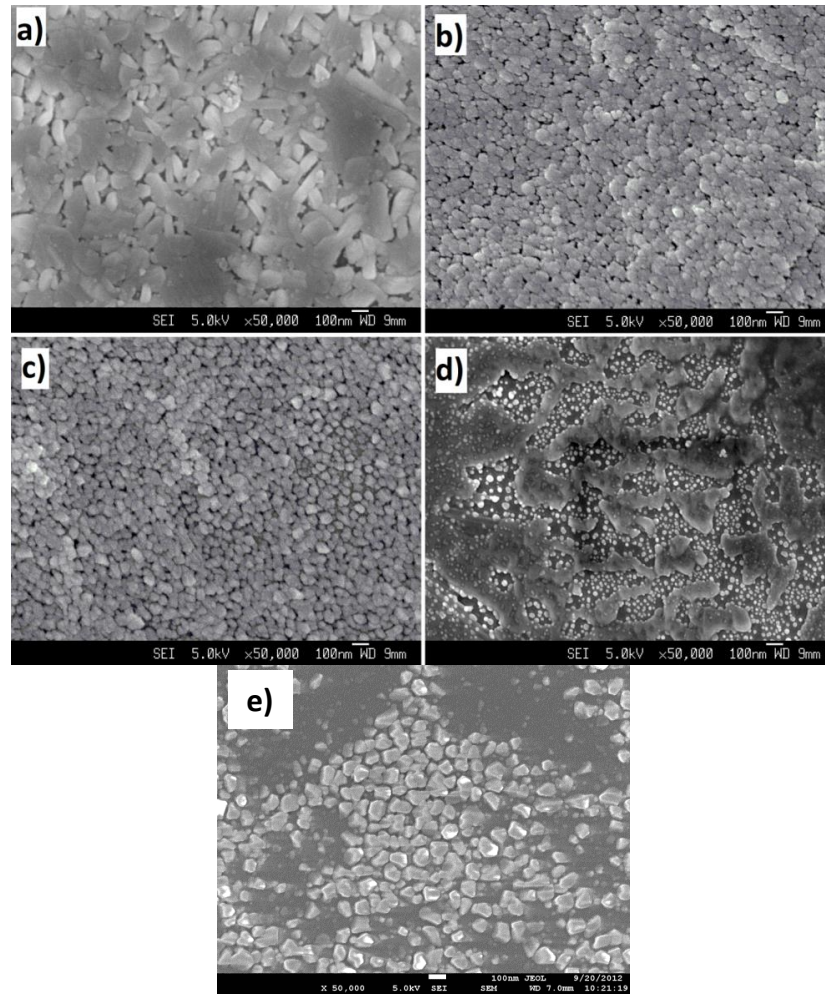


Figure 4.2 FESEM images of the Eu-doped VO₂ films at the doping level 1 at% (a), 3 at% (b), 4 at% (c), 5 at% (d) and 2 at% (e).^[26]

Thermochromic properties. The UV-Vis-NIR transmittance spectra for the Eu-doped VO₂ thin films were measured in a wavelength range 250 to 2500 nm at the temperature 20 and 90 °C, respectively (Figure 4.3). The %T contrast across the MIT (below and above the τ_c or 20/90 °C) at the wavelength 2500 nm for the thin films with Eu doping level 0-5 at.% is 71%, 58%, 59%, 53%, 51% and 47% respectively, suggesting the decreasing tendency of the IR modulation along with the increase of Eu doping levels, which may arise from the lattice distortion as well as the increase of h^+ free carriers. The slight increase of the %T contrast for 2 at% Eu doping should be due to the morphology change from the rod to nanograin, which could reduce the light scattering.

The calculated thermochromic performance in terms of T_{lum} and ΔT_{sol} for the Eu doped VO₂ thin films based on Figure 4.3 have been tabulated in Table 4.2. Compared with the pristine undoped VO₂ thin film, the T_{lum} only showed a slight difference for the 1 and 2 at% Eu-doped VO₂ thin films, indicating the almost unchanged refractive index in the visible region. Upon further increasing the Eu doping level to 3 and 4 at.%, a large enhancement of average T_{lum} by ~10 % could be observed, which indicated the reduce of refractive index. Notably, the enhancement of T_{lum} seemed not to sacrifice the ΔT_{sol} , as an enhanced ΔT_{sol} up to 6.7 % was attained simultaneously at the Eu doping level of 4 at.%, which was almost 40 % relatively larger than that for the pristine undoped VO₂ thin film ($\Delta T_{sol} = 4.9$ %), which should be due to the uniform grain size (T_{lum} decrease) and the close packing (ΔT_{sol} increase). This favorable simultaneous enhancement of T_{lum} and ΔT_{sol} has not been achieved before for the continuous VO₂ thin films. Furthermore, a sudden drop of ΔT_{sol} at the 5 at% Eu doping was observed, which should be due to the agglomeration of the VO₂ nanograins, which may result in a serious light scattering to reduce the transmittance.

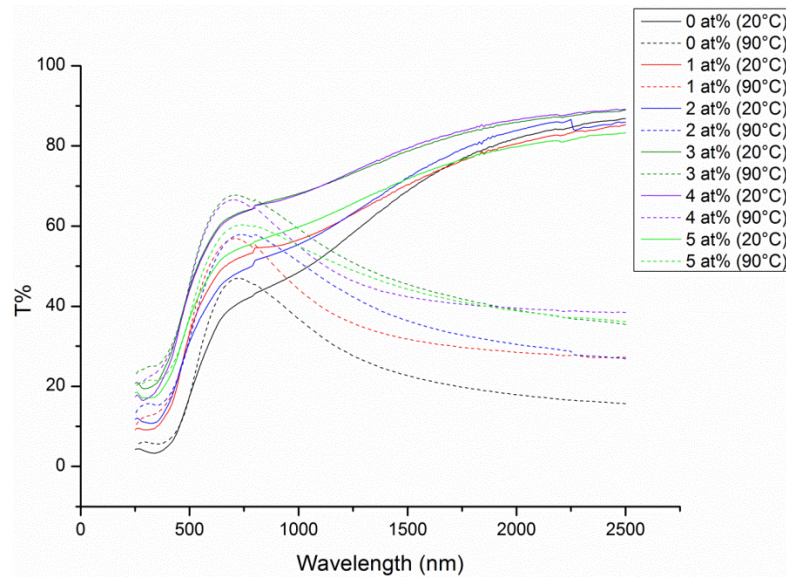


Figure 4.3 UV-Vis-NIR %T spectra recorded at 20 (solid lines) and 90 °C (dash lines) for the Eu-doped VO₂ films with the doping level 0-5 at%.^[26]

Regarding the phase transition temperature, as depicted in Figure 4.4 and Table 4.2, with increasing the Eu doping level from 1 to 4 at.%, the τ_c was steadily reduced from 67.5 to 47.5 °C with a τ_c reducing rate of 6.5 °C/at%. Meanwhile, the loop width ($\Delta\tau_c = \tau_{c,heat} - \tau_{c,cool}$) was gradually increased from 5 to 15 °C, indicating the $\Delta\tau_c$ widening effect of Eu doping, which may be ascribed to the grain size effect from the steadily reduced grain size along with the Eu doping. As for the τ_c reducing mechanism, when the Eu³⁺ doping level was gradually increased, the h^+ extra carrier density was also increased accordingly, which should increase the τ_c [65]. On the other hand, the atom substitution of V⁴⁺ by Eu³⁺ with larger ionic radius should lead to the lattice deformation and reduce the energy barrier for the MIT, which should reduce the τ_c . Therefore, the τ_c modulation of Eu doping should be achieved by the competition between the h^+ charge carrier and the lattice deformation. In other words, at low Eu doping levels, the lattice distortion dominates the MIT and the τ_c was steadily reduced. At high Eu doping level (5 at.%), the increased h^+ charge carrier controlled the MIT and the τ_c began to be increased. The best combination of thermochromic performance for the Eu-doped VO₂ thin films was obtained at the doping level 4 at% with an average $T_{lum} \sim 54\%$, $\Delta T_{sol} \sim 6.7\%$ and a reduced τ_c of 47.5 °C.

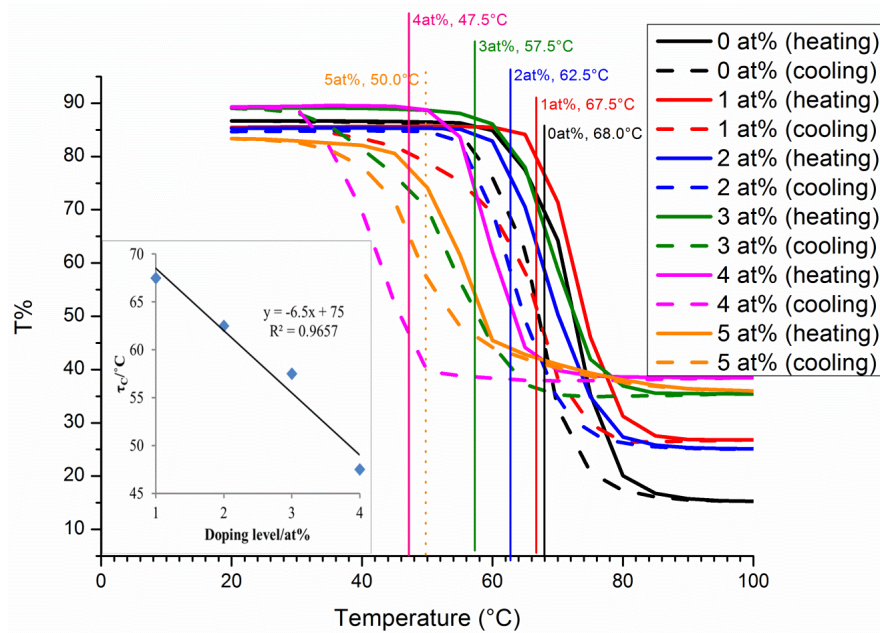


Figure 4.4 %T hysteresis loop at a fixed wavelength 2500 nm in a temperature range 20-100 °C for the Eu-doped VO₂ films with the doping level 0 to 5 at%. The inset is the plots of τ_c v.s. Eu doping level with a least-square linear fit. ^[26]

Table 4.2 Calculated thermochromic properties for Eu-doped VO₂ films. ^[26]

Doping level/at%	$T_{lum}(20^\circ\text{C}/90^\circ\text{C})$	$\Delta T_{sol}^a)$	$\tau_c/^\circ\text{C}^b)$	$\Delta \tau_c/^\circ\text{C}^c)$
0	42.4%/45.8%	4.9%	68.0	5
1	41.0%/44.7%	6.8%	67.5	5
2	39.2%/43.0%	4.1%	62.5	5
3	52.4%/56.4%	5.3%	57.5	15
4	51.8%/55.8%	6.7%	47.5	15
5	44.1%/47.5%	3.3%	50.0	10

In summary, series of Eu-doped VO₂ thin films were prepared through a sol-gel method with the V₂O₅-H₂O₂ precursor. In this research, it is found that doping with the rare earth cation Eu³⁺ could effectively reduce the phase transition temperature as well as enhance the thermochromic properties of VO₂ thin films. Compared with the pristine undoped VO₂ thin film, the 4 at.% Eu-doped VO₂ thin film gave a best combination of high visible transmittance (T_{lum} = 53.8%) and a high solar modulating ability (ΔT_{sol} = 6.7%) with a reduced τ_c = 47.5 °C. Furthermore, at the low Eu doping level below 5 at.%, the Eu³⁺ cation was found to be effective in reducing the τ_c with a decreasing rate of 6.5 °C/at%. At the high doping level 5 at.%, the τ_c underwent a recover due to the competition between the introduced h⁺ charge carrier and the lattice deformation. The enhanced thermochromic performance with the reduced τ_c , increased T_{lum} as well as the simultaneously enlarged ΔT_{sol} exceled among all other reported doping cases, and should be of great practical significance for thermochromic smart window applications.

4.3.1.2 Tb doped VO₂ thin Film

Synthesis of Tb-doped VO₂ thin films. With coating the Tb doped V₂O₅-H₂O₂ precursor sol onto fused silica substrates and annealing in the Ar atmosphere, the Tb doped VO₂ thin films were attained. The XRD patterns of the Tb doped VO₂ thin films were measured with a 2 theta scan mode in a 2-theta angle range of 20-60°. As shown in

Figure 4.5a, all of the doped samples V_{1-x}Tb_xO₂ (x=0-10 at.%) only exhibited the characteristic (011) peak at ~28° (2θ), revealing the successful formation of the pure VO₂(M) phase (JCPDS #82-661). The large background noise at low angles should be due to the fluoresced X-rays. No other XRD peaks for vanadium oxide and/or terbium compounds could be observed in the XRD patterns, proving the high phase purity of the attained VO₂ thin films. High resolution V 2p and Tb 3d XPS scan was carried out in the binding energy range of 507-535 eV and 1235-1287 eV, respectively for the sample V_{0.9}Tb_{0.1}O₂. As depicted in Figure 4.5b, the broad V 2p3/2 peak can be fitted by V⁵⁺ 2p3/2 and V⁴⁺ 2p3/2 peaks located at 518.6 and 517.8 eV, respectively. The appearance of V⁵⁺ 2p3/2 in the VO₂ thin film should be ascribed to the partial oxidation of the VO₂ within several nanometers scale near the top surface. The Tb 3d peaks as observed in Figure 4.5c could be assigned to Tb 3d3/2 and Tb 3d5/2 peaks locating at 1278.4 and 1243.4 eV, respectively, indicating the successful doping of Tb in the VO₂ thin films. After calculating based on the Equation 3.6, it is observed that the doping level of Tb³⁺ in the V_{0.9}Tb_{0.1}O₂ thin film based on the XPS peaks of V 2p and Tb 3d was ~10.3 at.%, consistent with the stoichiometry of the sample V_{0.9}Tb_{0.1}O₂.

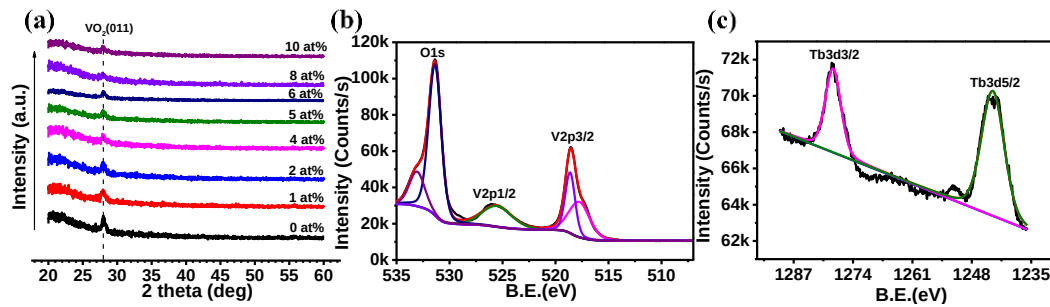


Figure 4.5 (a) XRD patterns of the Tb-doped VO₂ thin films with the doping level from 0 to 10 at.%. (b-c) High resolution XPS scan of V 2p (b) and Tb 3d (c) for the VO₂ thin film with the stoichiometry V_{0.9}Tb_{0.1}O₂.^[27]

The morphology of the Tb doped VO₂ thin films has been characterized with AFM as shown in Figure 4.6 and the mean particle size of the thin films has been analysed with the NanoScope Analysis 3.0 software. As illustrated in Figure 4.6, most of the mean grain size for the Tb doped VO₂ thin films ranged from 50 to 80 nm, only the 10 at.% Tb doped VO₂ thin film exhibited a larger mean grain size ~100 nm as shown in Figure 4.6i.

The sub-100 nm grain size of the VO₂ thin films should benefit the thermochromic performance with high T_{lum} , since the scattering could be largely reduced by the small grain size.^[45] The measured average roughness (Ra) for the Tb-doped VO₂ thin films was in a range of 0.7 to 4.5 nm, indicating the smooth surface with low roughness, which may also be useful to get the high T_{lum} owing to the low scattering. The morphology and the crystallinity of the Tb-doped VO₂ thin films have been further investigated through TEM analysis. As shown in Figure 4.7, the V_{0.98}Tb_{0.02}O₂ thin film showed an average grain size ~62 nm (Figure 4.7a), which was in accord with the AFM analysis. As for the crystallinity, the Selected Area Electron Diffraction (SAED) pattern (Figure 4.7b) can be indexed with (011), (-211), (-212) and (220) faces of the crystalline VO₂(M) (ICSD #602360, $P2_1/c$, $a=5.755$ Å, $b=4.525$ Å, $c=5.386$ Å, $\alpha=\gamma=90^\circ$, $\beta=122.61^\circ$). The crystal lattice was studied by the HRTEM as shown in Figure 4.7c, where the lattice distortion region could be observed that may arise from the atom replacement of V by Tb [ionic radius ratio: 0.92 Å (Tb³⁺) v.s. 0.58 Å (V⁴⁺)]. The Tb doping was further investigated with the EDX mapping. As shown in Figure 4.7d and e, the mapping of Tb and V element in the VO₂ grains showed a continuous distribution for both Tb and V, indicating the uniform doping of Tb in the VO₂ thin film. The successful doping of Tb revealed the advantage of the presented inorganic sol-gel method in preparing the cation doped VO₂ nanomaterials.

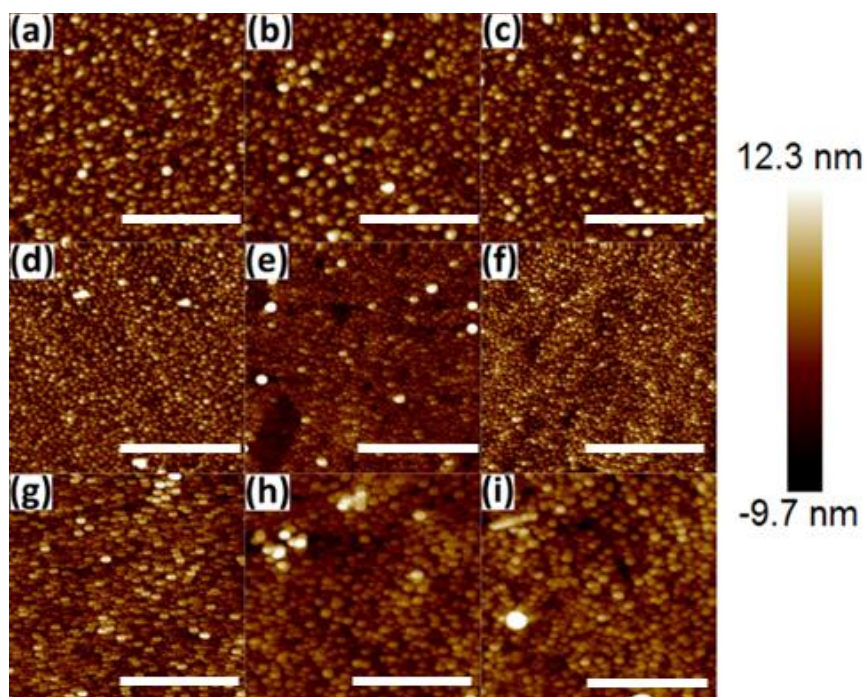


Figure 4.6 2D AFM height images of Tb-doped VO₂ thin films at the doping level 0 at.% (a), 1 at.% (b), 2 at.% (c), 3 at.% (d), 4 at.% (e), 5 at.% (f), 6 at.% (g), 8 at.% (h) and 10 at.% (i). The scan area for all the images is $2 \times 2 \mu\text{m}^2$ and the scale bar in the images represent $1 \mu\text{m}$.^[27]

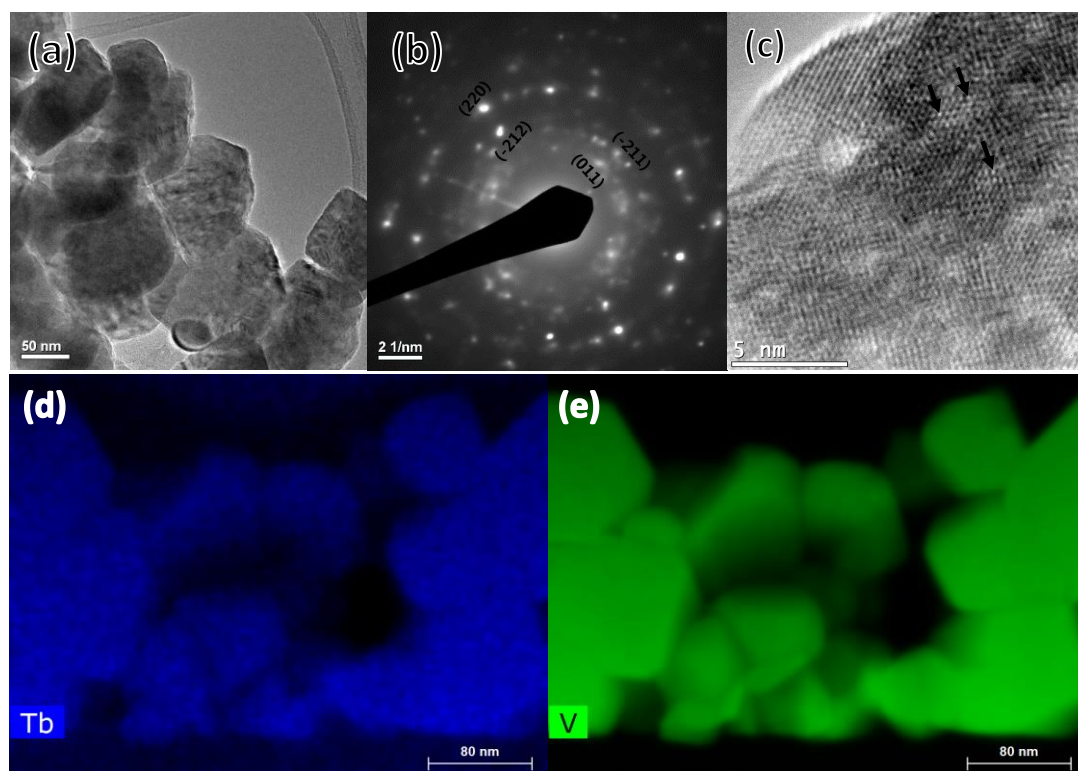


Figure 4.7 Low-magnification TEM image (a), SAED pattern (b) and the HRTEM image (c) for the sample V_{0.98}Tb_{0.02}O₂. (d) and (e) are the elemental EDX mapping for the Tb, V element distribution within a cross-section TEM sample, respectively. ^[27]

Thermochromic properties. The UV-Vis-NIR transmittance spectra for the Tb-doped VO₂ thin films were measured in the wavelength range 250-2500 nm at the temperature 20/90 °C. As shown in Figure 4.8, with increasing the Tb doping level, the transmittance in the whole wavelength range was steadily increased at both 20 ($\tau < \tau_c$) and 90 °C ($\tau > \tau_c$), and the %T contrast across the MIT could be clearly observed especially in the IR range ($\lambda > 780$ nm). The thermochromic properties calculated based on the temperature dependent %T spectra were tabulated in Table 4.3, where a steady increase of average T_{lum} from 45.8% to 79.0% along with the increasing Tb doping level from 0 to 6 at.% could be observed, and then it fell back slightly to 75.1%/62.3% at the doping level 8 at.%/10 at.%. As observed in the %T spectra, both visible and IR transmission could be enhanced by the Tb doping no matter at high or low temperatures. It is found that with increasing the Tb doping level, the %T contrast at $\lambda = 2500$ nm was gradually decreased, which should be due to the lattice distortion as a result of atom substitution of V⁴⁺ by Tb³⁺. An interference effect^[67] for the temperature dependent %T was observed from 0 to 2 at.% Tb doping, where the crossover point of the %T curves at low and high temperatures exhibited a blue shift when increasing the Tb doping level, which could result in an enhancement of ΔT_{sol} from 7.7% to 8.3%. However, with further increasing the doping level above 2 at.%, the interference effect discontinued and the ΔT_{sol} began to decrease accordingly. The overall changing trend of average T_{lum} and ΔT_{sol} as a function of Tb doping level has been illustrated in Figure 4.8b. It is noticed that the Tb doping level of 6 at.% was a turning point for both T_{lum} and ΔT_{sol} , at which the average T_{lum} was at the maximum whilst the ΔT_{sol} was at the lowest point. It should be noticed that the relative enhancement of T_{lum} by ~80% through 6 at.% Tb doping has surpassed the best reported doping cases as shown in Table 4.4. The best thermochromic performance was reached at 2 at.% Tb-doping, where a relative enhancement (~ 18%) of average T_{lum} and an increase of ΔT_{sol} from 7.7% to 8.3% compared with the pristine undoped VO₂ thin film could be achieved. The %T hysteresis loops measured at the wavelength 2500 nm

were recorded in a heating/cooling cycle within a temperature range 20-100 °C. As depicted in Figure 4.8c, all the hysteresis loops show the sharp %T change around the transition temperature, in accordance with the first order MIT nature of the VO₂ material. The temperatures during the heating and cooling cycles at which the sharpest %T change happens were recorded as phase transition temperature $\tau_{c, \text{ heating}}$ and $\tau_{c, \text{ cooling}}$. The τ_c was calculated from the average of $\tau_{c, \text{ heating}}$ and $\tau_{c, \text{ cooling}}$, while the τ_c movement from heating to cooling cycle ($\Delta\tau_c = \tau_{c, \text{ heating}} - \tau_{c, \text{ cooling}}$) was termed as the hysteresis loop width. As illustrated in Table 4.3, below the doping level of 5 at.%, the τ_c reducing rate of Tb-doping could be calculated as 1.5 °C/at.%, and then τ_c returned to the value of pristine undoped VO₂ thin film (67.5 °C) at the doping level 6 at.%. The mechanism of τ_c modulation with Tb doping may be explained rationally by the competition between the lattice distortion from the atom replacement of V by Tb with larger ionic radius (increasing extra strain) and the generated h^+ carrier by the Tb doping simultaneously. In details, after the atom replacement, the larger Tb³⁺ ionic radius could give rise to the τ_c reduction only at low doping levels (< 5 at.%), since the lattice distortion was superior to the h^+ carrier density at these doping levels^[68], and then the high concentration of h^+ carriers resulted in the increment of τ_c at high Tb doping levels, as the h^+ carrier density has been superior to lattice distortion at this time.^[1] In addition, the decrease of τ_c with Tb doping was consistent with the DFT study on RE-doped VO₂ by Gao, et al. (2014).^[69] Overall, compared with the reported F-,^[70] Mg-,^[25] Zr-doped and W-Zr-codoped VO₂ thin films,^[25] the Tb-doped VO₂ thin films exhibited the largest luminous transmittance, although solar modulating ability was largely sacrificed simultaneously.

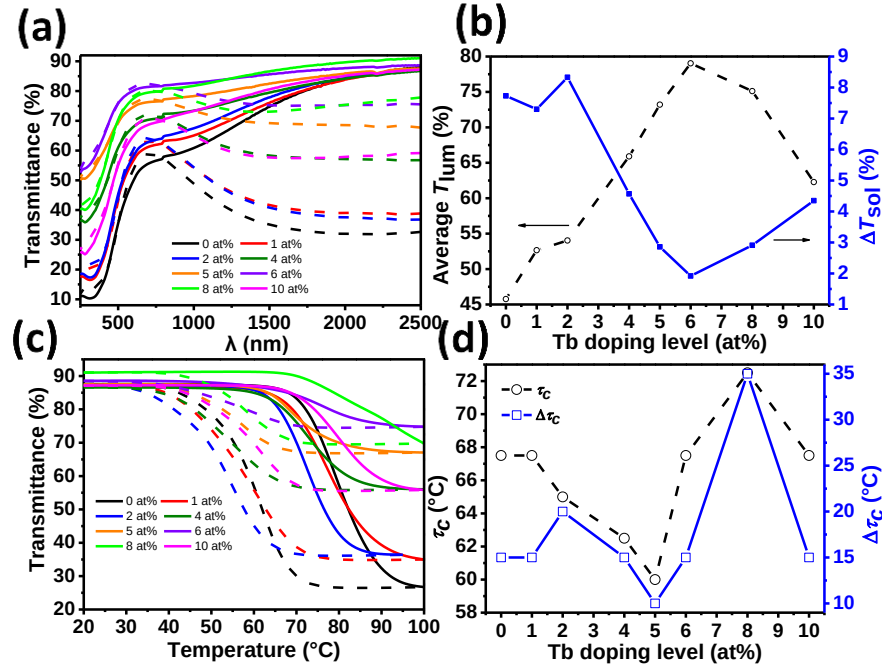


Figure 4.8 a) UV-Vis-NIR %T spectra of Tb-doped VO₂ thin films with the doping level from 0 to 10 at.%, all the spectra were collected at 20 °C (solid lines) and 90 °C (dashed lines). b) Plots of average $T_{lum}/\Delta T_{sol}$ v.s. doping level for Tb-doped VO₂ thin films. c) %T hysteresis loop of Tb-doped VO₂ thin films recorded at $\lambda = 2500$ nm. Solid lines represent the heating cycle and the dashed lines are the cooling cycles; d) Plots of Phase transition temperature (τ_c)/hysteresis loop width ($\Delta\tau_c$) v.s. doping level for Tb-doped VO₂ thin films. ^[27]

Table 4.3 Parameters and calculated thermochromic performance for Tb-doped VO₂ thin films. ^[27]

Doping level (at.%)	Thickness (nm) ^{a)}	T _{lum} (%)		ΔT _{lum} (%)	T _{sol} (%)		ΔT _{sol} (%)	τ _c (°C)	Δτ _c (°C)	Grain size (nm) ^{b)}
		20	90		20	90				
		°C	°C		°C	°C				
0	100	44.5	47.1	-2.6	51.6	43.9	7.7	67.5	15	60.7
1	100	52.0	53.3	-1.3	57.1	49.8	7.3	67.5	15	60.0
2	100	53.4	54.7	-1.3	58.7	50.3	8.3	65.0	20	61.5
4	100	65.4	66.4	-1.0	68.1	63.5	4.6	62.5	15	71.0
5	100	72.8	73.6	-0.8	74.6	71.7	2.9	60.0	10	60.1
6	100	78.6	79.5	-0.9	79.4	77.5	1.9	67.5	15	57.5
8	100	74.8	75.4	-0.6	76.4	73.5	2.9	72.5	35	73.6
10	100	61.3	63.3	-2.0	65.4	61.1	4.4	67.5	15	97.8

^{a)} The thickness derivation is within 10 nm. ^{b)} The mean grain sizes were obtained from the respective AFM images.

Table 4.4 Effects of selected dopants on τ_c and T_{lum} of VO₂.^[27]

Dopant	Limit	Effect on τ_c	Effect on T_{lum}
Eu ³⁺ ^[26]	4 at. %	-6.5 °C/at. %	Increased by 22% at 4 at. %
Mg ²⁺ ^[34, 71, 72]	7 at. %	-3 °C/at. %	Increased by 11% at 7 at. %
W ⁶⁺ ^[73]	2.5 at. %	-23 °C/at. %	Decreased by 10% at 2.5 at. %
F ⁻ ^[73]	2.1 at. %	-20 °C/at. %	unchanged
Mo ⁶⁺ ^[21]	2.5 at. %	-12 °C/at. %	Decreased by 10% at 3 at. %
Nb ⁵⁺ ^[21]	4 at. %	-8 °C/at. %	Decreased by 50% at 11 at. %
P ³⁻ ^[74]	1 at. %	-13 °C/at. %	Not available
Fe ³⁺ ^[38]	1.4 at. %	-6 °C/at. %	Not available
Sb ³⁺ ^[12]	7 at. %	-1 °C/at. %	35% at 3 at. %.
Zr ⁴⁺ ^[75]	11 at. %	unchanged.	Increased by 65%

Band gap of the thin films. As demonstrated in the literature,^[76] the optical band gap of semiconducting materials can be determined by the expression $(\alpha\hbar\omega)^m = A(\hbar\omega - E_g)$, where the value of m assigned to 1/2, 1/3, 2 and 2/3 represents the corresponding indirect-allowed, indirect-forbidden, direct-allowed and direct-forbidden optical transitions. Moreover, the band gap detected by the optical measurement is usually the direct band gap, since the momentum conservation has low-excitation probability during the optical transition between two different symmetry points.^[77] With this in mind, the direct band gap of the pristine and Tb-doped VO₂ thin films was determined by least-square fitting the linear part of plots of $(\alpha\hbar\omega)^2$ v.s. $\hbar\omega$ (Figure 4.9a) according to the equation $(\alpha\hbar\omega)^2 = A(\hbar\omega - E_g)$, where α is the absorption coefficient derived from $\alpha d = -\ln(T/1-R)$, A is a constant and $\hbar\omega$ is the incident light energy. As shown in Figure 4.9b, below the doping level of 6 at. %, the band gap E_g was gradually widened from 2.67 to 3.0 eV along with the Tb doping from 0 to 6 at. %, which should be the reason of the increase of T_{lum} as illustrated in Table 4.3. Such similar band gap widening effect has also been reported in

Mg-doped VO₂ thin films. [34, 71, 72] However, further increment of the doping level results in a slight decay of E_g , and also resulted in a moderate decrease of T_{lum} , which should be due to the competition between the extra strain energy and the h^+ carrier density introduced by the Tb³⁺ doping in the VO₂ lattice.

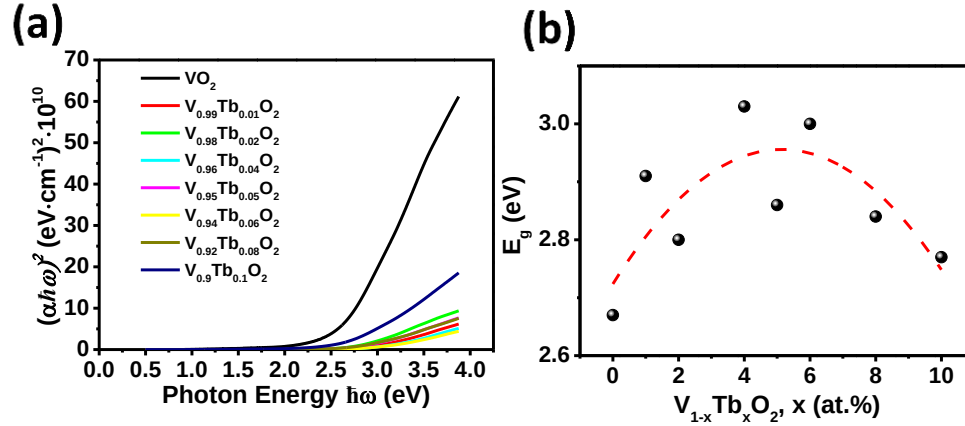


Figure 4.9 Plots of $(\alpha\hbar\omega)^2$ v.s. $\hbar\omega$ (a) and the doping level dependent band gap E_g (b) of the Tb-doped VO₂ thin films. [27]

In summary, the Tb³⁺ cation was firstly doped into the VO₂ lattice to investigate its effect on enhancing the thermochromic properties in terms of τ_c reduction as well as T_{lum} increment. With continuously doping with Tb³⁺ from 0 at.% to 5 at.%, the T_{lum} was found to be largely improved from 45.8% (pristine undoped VO₂) to 73.2% (5 at.% Tb doping) whilst the τ_c was found to be marginally reduced from 67.5 °C (pristine undoped VO₂) to 60 °C (5 at.% Tb doping). However, with further improving the doping level to 10 at.%, the T_{lum} was found to be slightly depressed to 62.8% and the τ_c was increased to 67.5 °C, which should be mainly due to the competition between the lattice distortion and the free h^+ carrier density arising from the cation substitution of V⁴⁺ by Tb³⁺. With respect to the smart window applications, the future investigate on Tb/M (M=W, Mg, F, Zr)-codoped VO₂ thin films will be performed to explore an alternative approach to dig out the combination of high T_{lum} and large ΔT_{sol} , in light of the cost of solar modulating abilities in increasing the luminous transmittance for single Tb doping.

4.3.1.3 La doped VO₂ thin Film

Synthesis of La-doped VO₂ thin films. The XRD analysis of the pristine and La-doped VO₂ thin films was performed using a 2 theta scanning mode with a grazing angle of 0.3°. As shown in Figure 4.10a, the broad diffraction bumps around 20° (2θ) in the XRD patterns should be assigned to the XRD peak of the amorphous fused silica substrate. The high diffraction noise at low angles should be due to the fluorescent background diffraction. All of the pristine and La-doped VO₂ thin films exhibit the characteristic (011) XRD peak of VO₂(M) (monoclinic, $P 2_1/c$, JCPDS #82-661) around 28° (2θ), and no other vanadium or lanthanum impurity phases could be observed in the patterns, which indicates the successful synthesis of La-doped VO₂(M) thin films. With regard to the peak shift due to the La doping, compared with the pristine VO₂ thin film, the (011) peak position for the 5 at.% La doped VO₂ thin film was shifted to the left by 0.2° from 28.0° to 27.8°, in accordance with the lattice expansion due to the cation substitution of V⁴⁺ by the larger La³⁺ (ionic radius, 1.032 Å v.s. 0.58 Å), and was also consistent with the DFT calculations.^[69] The La doping levels for the La-doped VO₂ thin films were confirmed by EDX analysis with a 10% derivation. As illustrated in Figure 4.10b, the doping levels detected by EDX agree well with the expected values in the experiment, which made sure the reasonable discussions below according to the La doping levels.

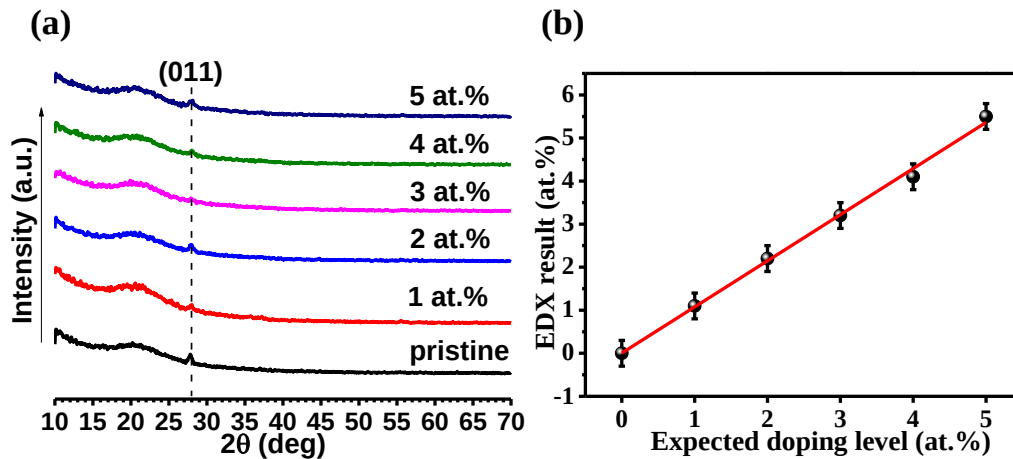


Figure 4.10 (a) XRD patterns of the pristine and La-doped VO₂ thin films with the doping level from 1 to 5 at.%. (b) Correlation between the expected La doping level and the values determined by EDX analysis with a 10% derivation.^[69]

The morphology evolution of the pristine and La doped VO₂ thin films was characterized using FESEM. As shown in Figure 4.11, all the La-doped VO₂ thin films showed a nanograin dense-packed morphology. The mean grain size for the thin films with the doping level 0/1/2/3/4/5 at.% was 61, 72, 84, 79, 62 and 73 nm, respectively, indicating the slight increase of the grain size along with the La doping. The average roughness (*Ra*) and the mean thickness of the La-doped VO₂ thin films have been measured with AFM under tapping scanning mode, and the determined values have been tabulated in Table 4.5. The *Ra* for the thin films was in a range of 3.0-5.5 Å, and the mean thickness of the thin films was within a range of 72-90 nm, which should have no significant influence on the thermochromic properties. A further morphology/phase investigate on the 3 at.% La doped VO₂ thin film was carried out with the TEM. As depicted in Figure 4.12(a,b), the bright-field TEM images confirmed that the average grain size for the 3 at.% La doped VO₂ thin film was ~80 nm, in agreement with the FESEM analysis. The SAED pattern as shown in Figure 4.12c showed the polycrystalline diffraction concentric rings that can be indexed with (011), (200), (021) and (022) crystalline faces of VO₂(M) phase, which indicates the high phase purity as well as the polycrystalline nature of the VO₂ thin film. The STEM was used to investigate the La doping at the lattice scale in depth. As illustrated in Figure 4.12d, the atom substitution of V by La in the lattice could be observed in the high resolution HAADF (high angle annular dark field) image, where the La atoms were brighter than the V atoms as La element has larger atomic number (57 v.s. 23), which contributed more HAADF (elastic scattering) signals collected by the detector ($\propto Z^{3/2}$). Furthermore, the STEM-EDX elemental mapping was used to determine the La element distribution in the VO₂ lattice. As shown in Figure 4.12(e, f), the elemental mapping showed that the La atoms have been incorporated in the VO₂ lattice successfully since the distribution of La signal matched well with the lattice plane arrangement.

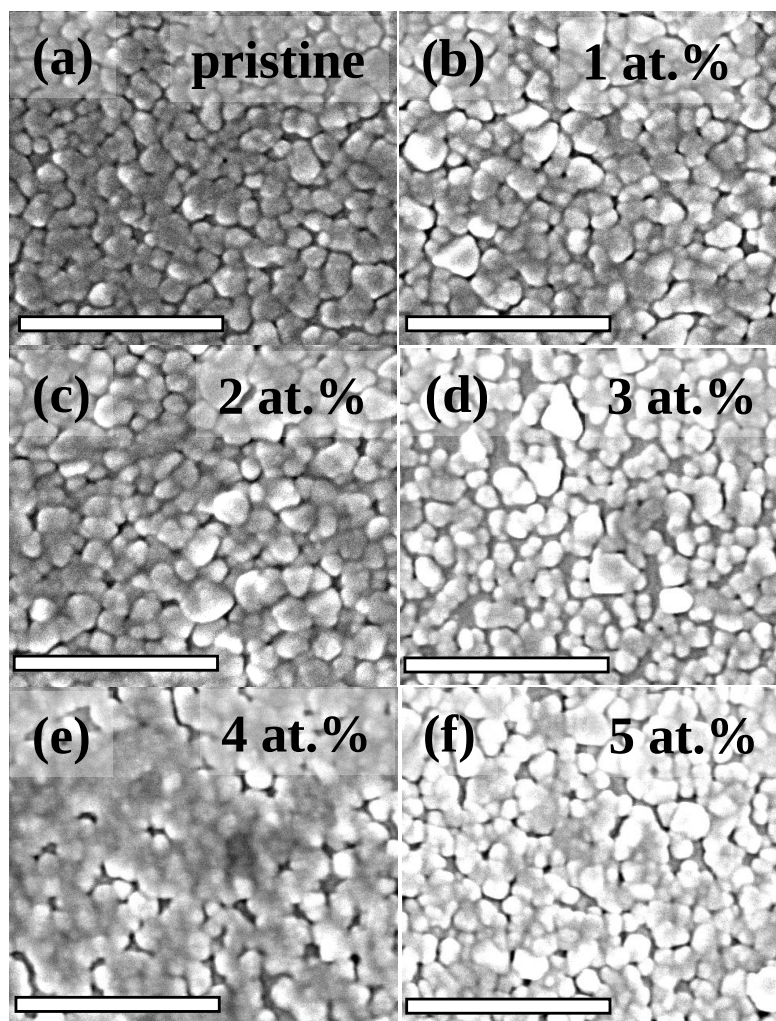


Figure 4.11 FESEM images for the pristine (a) and La doped VO₂ thin films with the doping level 1 at.% (b), 2 at.% (c), 3 at.% (d), 4 at.% (e) and 5 at.% (f). The scale bar in the images is 500 nm in length.^[69]

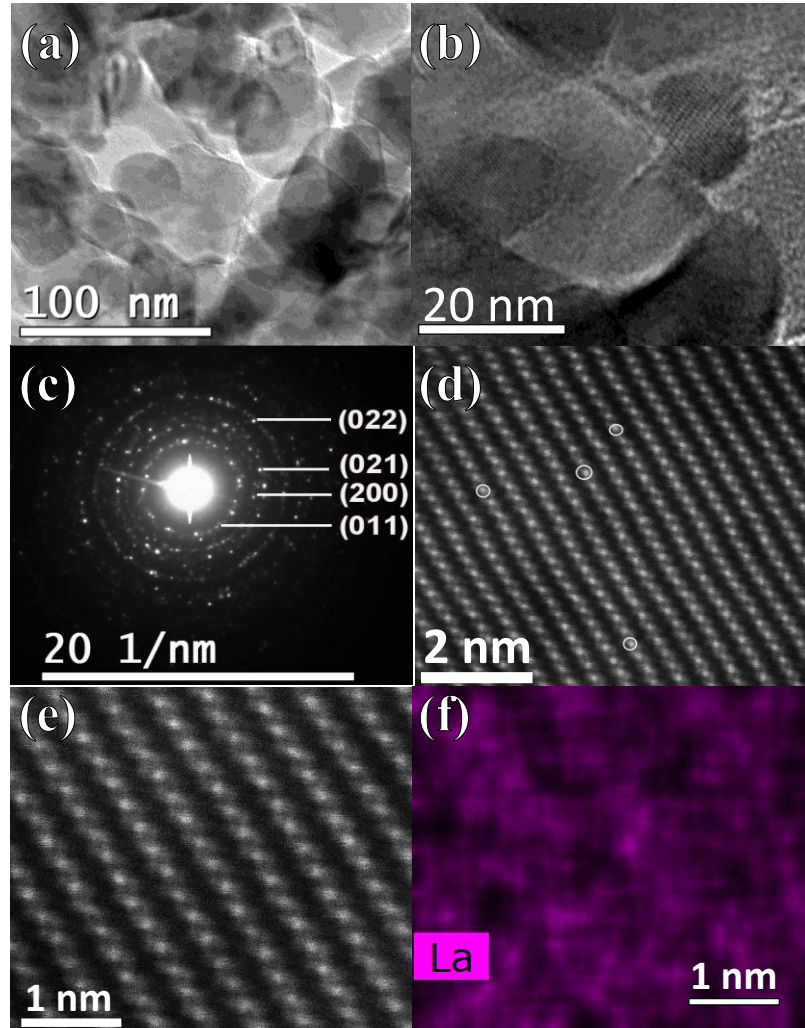


Figure 4.12 Low-magnification TEM (a) and enlarged TEM image (b) of the 3 at.% La doped VO₂ thin film. (c) Corresponding SAED pattern of the polycrystalline 3 at.% La doped VO₂ thin film. (d) High-resolution HAADF image of the 3 at.% La doped VO₂ thin film. (e) HAADF image of 3 at.% La doped VO₂ thin film for EDX mapping. (f) The corresponding La element mapping in the whole area of (e).^[69]

Thermochromic properties. Figure 4.13a shows the UV-Vis-NIR transmittance spectra ($250 \leq \lambda \leq 2500$ nm) of the La-doped VO₂ thin films at the temperature 20/90 °C. With heating from 20 to 90 °C, a large %T contrast across the MIT at the wavelength 2500 nm was observed for all the La-doped VO₂ thin films, consistent with the optical modulating abilities for VO₂(M).^[43, 55, 78] The integrated T_{lum} and ΔT_{sol} were calculated based on the %T spectra, and were tabulated in Table 4.5. Figure 4.13b shows plots of average T_{lum} v.s. ΔT_{sol} at different La doping levels. The best thermochromic performance in terms of a

combination of $T_{\text{lum}}=50\%$, $\Delta T_{\text{sol}}=10.3\%$ could be reached with 4 at.% La doping, which has surpassed the best value for RE-doped VO₂ thin films,^[26, 27, 39] and was comparable to other non-RE doped VO₂ thin films.^[12, 25, 79-82] It is interesting to find that both the average T_{lum} and ΔT_{sol} (69.2 %, 9.0 %) at 5 at.% La doping were larger than that of pristine VO₂ (64.8%, 7.3 %) (Figure 4.13b), which should be owing to the appearance of Surface Plasmon Resonance peak around the wavelength 1250 nm as shown in Figure 4.13a. The peaks at 2500 nm were the noise from the spectrometer. The hysteresis loop of transmittance was measured from 20 to 100 °C at a fixed wavelength 2000 nm. As shown in Figure 4.13c, the MIT of VO₂ with La doping tended to move toward lower temperatures below the doping level of 4 at.%, and the similar trend has also been found in the Eu-doped VO₂ thin films.^[26] The La doping level dependent τ_c has been analyzed in Figure 4.13d, where a τ_c reducing rate -1.1 °C/at.% was deduced from the least-square fitting of the τ_c values below 4 at.% La doping. The τ_c reducing rate of La was similar to that of Tb doping (-1.5 °C/at.%), but much lower than that of Eu doping (-6.5 °C/at.%) (Table 4.6). It is the first time to investigate the τ_c reducing efficiency of La doping experimentally, since a DFT simulation work has uncovered the τ_c reducing ability of La.^[69] As for the τ_c reduction mechanism, the lattice distortion from the atom replacement of vanadium by larger lanthanum atoms should contribute to the decrease of τ_c as calculated by DFT,^[69] and the propagation of V⁵⁺ or the increment of hole carrier density (h^+) induced by the La doping ($\text{V}^{4+}_{1-2x}\text{V}^{5+}_x\text{La}^{3+}_x\text{O}_2$) should result in the increase of τ_c .^[65] Therefore, the competition between the above two factors should be an acceptable reason why τ_c was reduced at low La doping levels, but began to recover at high La doping levels.

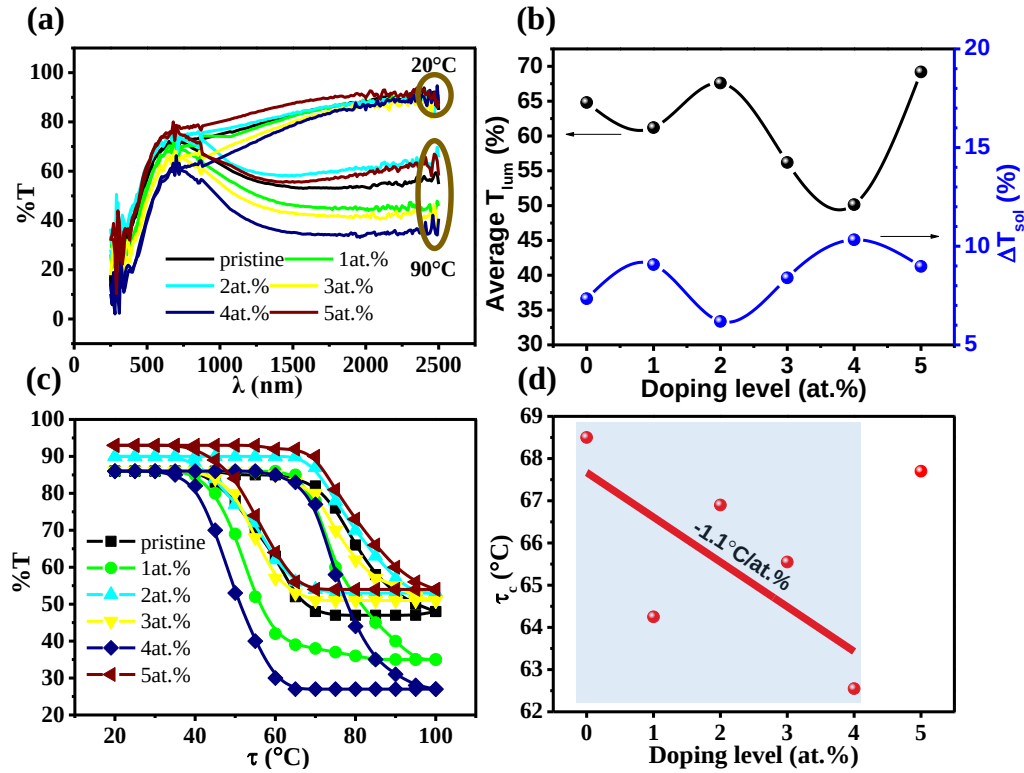


Figure 4.13 (a) UV-Vis-NIR %T spectra of the pristine and La doped VO₂ thin films (doping level 1-5 at.%) under the temperature 20 and 90 °C. (b) La doping level dependent average T_{lum} and ΔT_{sol} for the La-doped VO₂ thin films. (c) %T hysteresis loop of the pristine and La doped VO₂ thin films (doping level 1-5 at.%). (d) Plots of τ_c v.s. La doping level with linear fitting below 4 at.%. [69]

As listed in Table 4.6, compared to previously reported Eu³⁺ and Tb³⁺ doping, the much larger ionic radius of the La³⁺ cation should be able to result in more significant enhancement of thermochromic properties of VO₂ thin films. As illustrated, the average T_{lum} declined steadily along with the ascending ionic radius of the RE cations doping in the VO₂ thin films, and it was consistent with the larger refractive index arising from the greater electronic polarization and slower velocity of light for larger cations. The ionic radius increased from 0.92 to 0.95 Å from Tb³⁺ to Eu³⁺, whilst the τ_c reducing rate increased from 1.5 to 6.5 °C/at%, indicating the high efficiency of large cations in reducing the τ_c due to the larger lattice distortion. Unexpectedly, the La³⁺ cation doping with the largest ionic radius showed the lowest τ_c reducing rate, which could not be explained reasonably till now. But the expected dot defects in terms of La insertion rather

than V replacement in the distorted lattice arising from La doping may partially contribute to this phenomenon.

The %A and %R UV-Vis-NIR spectra of the pristine and La-doped VO₂ thin films are shown in Figure 4.14a. The %A and %R spectra were found to be modulated by the La doping with the doping levels from 1 to 5 at.%, where the 5 at.% La doping exhibited the lowest %A or %R and 4 at.% La doping showed the highest %A or %R, indicating the highest and lowest %T at 5 at.% and 4 at.% doping level, respectively. In order to further evaluate the doping effects of La³⁺ cation on the optical properties of VO₂ thin films, a least-square fitting of the linear part of $(\alpha\hbar\omega)^2$ v.s. E was carried out to calculate the direct bandgap (E_g) of the La-doped VO₂ thin films (Figure 4.14b) according to the equation $(\alpha\hbar\omega)^2 = A(E - E_g)$, where α is the absorption coefficient that can be calculated from $\alpha d = -\ln(T/1-R)$, A is a fitting constant and $\hbar\omega$ or E is the incident light energy. As shown in the inset of Figure 4.14b, with continuously doping with La, the E_g of the VO₂ thin films was gradually decreased, and reached the lowest value 2.42 eV at the doping level of 3 at.%. Thereafter, the E_g began to recover with further La doping. The E_g decrease below the doping level of 3 at.% seemed to be similar to the tungsten (W) doping, which has been ascribed to the larger ionic radius of W⁶⁺,^[83] and the subsequent E_g widening should be attributed to the competition between the large ionic radius effect and the increasing h^+ carrier density. As the change of band gap is of electronic nature,^[83] the E_g decrease below 3 at.% La doping should also be related to the band structure modification in the La doped VO₂ lattice. As shown in Figure 4.14c, the 5 at.% La doped VO₂ thin film exhibited the reduced cold-state refractive index ($n < 1.9$) compared with the reported value ($n > 2.0$) for undoped VO₂ thin films^[84], which could also be used to explain the higher T_{lum} and the larger ΔT_{sol} than that of the pristine VO₂ thin film.

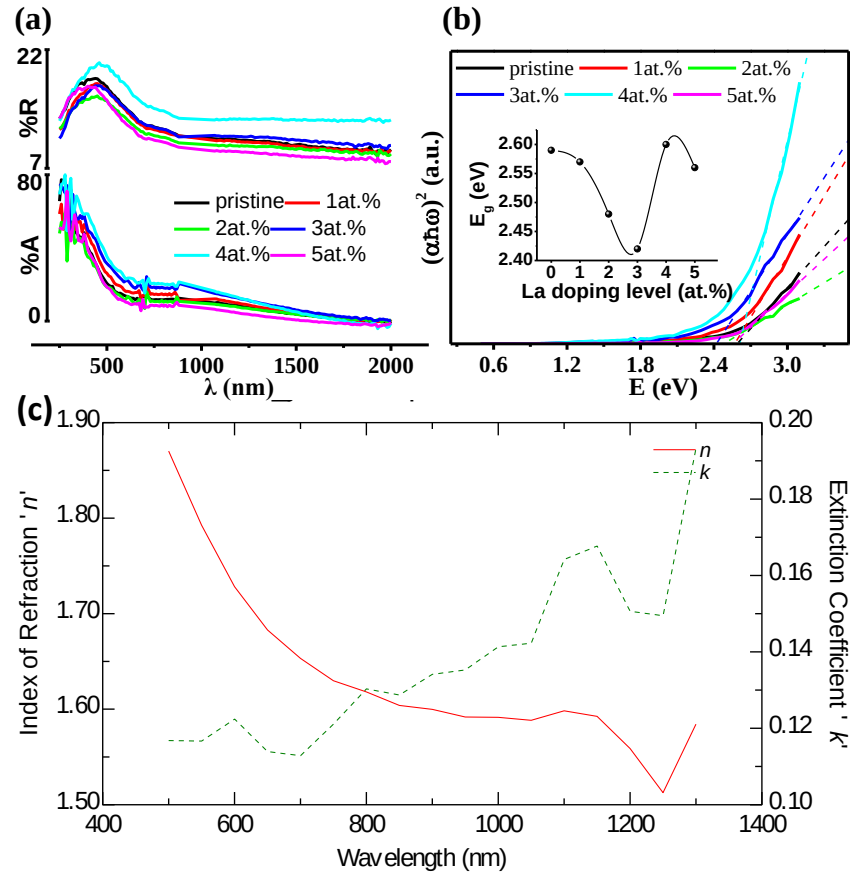


Figure 4.14 (a) %A and %R UV-Vis-NIR spectra of the pristine and La doped VO₂ thin films (doping level 1-5 at.%) at room temperature. (b) Plots of $(\alpha\hbar\omega)^2$ v.s. E . The inset is the band gap E_g under different La doping levels. ^[69] (c) Optical parameters 'n' and 'k' measured at cold-state with ellipsometer for 5 at.% La doped VO₂ thin film.

Table 4.5 Calculated thermochromic properties of the La-doped VO₂ thin films. ^[69]

Doping level/at.%	Thickness/nm	Ra ^a /nm	T _{lum} (20 °C/90 °C)/%	ΔT _{sol} ^b /%	τ _c (heating/cooling)/ °C
0	74	3.0	64.8/64.8	7.3	79.9/57.1
1	83	4.4	61.1/61.3	9.1	76.1/52.4
2	60	8.6	67.5/67.7	6.2	79.6/54.2
3	72	4.4	55.8/56.6	8.4	76.2/54.9
4	90	4.1	49.9/50.4	10.3	75.9/49.2
5	80	5.5	69.5/68.9	9.0	80.2/55.2

^a Ra is the average roughness; ^b $\Delta T_{\text{sol}} = T_{\text{sol}}(20\text{ }^{\circ}\text{C}) - T_{\text{sol}}(90\text{ }^{\circ}\text{C})$.

Table 4.6 Summarized doping effect on thermochromic properties of the VO₂ continuous thin films. ^[69]

RE doping						
cation	Ionic Radius/Å	Doping /at.%	Ave. T_{lum} /%	ΔT_{sol} /%	d τ_c /d at.%	Ref.
Eu ³⁺	0.95	4	54	6.7	-6.5	[26]
Tb ³⁺	0.92	4	65.9	4.6	-1.5	[85]
La ³⁺	1.03	4	50.1	10.3	-1.1	This work
Other doping						
W ⁶⁺	0.6	2	45.1	6.9	20	[86]
Ti ⁴⁺	0.605	-	40	4.6	-	[87]
Mg ²⁺	0.72	5	82.1	4.8	1.4	[63]

Notes: The thickness, roughness and grain size of the thin films are at the same level.

In summary, the first experimental studies on La-doped VO₂ thin films were carried out with fully characterization starting from a facile sol-gel synthesis method. The obtained La-doped VO₂ thin films were found to exhibit high visible transmission as well as large solar modulating abilities, which could facilitate the smart window applications. Remarkably, the combination $T_{\text{lum}}=50.1\%$, $\Delta T_{\text{sol}}=10.3\%$ obtained at the 4 at.% La doping has reached the best value for the thermochromic performance of continuous VO₂ thin films as far as our knowledge. Furthermore, the 5 at.% La doped VO₂ thin film exhibited a simultaneously increment of T_{lum} and ΔT_{sol} . A comparison between the La and the Eu/Tb doping effect on the thermochromic performance of VO₂ thin films has been investigated, and the T_{lum} was found to decrease with increasing the ionic radius of the RE dopants, which could be ascribed to the lattice distortion arising from the RE doping. In addition, the τ_c reduction ability of the La doping as suggested by the DFT calculation was firstly confirmed in experiment, and a τ_c reducing rate -1.1 $^{\circ}\text{C/at.}\%$ below the doping level of 4 at.% could be induced by least-square fitting. The τ_c increase at 5 at.% La

doping should be due to the competition between the lattice distortion and the h^+ carrier density that were coexistent in the La-doped VO₂ thin films. Lastly, a band gap narrowing down phenomenon was observed below 3 at.% La doping, which should be due to the band structure changes caused by the La doping. All in all, the presented systematic study of La doping effects on VO₂ thin films opened another window for rationally analysis of the doping with the cations showing the large ionic radius and the low valence state as well.

4.3.2 Mg/W codoped VO₂ thin Film

Phase and topography analysis. The crystalline phase of the pristine and Mg/W-codoped VO₂ thin films was determined by XRD with a 2 theta scanning mode in the range of 10 to 70 °(2 θ) with a grazing angle 1 °. As shown in Figure 4.15, only the characteristic (011) peak at around 2 θ =28 ° for the monoclinic VO₂(M) phase ($P2_1/c$, JCPDS #82-661) could be observed in all of the XRD patterns. No diffraction peaks for other vanadium oxide phases or magnesium/tungsten oxide phases could be found in the XRD patterns, which proves the phase purity of the obtained VO₂(M) phase as well as the successful Mg/W codoping in the VO₂ lattice. The broad bump around 2 θ =20 ° should be ascribed to the silica diffraction from the fused silica substrates, and the increased background noise at low angles should be owing to the X-rays fluoresced by vanadium atoms.

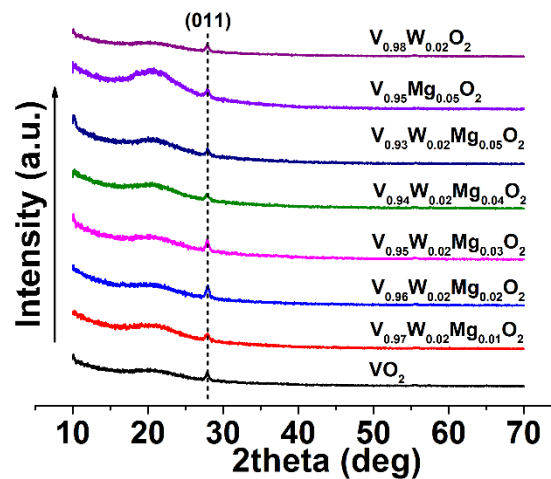


Figure 4.15 XRD patterns for the Mg/W-codoped VO₂ thin films.^[63]

The topography for the pristine and Mg/W-codoped VO₂ thin films was characterized by AFM with a tapping mode. As shown in Figure 4.16, all the VO₂ thin films exhibited a dense-packed nanograin array topography with a narrow grain size distribution below ~100 nm, which could help to reduce the light scattering and enhance the thermochromic performance.^[45] The average grain size for the pristine and codoped VO₂ thin films was in a range of 60-80 nm, and the single Mg doped VO₂ exhibited a relatively smaller grain size ~50 nm.

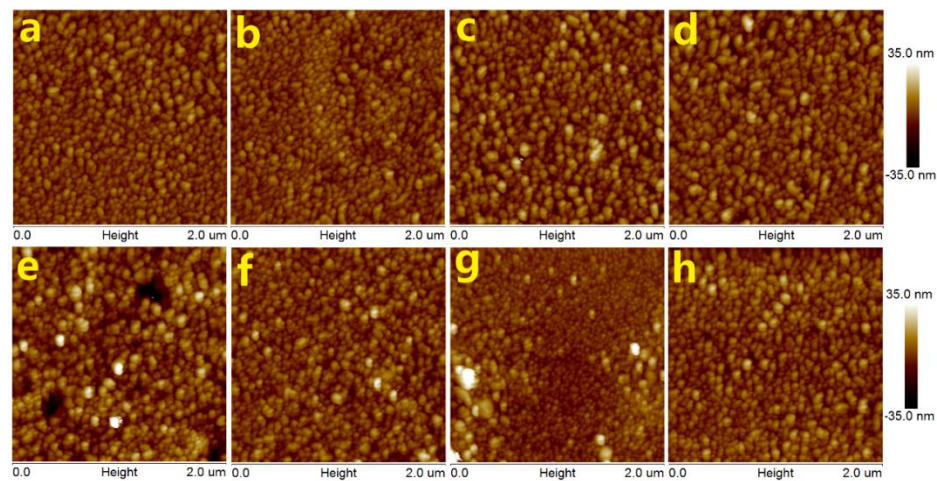


Figure 4.16 2D AFM images for the VO₂ thin films: pristine VO₂ (a); V_{0.98-x}W_{0.02}Mg_xO₂, x=0.01/0.02/0.03/0.04/0.05 (b-f); V_{0.95}Mg_{0.05}O₂ (g); V_{0.98}W_{0.02}O₂ (h) with the scanning area 2 × 2 μm².^[63]

The morphology and the crystallinity of the V_{0.94}W_{0.02}Mg_{0.04}O₂ thin film was further characterized by TEM. As shown in Figure 4.17, the low-magnification bright-field TEM image (Figure 4.17a) indicated the sub-100 nm grain size and the narrow size distribution, which was in accordance with the AFM analysis. The HRTEM image (Figure 4.17b) suggested the well crystallinity of the codoped VO₂ thin film with clearly indexed (011) face belonging to the VO₂(M) phase. The corresponding selected area electron diffraction (SAED) pattern (Figure 4.17c) showed the polycrystalline nature of the VO₂ thin film, and could be indexed by (011)/(-211)/(-212)/(220) faces of VO₂(M) phase, further proving the phase purity of the attained VO₂(M) thin film as analyzed in the XRD results.

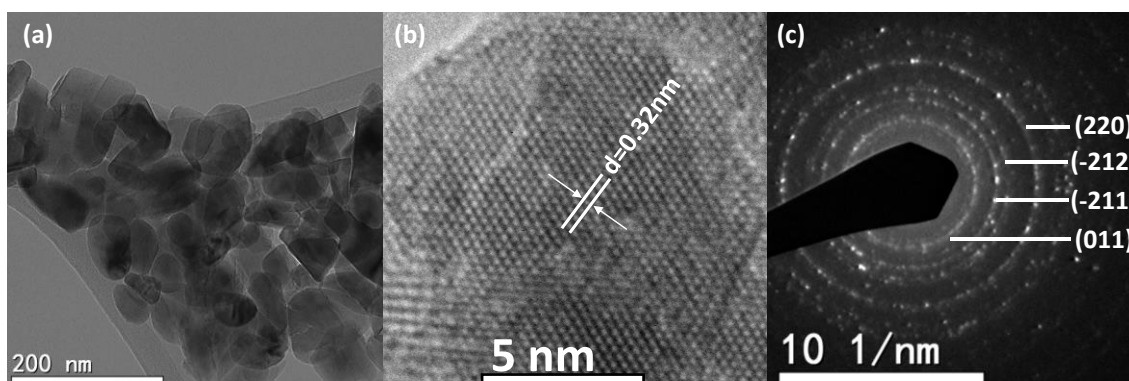


Figure 4.17 Low-magnification bright field TEM image (a), HRTEM image (b) and SAED pattern (c) for the $V_{0.94}W_{0.02}Mg_{0.04}O_2$ thin film.^[63]

Thermochromic properties. The UV-Vis-NIR %T spectra for the Mg/W-codoped VO₂ thin films were measured at 15 and 90 °C, respectively. As shown in Figure 4.18, a %T contrast was observed for all thin films across the phase transition temperature (15/90 °C), which should be ascribed to the intrinsic MIT characteristics of VO₂. Among the thin films, the single Mg-doped sample $V_{0.95}Mg_{0.05}O_2$ exhibited the highest transmittance across the whole spectrum (250-2500 nm) at both 15 and 90 °C, indicating the capability of Mg²⁺ doping in enhancing the T_{lum} . In comparison, the single W-doped VO₂ thin film $V_{0.98}W_{0.02}O_2$ showed the lowest transmittance below and above MIT, uncovering the weakness of W⁶⁺ doping in increasing the T_{lum} due to the absorption. Interestingly, based on 2 at.% W doping, a further codoping with Mg²⁺ was found to be effective to improve T_{lum} , and gave a close result comparing with the single Mg doping ($V_{0.94}W_{0.02}Mg_{0.04}O_2$). This tendency could also be found in the calculated T_{lum} and ΔT_{sol} based on the temperature dependent %T spectra (Table 4.7). The reflection (%R) and absorption (%A) spectra of the Mg/W-codoped VO₂ thin films are shown in Figure 4.18b, where the %A was calculated as 1-%R-%T. The %R at $\lambda=580$ nm for all the thin films fell into a range 14.9-17.8%. Single W⁶⁺ doping led to the highest absorption from 380 to 2500 nm, which indicated that the W⁶⁺ doping had the ability to increase the absorption coefficient of VO₂, largely contributing to the depressed T_{lum} (Table 4.7). On the contrary, single Mg doping was found to give the lowest absorption over most of the wavelengths, proving the capability of Mg doping in enhancing the visible transmission by largely reducing the

absorption coefficient of VO₂.^[25, 33] In addition, compared with 2 at.% W⁶⁺ single doping, the further codoping with Mg²⁺ could also decline the %A ($\lambda=580$ nm), and the lowest absorption could be got for the sample V_{0.94}W_{0.02}Mg_{0.04}O₂, leading to its high T_{lum} as calculated in Table 4.7.

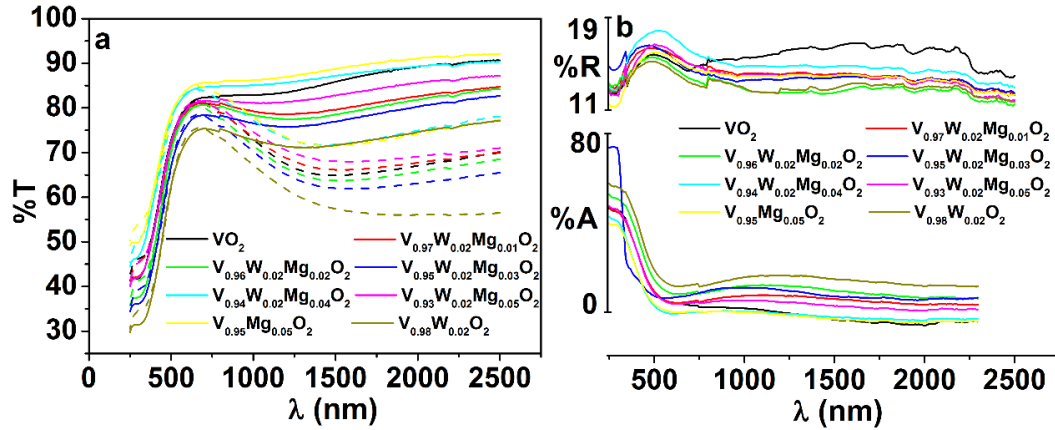


Figure 4.18 (a) Transmittance spectra in the wavelength range 250-2500 nm range for the Mg/W-codoped VO₂ thin films. The solid and dash lines represent the %T spectra tested at 15 and 90 °C, respectively. (b) Recorded %R and %A spectra for the pristine and Mg/W-codoped VO₂ thin films.^[63]

Based on the temperature and doping level dependent %T spectra as shown in Figure 4.18a, the calculated average $T_{lum} = (T_{lum, 15\text{ °C}} + T_{lum, 90\text{ °C}})/2$ and $\Delta T_{sol} = T_{sol, 15\text{ °C}} - T_{sol, 90\text{ °C}}$ for the pristine and Mg/W-codoped VO₂ thin films were tabulated in Table 4.7. Compared with the pristine VO₂, the single 5 at.% Mg-doped VO₂ thin film exhibited an enhanced average T_{lum} from 77.5% to 82.1%, whilst the single 2 at.% W-doped VO₂ thin film showed an decreased average T_{lum} of 69.5%. Based on doping with 2 at.% W, the further doping with Mg re-improve the average T_{lum} above 70%, and the highest value 81.3% could be reached for the sample V_{1.94}W_{0.02}Mg_{0.04}O₂, confirming the ability of Mg doping in enhancing the T_{lum} , even in the Mg/W codoping system.

Table 4.7 Calculated thermochromic properties of the pristine, single and codoped VO₂ thin films.

Sample	%R(580nm)	%A(580nm)	Average T_{lum} /%	ΔT_{sol} /%	τ_c / °C	$\Delta \tau_c$ / °C	E_g /eV
VO ₂	15.6	5.0	77.5	5.9	63.89	19.8	2.88
V _{0.98} W _{0.02} O ₂	14.9	13.5	69.5	3.4	27.05	8.7	2.67

V _{0.95} Mg _{0.05} O ₂	15.9	0.6	82.1	4.8	61.05	16.7	2.99
V _{0.97} W _{0.02} Mg _{0.01} O ₂	16.2	5.2	77.0	3.3	30.45	8.7	2.83
V _{0.96} W _{0.02} Mg _{0.02} O ₂	16.0	8.9	76.0	3.9	29.55	7.9	2.7
V _{0.95} W _{0.02} Mg _{0.03} O ₂	16.0	5.7	73.3	3.7	32.55	8.5	2.75
V_{0.94}W_{0.02}Mg_{0.04}O₂	17.8	0.0	81.3	4.3	35.05	8.9	3.02
V _{0.93} W _{0.02} Mg _{0.05} O ₂	16.5	4.6	77.4	3.7	35.08	8.3	2.83

With respect to the phase transition temperature, the %T at the wavelength 2500 nm heating and cooling in a temperature range 10 to 90 °C was in-time recorded, and has been plotted as %T v.s. T/°C hysteresis loops (Figure 4.19a). As shown in Figure 4.19a, across the heating and cooling cycles, the single Mg and single W doping gave the highest and lowest transmission, respectively. As tabulated in Table 4.7, the pristine undoped VO₂ thin film exhibited the highest τ_c = 63.9 °C and the widest $\Delta \tau_c$ = 19.8 °C. It should be noticed that the τ_c of the pristine VO₂ was slightly lower than the reported value 68 °C for bulk counterparts, which should be due to the grain size effect arising from the sub-100 nm grain size, and the nanograin size effect should also contribute to the widened $\Delta \tau_c$ (19.8 °C).^[64] In comparison, the single Mg/W-doped VO₂ thin films with 5 at.% Mg/2 at.% W could reduce the τ_c to 61.05 °C and 27.05 °C while narrowing down the $\Delta \tau_c$ to 16.7 °C and 8.7 °C, respectively. The much efficient reduction of τ_c and $\Delta \tau_c$ with single W doping should be owing to the high valence state of W⁶⁺, which introduced free electrons to decrease the MIT energy barrier. As for the Mg/W-codoping cases, an unpredicted τ_c increasing tendency was observed (Figure 4.19b), where the Mg doping along with the pre-existence 2 at.% W doping gave rise to a slight τ_c increase from 27.05 °C (V_{0.98}W_{0.02}O₂) to 35.08 °C (V_{0.93}W_{0.02}Mg_{0.05}O₂) with a reducing rate of 1.6 °C/at.%. As is well known, doping with higher/lower valence state cations than V⁴⁺ in the VO₂ lattice could result in the free electron (e⁻)/hole (h⁺) charge carriers that create the V³⁺/V⁵⁺ defect sites, respectively.^[1] The coexistence of W⁶⁺ and Mg²⁺ dopants in the VO₂ lattice may decrease the equilibrium free charge carrier density due to the possible combination of e⁻ and h⁺ charge carriers, which therefore was responsible for the increased τ_c under Mg/W-codoping conditions since τ_c was closely related to the equilibrium carrier density.^[65] It was interesting to observe that the τ_c increasing rate 1.6 °C/at.% arising from W/Mg-codoping was close to the τ_c decreasing rate 1.4 °C/at.%

for the single Mg doping case, which uncovered the critical roles of the equilibrium carrier density in modulating the τ_c .

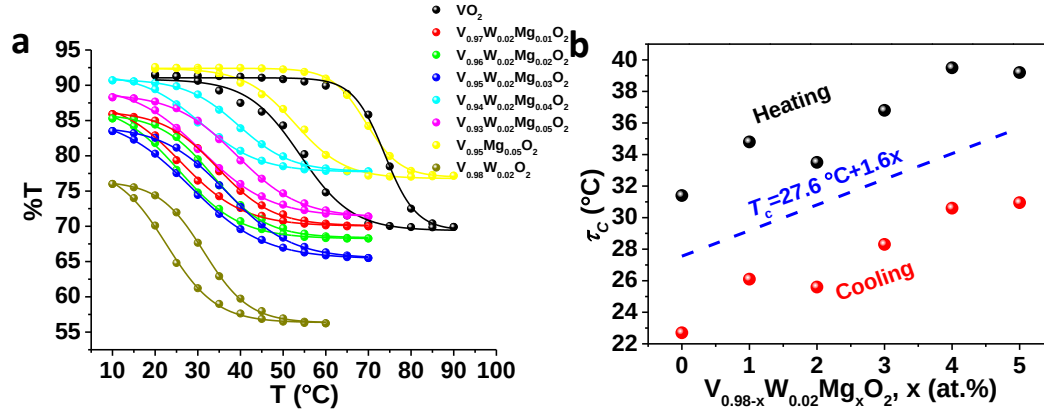


Figure 4.19 (a) %T hysteresis loop for Mg/W-codoped VO₂ thin films at the wavelength 2500 nm in a temperature range 10–100 °C. (b) Plots of doping level dependent τ_c . The solid lines in (a) represent the best fitting results based on Equation 4.2.^[63]

As investigated by Li et al. (2013),^[33] doping with Mg²⁺ had the ability to widen the band gap (E_g) of the VO₂ thin films, and thus resulted in the enhancement of visible transmission. For the Mg/W-codoped VO₂ thin films, the band gap (E_g) was calculated from the linear part of $(\alpha\hbar\omega)^2$ v.s. $\hbar\omega$ (Figure 4.20a) through the least square fitting with the equation

$$(\alpha\hbar\omega)^2 = A(\hbar\omega - E_g) \quad (4.3)$$

Where, α is the absorption coefficient ($\alpha d = -\ln \frac{T}{1-R}$), A is a fitting constant and $\hbar\omega$ is the incident light energy ($\lambda(nm) = \frac{1240}{\hbar\omega(eV)}$). As shown in Table 4.7, under single Mg doping, E_g could be widened from 2.88 to 2.99 eV with 5 at.% Mg doping ($V_{0.95}Mg_{0.05}O_2$) which was consistent with the reported result from Li et al. (2013).^[33] Comparatively, with Mg/W-codoping ($V_{0.98-x}W_{0.02}Mg_xO_2$) in VO₂ thin films, the E_g was also found to be widened upon increasing the Mg²⁺ doping levels, and the E_g increasing rate could be calculated as 0.04 eV/at.% (inset in Figure 4.20b). The relationship between the E_g and the T_{lum} was also investigated as shown in Figure 4.20b. A similar increasing tendency

along with the increase of Mg doping level was found for E_g and T_{lum} , where the curve E_g v.s. T_{lum} follows a linear relationship, which should be ascribed to the simultaneous decline of absorption coefficient as well as the widening of E_g arising from the doping with Mg²⁺ in the VO₂ lattice.

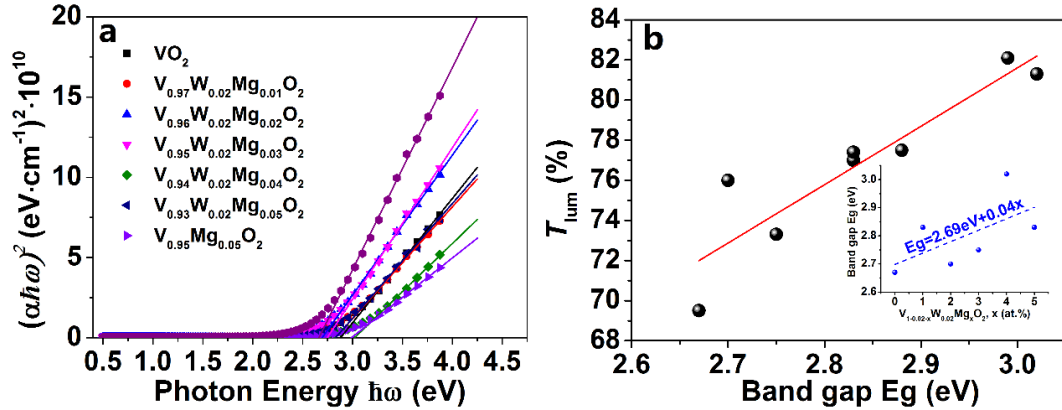


Figure 4.20 (a) Plots of $(\alpha\hbar\omega)^2$ v.s. $\hbar\omega$, where α is the absorption coefficient and $\hbar\omega$ is the photon energy. Band gap E_g is extracted with linear fittings. (b) Relationship between the average T_{lum} and E_g . The solid line in (b) is a linear fit. The inset in (b) is plots of Mg doping level dependent E_g under codoping conditions.^[63]

The high resolution XPS scan of V 2p, Mg 1s and W 4f for the Mg/W-codoped VO₂ thin films was carried out in the corresponding binding energy regions. As depicted in Figure 4.21, it was clearly to see that there exist Mg1s and W4f5/2 / W4f7/2 peaks in the Mg 1s and W4f scan, respectively, indicating the successful Mg/W-codoping in the VO₂ thin films since no magnesium or tungsten compounds could be observed through XRD analysis. Furthermore, the quantitative elemental analysis based on the high resolution XPS, as tabulated in Table 4.8, matched the expected doping levels very well for the Mg/W-codoped VO₂ thin films. As depicted in Figure 4.21(a-e), the V 2p3/2 peak in the V 2p scan could be fitted by two peaks, i.e. V⁴⁺ 2p3/2 around 516 eV and V³⁺ 2p3/2 around 514 eV, suggesting the non-stoichiometry in the VO₂ phase arising from the replacement of V atoms by Mg, W dopants in the lattice. Moreover, as shown in Figure 4.22, with increasing the doping level of Mg²⁺ from 1 to 5 at.% in the lattice, the cation ratio $V^{3+}/(V^{3+}+V^{4+})$ calculated from the XPS result was gradually decreased from 0.42 to 0.22, which was in accord with the decrease of free electron carriers (from the W⁶⁺

doping) due to the neutralization by the hole carriers arising from the Mg²⁺ doping in the Mg/W-codoping system.

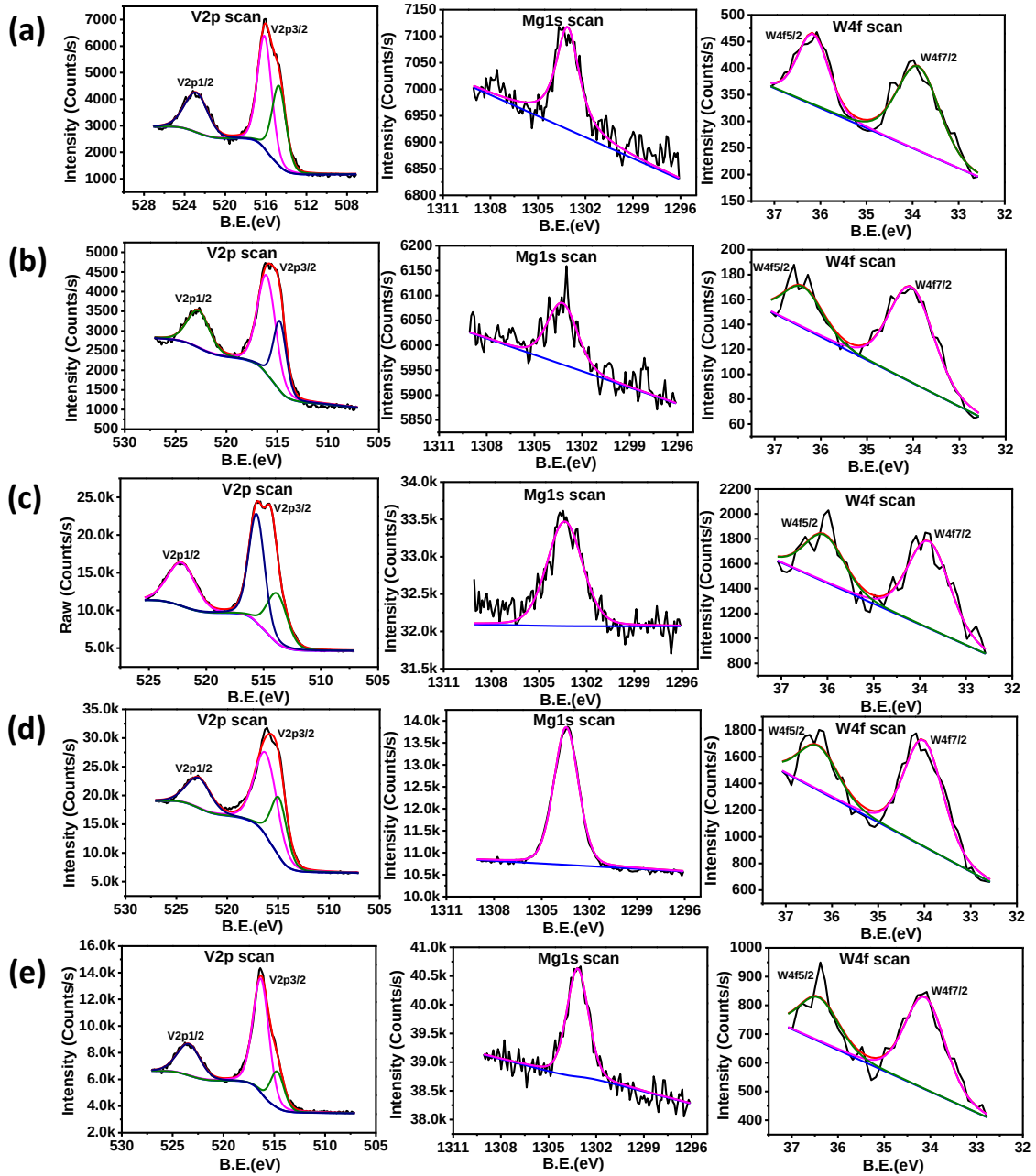


Figure 4.21 High resolution XPS scan of V 2p, Mg 1s and W 4f for the Mg/W-codoped VO₂ thin films, V_{0.98-x}W_{0.02}Mg_xO₂ (a, x=0.01; b, x=0.02; c, x=0.03; d, x=0.04; e, x=0.05).^[63]

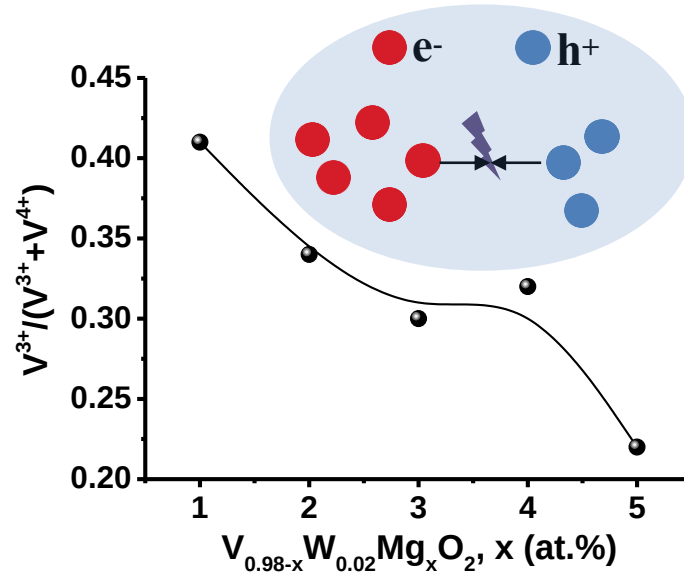


Figure 4.22 XPS result of the $V^{3+}/(V^{3+}+V^{4+})$ for $V_{0.98-x}W_{0.02}Mg_xO_2$ thin film.^[63]

Table 4.8 Doping level and stoichiometry of the Mg/W codoped VO₂ samples.^[63]

Samples	Doping level of Mg, W		Stoichiometry $V^{3+}/(V^{3+}+V^{4+})$
	Exp. (at.%)	XPS result (at.%)	
$V_{0.98}W_{0.02}O_2$	0.0, 2.0	0.0, 2.1	0.45
$V_{0.95}Mg_{0.05}O_2$	5.0, 0.0	5.0, 0.0	0.16
$V_{0.97}W_{0.02}Mg_{0.01}O_2$	1.0, 2.0	1.2, 1.8	0.41
$V_{0.96}W_{0.02}Mg_{0.02}O_2$	2.0, 2.0	1.9, 2.1	0.34
$V_{0.95}W_{0.02}Mg_{0.03}O_2$	3.0, 2.0	2.7, 1.9	0.30
$V_{0.94}W_{0.02}Mg_{0.04}O_2$	4.0, 2.0	3.8, 1.8	0.32
$V_{0.93}W_{0.02}Mg_{0.05}O_2$	5.0, 2.0	5.3, 2.1	0.22

In summary, the first case of Mg/W-codoped VO₂ thin film was synthesized with a facile solution method. The Mg/W codoping was found to be able to benefit the VO₂ thin films with the reduced τ_c from W and the enhanced T_{lum} from Mg. Different from the τ_c reducing ability of the single Mg or W doping, the Mg/W-codoping with a fixed W doping level was found to be able to increase the τ_c at the rate of 1.6 °C/at.% Mg. The τ_c increasing rate (1.6 °C/at.%) under Mg/W-codoping was found to be close to the τ_c reducing rate (1.4 °C/at.%) under single Mg doping, which indicates the critical roles of the equilibrium carrier density in tuning the τ_c of VO₂ indirectly, in terms of the counteraction between the h^+ and e^- carriers. Similar to the single Mg doping, the band gap E_g widening effect was also found in the Mg/W-codoped VO₂ thin films, which could lead to the enhancement of T_{lum} . The best thermochromic performance was found to be

the combination of $T_{\text{lum}} = 81.3\%$, $\Delta T_{\text{sol}} = 4.3\%$ and $\tau_c = 35.05\text{ }^\circ\text{C}$ with the formula $\text{V}_{0.94}\text{W}_{0.02}\text{Mg}_{0.04}\text{O}_2$. The low τ_c as well as the high T_{lum} was promising for practical applications of VO₂ smart windows.

4.4 Conclusions

In conclusion, the fabrication and thermochromic properties of the RE-doped and Mg/W-codoped VO₂ thin films were investigated systematically in this chapter, and the achievement could be concluded as the following:

i) A series of RE-doped VO₂ thin films (RE=Eu, Tb, La) were fabricated with a facile inorganic sol-gel method starting from the V₂O₅-H₂O₂ precursor. The doping of Eu³⁺ in the VO₂ lattice was found to be able to effectively reduce the phase transition temperature and improve the thermochromic properties of VO₂ thin films. The thermochromic properties of VO₂ thin films were improved steadily with the Eu doping, and the best combination of $T_{\text{lum}} = 53.8\%$, $\Delta T_{\text{sol}} = 6.7\%$, $\tau_c = 47.5\text{ }^\circ\text{C}$ could be achieved at the 4 at.% Eu doping which could be comparable to the best value of reported continuous VO₂ thin films. With respect to the phase transition temperature τ_c , the Eu doping below 4 at.% could effectively reduce the τ_c with a rate of $-6.5\text{ }^\circ\text{C/at}\%$, however the τ_c could be slightly increased when further increasing the doping level to 5 at.%. The reason for the τ_c recover under Eu doping should be due to the competition between the free h⁺ charge carrier and the lattice distortion arising from the cation substitution of V⁴⁺ by Eu³⁺, where the h⁺ carrier could increase the τ_c whilst the lattice distortion could reduce the τ_c . The improved thermochromic performance in terms of low τ_c , high T_{lum} as well as the large ΔT_{sol} make Eu³⁺ a promising candidate among the cations to improve the thermochromic properties of VO₂.

With respect to the Tb³⁺ doping, its effect on enhancing the thermochromic properties by reducing the τ_c and increasing the T_{lum} was investigated. With increasing the Tb³⁺ doping level from 0 at.% to 5 at.%, the T_{lum} was steadily improved from 45.8% to 73.2% (~60% relative increment) and the τ_c was slightly reduced from 67.5 to 60 $^\circ\text{C}$ (~1.5 $^\circ\text{C/at}\%$).

Nevertheless, further increasing the Tb doping level to 10 at.% could only slightly decrease the T_{lum} to 62.8% and increase the τ_c back to 67.5 °C, which should be mainly ascribed to the competition between the lattice distortion and the free h^+ carrier density arising from the cation substitution of V⁴⁺ by Tb³⁺, similar to the La doping.

Regarding to the La doping, it was found that the La-doped VO₂ thin films exhibited the combination of high visible transmission (> 50%) and large solar modulating abilities (> 10%), representing the best thermochromic performance for reported VO₂ continuous thin films. Remarkably, the combination T_{lum} =50.1% and ΔT_{sol} =10.3% achieved at 4 at.% La doping was a big improvement for the smart window applications of VO₂ thin films. In light of the Eu, Tb and La doping researches, a comparison between the RE doping effects on the thermochromic performance of VO₂ thin films was investigated. The T_{lum} was found to be decreased gradually upon increasing the ionic radius of the RE dopants, which could be owing to the enhanced lattice distortion from the atom replacement of V by RE with larger ionic radius. The τ_c reducing ability of La doping for VO₂ thin films as reported by the DFT calculation was confirmed in experiment at the first time, and a τ_c reducing rate -1.1 °C/at.% below 4 at.% has been figured out for the la doping. The τ_c recovering at 5 at.% should be also due to the competition between the lattice distortion and the h^+ carrier density as discussed in the Eu and Tb doping. Finally, the systematic study of RE doping effects on the thermochromic properties of VO₂ continuous thin films provides a meaningful viewpoint for analyzing the doping effects for the cations with the large ionic radius as well as the low valence state.

All in all, a facile inorganic sol-gel technique was proposed for the VO₂ continuous thin film fabrications, and a progress for enhancing the thermochromic properties of VO₂ thin films has been achieved through Mg/W-codoping and RE doping in the VO₂ lattice.

ii) A facile solution method was utilized to prepare the first case of Mg/W-codoped VO₂ thin films that may fully make use of the advantages of single Mg and W doping on T_{lum} increment and τ_c reduction, respectively. In accord with the expectation, the Mg/W codoping was found to be able to enhance the thermochromic properties of VO₂ thin

films in terms of the reduced τ_c and the enhanced T_{lum} . Interestingly, different from the τ_c reduction observed from the single Mg or W doping, the Mg/W-codoping with a fixed 2 at.% W doping could result in a slight increase of τ_c with a rate of 1.6 °C/at.% Mg. The τ_c increasing rate (1.6 °C/at.%) was very similar to the τ_c reducing rate (1.4 °C/at.%) from single Mg doping, indicating the critical roles of the equilibrium carrier density (h^+/e^-) in modulating the τ_c , since the counteraction between the h^+ and e^- carriers could occur along with the Mg/W-codoping. Similar to the band gap widening effect from the single Mg doping, the band gap E_g was also found to be widened steadily in the Mg/W-codoped VO₂ thin films, and the E_g widening could also give rise to the enhancement of T_{lum} . The best result for the thermochromic performance of the Mg/W-codoped VO₂ thin films was a combination of T_{lum} = 81.3%, ΔT_{sol} = 4.3% and τ_c = 35.05 °C under 4 at.% Mg and 2 at.% W codoping conditions. The high T_{lum} and the low τ_c for the Mg/W-codoped VO₂ thin films should be meaningful to promote the practical applications of thermochromic smart windows.

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Chapter 5*

Patterned VO₂ Nanostructures on Substrate

The patterned VO₂ nanostructures on supporting substrates were fabricated thorough the top-down etching and the bottom-up annealing approaches. The top-down bioinspired multifunctional VO₂ nipple array was fabricated on patterned fused silica substrates, which exhibited the improved hydrophobicity and the enhanced thermochromic properties with both high visible transmission and large solar modulating abilities. The bottom-up patterned VO₂ surfaces annealed under different temperatures and inert atmospheres showed the morphology evolution from continuous to island-like structures. The mechanisms for the thermochromic performance modulation with patterning were investigated in detail.

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5.1 Introduction

As a phase transition material, vanadium dioxide (VO₂) is well known for its first order phase transition from the low-temperature insulating state to the high-temperature metallic state (MIT) at a critical temperature ($\tau_c \sim 68^\circ\text{C}$). Along with the MIT, there is also an optical transmittance sharp change across the τ_c in the infrared (IR) region, i.e. it allows IR transmission below τ_c , but is highly reflective and absorptive above τ_c , resulting in large transmission contrast across the τ_c . Meanwhile, the visible transmission is almost unaffected during the MIT.^[1-3] Therefore, VO₂ thin films are seemed as excellent candidate for functional applications, e.g. IR bolometers,^[4] thermochromic smart windows,^[5-7] field effect transistors (FETs),^[8] highly damping materials^[9] and smart devices for spacecraft in radiator.^[10]

Basically, an ideal thermochromic smart window requires a high luminous transmittance ($T_{\text{lum}} > 70\%$), a large solar modulating ability ($\Delta T_{\text{sol}} > 10\%$) and a low phase transition temperature ($\tau_c < 30^\circ\text{C}$).^[11] However, there is no such material that can solely meet all the above requirements to date, and the trade-offs are always existed between the requirements. With respect to the VO₂ thermochromic smart windows, the low T_{lum} , small ΔT_{sol} as well as the trade-off between them are the main drawbacks waiting to be solved.^[6, 10] There are already important works, e.g. Mg- and Eu-doping,^[12, 13] multilayer-stacking design,^[14, 15] nanocomposite,^[7, 16] porous structure^[17] and anti-reflective coatings(ARC),^[18, 19] to increase the visible transmission by sacrificing the solar modulation ability except for the five-layer TiO₂/VO₂/TiO₂/VO₂/TO₂ multilayer stacking films with enhanced T_{lum} and ΔT_{lum} simultaneously, but it is complicated to construct at the same time.^[15]

Biomimetic nanostructures have been extensively investigated for antireflection applications due to their ability in dramatically decreasing the reflection as well as enhancing the transmission over a wide range of wavelength and incident angles.^[20-23] The biomimetic surface designed in this chapter is characterized as tapered cone arrays similar to the surface of moth eyes.^[21, 22, 24, 25] The antireflection of the Moth-eye

biomimetic surface can be illustrated by the fact that the tapered cone-array structure offers a gradual increase of refractive index from the top of the cone ($n_{\text{air}} = 1$) to the bottom according to the Equation 1.1.^[24, 26] The net reflectance should be the propagation of each layer across the cone height with gradually increased refractive index from the top to the bottom.^[24] At different depth of the cone, the reflectance changes along with the refractive index, and exhibits the different phase of the optical wave. When the reflection occurs over an optical distance at half wavelength ($\lambda/2$) presenting all phases, the reflectance could be theoretically diminished to zero due to the destructive interference.^[24] The antireflection of the Moth-eye biomimetic nanostructure should be able to enhance the transmission effectively. The efficiency of the reflection reduction over a broad range of light wavelength and incidence angles is correlated to three structural parameters for the Moth-eye biomimetic nanostructure: the height (h) of the tapered nipple arrays, the period (d) and the distance (s) between the neighboured/adjacent cones. In order to reduce the possible scattering from the nipple arrays, the d should be smaller than the wavelength of incident light, and the reflection could be further decreased by reducing the refractive gap between the air and the VO₂/substrate interface through increasing the h .^[24] In addition, the distance s could be almost neglected under the fixed d and h for the antireflection performance. The antireflection effect of the AR nanostructure is superior to that of the AR flat coating owing to its antireflection efficiency over a wide range of incident angles.^[27] *Hitherto* AR surfaces have been explored extensively to eliminate ghost images or veil glare arising from reflection, increase the transmittance and enhance the performance of devices.^[25, 27] With regard to the theoretical calculations, the Finite Difference Time Domain (FDTD) simulation has been utilized to estimate the functions of the Moth-eye biomimetic nanostructures composed of VO₂ coatings on the silica nipple arrays, where the SiO₂ tapered nipple arrays ($p \sim 130$ nm) coated by VO₂ (5-50nm thick) was found to be able to enhance the ΔT_{sol} up to 15.5% and increase the T_{lum} to $\sim 70\%$ simultaneously^[28]. In this chapter, the experimentally investigation of VO₂ thermochromic layer coated on Moth-eye biomimetic SiO₂ nipple arrays was carried out for the first time. Compared with multi- or single-layer flat antireflection coatings,^[14, 15] the nipple array structure could reduce the thermal stress induced by thermal cycling and the coefficient of thermal

expansion (CTE) mismatch between the nanostructure and the substrate. It is found that both T_{lum} and ΔT_{sol} can be enhanced by the Moth-eye biomimetic VO₂ nanostructures and the hydrophobicity can be increased by coating with an additional overcoat on the top of the VO₂ layer within the nanostructure. In addition, the bottom-up method for patterning the VO₂ surface under different annealing temperatures as well as different annealing atmospheres was also proposed to modulate the thermochromic performance.

5.2 Materials and methods

V-H₂O₂ precursor. 300 mg vanadium powder was added into 30 mL 30 wt.% H₂O₂ with rigorous stirring for 40 min in ice bath and a clear yellow solution was formed. Then the clear solution was warmed at 50 °C with continuous stirring until the color was changed to dark red. Prior to use, the dark red sol was aged at room temperature for 2-3 days until a stable uniform dark red gel was formed.

Bottom-up patterned VO₂ thin film preparation. The prepared V₂O₅-H₂O₂ precursors were transferred onto 15×15×0.5 mm³ fused silica substrates through spin coating or dip coating. The thin film thickness could be modified by tuning the coating rate. The dried gel was then annealed in a tube furnace under inert atmosphere (/CO₂/vacuum) for 2 hours at a temperature 350/450/550/650/750 °C with a gas flow rate 200 mL/min or under a vacuum level 1.2 ×10⁻³ Pa.

Top-down preparation of VO₂@SiO₂ Moth-eye patterned thin film: The Moth-eye biomimetic silica cone arrays on fused silica substrates with different periods (0, 210, 440, 580 and 1000 nm) were used to prepare the VO₂ nanostructures. The cone arrays were fabricated by reactive ion etching (RIE) using 2D polystyrene (PS) colloidal crystals as sacrificing template, and the details for RIE process could be found elsewhere in the literature.^[25] The V₂O₅-H₂O₂ precursor was prepared by dissolving vanadium pentoxide powder (300 mg, 99%, Alfa Aesar) in preheated hydrogen peroxide solution (30 mL, 30 wt.%, AnalaR NORMAPUR) under vigorous stirring at 70 °C.^[29] Before the coating process, the patterned substrates were successively precleaned with ammonia, acetone

and ethanol several times to modify the surface to be hydrophilic. Then the coating process was completed by immersing the patterned fused silica substrates into the precursor gel for 30 seconds, and then withdrawing at a speed of 10 mm/min (final VO₂ thickness ~140 nm) and 1 mm/min (final VO₂ thickness ~40 nm). After drying in air, the thin films were subsequently annealed at 550 °C for 2 hours in Ar flow with a heating/cooling rate 1 °C/min. The preparation of the fluorooctyl triethoxysilane (FOS) sol-gel AR overcoat could be found in the literature.^[19] In detail, a TEOS (tetraethyl orthosilicate) precursor was diluted in ethanol and water according to the molar ratio TEOS: ethanol (95%): H₂O = 1: 8.14: 2. HCl acid (37 wt.%) was then dropped into the solution until pH < 2. The solution was kept stirring for 2 h and then aging for at least 24 h before combining with FOS/methanol/H₂O mixture to form the FOS precursor.

Characterization: The XRD was carried out using a Bruker D8 Advance diffractometer (Cu K α , $\lambda = 0.15406$ nm) with a high voltage 40 kV and a current 30 mA. The surface morphology was characterized by an atomic force microscopy (AFM, DI-3100, Bruker, Germany) with the tapping mode and a field-emission scanning electron microscopy (FESEM, 6340F, JEOL, Japan) equipped with an energy-dispersive X-ray spectroscopy (EDS, Oxford, UK). The thickness of the thin film was measured by a surface profiler (Alpha-Step IQ, KLA-Tencor, USA.). The transmission electron microscopy (TEM) was used to characterize the morphology and the crystalline phase of the thin film on JEOL 2010 -TEM with a high voltage 200 KV and a probe current 106 μ A. The TEM cross-section sample was prepared with the lift-out technique in a focused ion beam (FIB) system. The temperature dependent UV-Vis-NIR spectra were measured with a spectrometer equipped with a heating/cooling stage (PE120, Linkam, UK). The reported data is the statistic value averaged from 5 tests on different points of the same sample. The integrated T_{lum} ($380 < \lambda < 780$ nm), T_{IR} ($780 < \lambda < 2500$ nm) and solar transmittance (T_{sol} , $280 < \lambda < 2500$ nm) were calculated from the Equation 3.20:

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

where $T(\lambda)$ represents the recorded %T spectra, $\varphi_{lum}(\lambda)$ is the standard luminous efficiency function of photopic vision in the wavelength range 380–780 nm, $^{[30]}\varphi_{IR}(\lambda)$ and $\varphi_{sol}(\lambda)$ is the IR and solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37 ° above the horizon). $^{[31]}\Delta T_{sol}$ is calculated as $\Delta T_{sol} = T_{sol,25\text{ }^{\circ}\text{C}} - T_{sol,90\text{ }^{\circ}\text{C}}$.

5.3 Outcomes

5.3.1 Top-down fabrication of Moth-eye biomimetic VO₂ surface

The three dimensional topography of the VO₂@SiO₂ nipple arrays is determined by atomic force microscopy (AFM) with a $2 \times 2\text{ }\mu\text{m}^2$ scanning area under the tapping mode. As shown in Figure 5.1(a–d), the biomimetic nanostructures exhibit uniform tapered nipple arrays perpendicular to the substrate. It also shows the continuous dispersion of VO₂ on the nipple-array area, including the place between the nipples. The hint of VO₂ aggregation cannot be found on the surface, indicating the continuous VO₂ covering. As illustrated in the cross-section profile (Figure 5.1e), the period of VO₂@SiO₂ nipple arrays are 210, 440, 580 and 1000 nm and the tapered nipple-array pattern can be figured out clearly. The FESEM cross-section image of the 210 nm patterned thin film (Figure 5.1f) depicts that the distance between the adjacent nipples varies from ~ 200 to ~240 nm and the height of the nipples is around 180 nm.

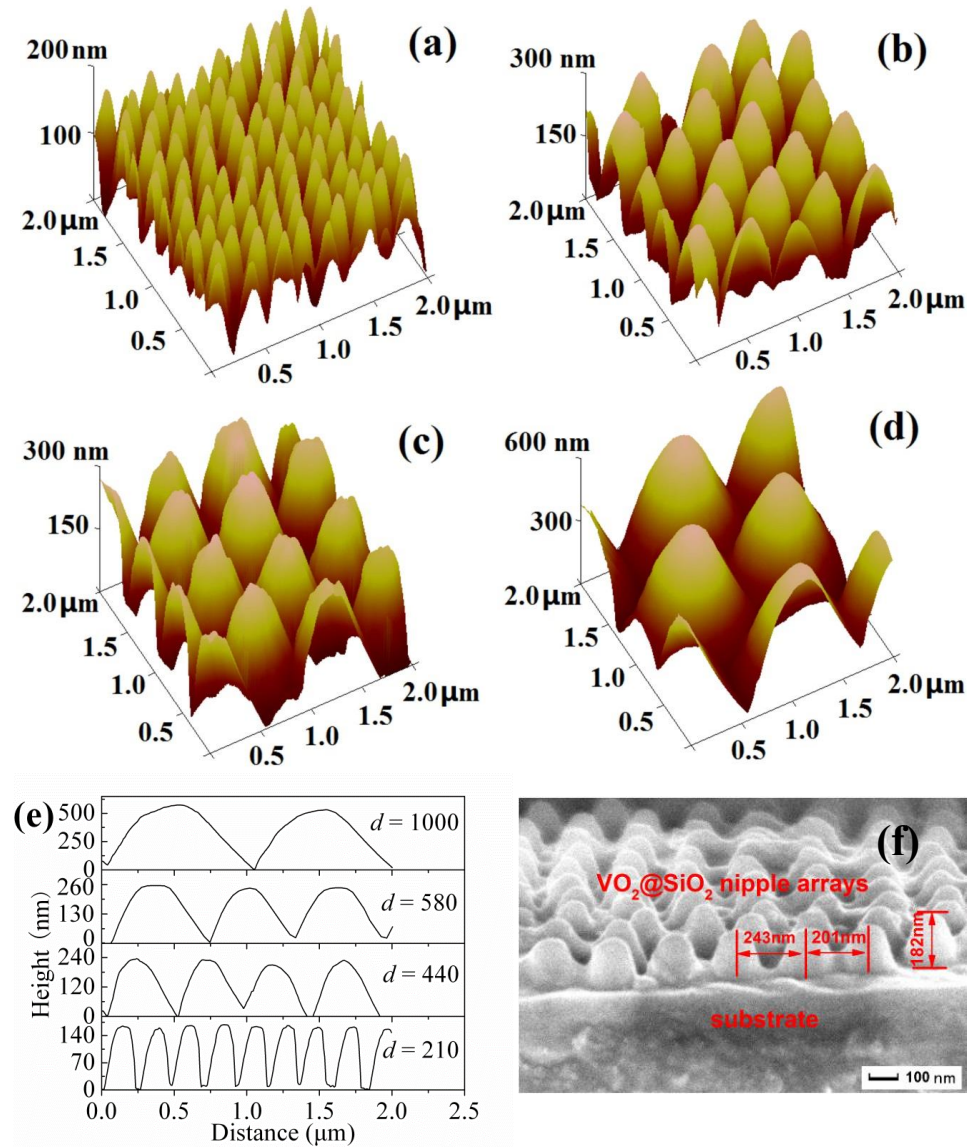


Figure 5.1 AFM images of VO₂@SiO₂ nipple arrays with different periods: (a) 210 nm, (b) 440 nm, (c) 580 nm, (d) 1000 nm, and the corresponding cross-section profile (e). (f) FESEM cross-section view of the VO₂@SiO₂ nipple array with the period 210 nm.^[32]

As the gradual change of refractive index across the VO₂@SiO₂ nipple arrays is essential for the antireflection efficiency and the solid content of VO₂ on the interface is critical for the solar modulating ability, the continuous VO₂ coverage on the surface is required for this biomimetic structure. The coverage of VO₂ on the silica nipple-array area is further examined by FESEM observation and the EDX line scanning. As shown in Figure 5.2a, the FESEM image for the VO₂@SiO₂ nipple array with the period ~440 nm is consistent

with the AFM cross-section profile, and shows the continuous VO₂ covering on the surface without aggregation. The EDX elemental line scanning profiles of O K α 1, Si K α 1 and V K α 1, as shown in Figure 5.2b, clearly show that the concentration of all three elements across the pattern is distributed evenly, which indicates the continuous covering of VO₂ on and between the SiO₂ nipple arrays.

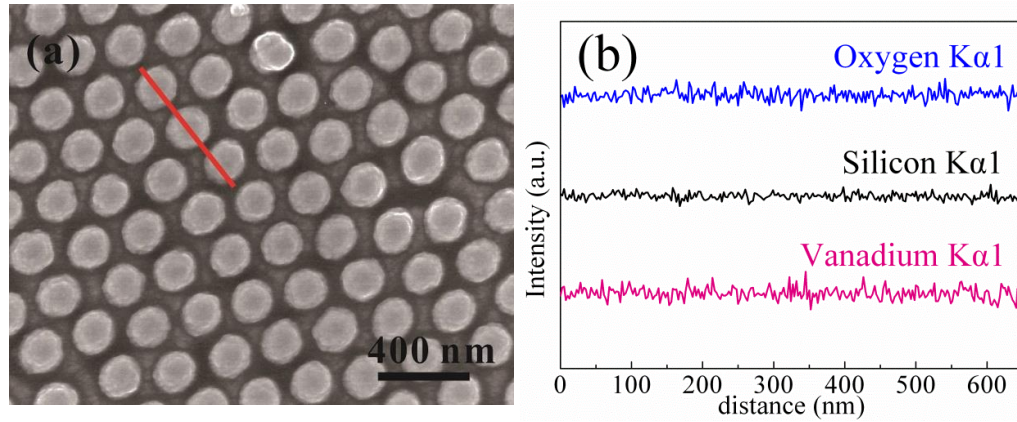


Figure 5.2 (a) Top-view FESEM image of VO₂@SiO₂ nipple arrays with the period 440 nm and the corresponding element line scan (b) along the red line in (a).^[32]

The UV-Vis-NIR transmittance spectra for the planar and patterned VO₂ thin films are measured in a wavelength range 250-2500 nm at the temperature 25 °C and 90 °C. As shown in Figure 5.3, the large transmission contrast between the cool and heat state in the IR range can be observed in all the VO₂ thin films, which is in accordance with the first-order MIT nature of VO₂(M).^[3, 12, 33] Two regions in the %T spectra are analysed separately, i.e. %T at visible (380< λ <780 nm) and IR (780< λ <2500 nm) ranges. At the temperature 25 °C, the VO₂@SiO₂ nipple arrays show the higher visible transmission than the planar thin film, and the visible transmission at the wavelength 700 nm reaches the maximum value 60.1% when the period of the pattern equals to 210 nm. As depicted, the larger period always results in a lower visible transmission, which should be due to the increased light scattering along with the enlarged period. All the %T spectra for the patterned VO₂ thin films show distinct features in terms of transmittance peaks and valleys whose position is dependent on the corresponding period. Compared with the planar VO₂ thin film, the patterned VO₂ thin film with the period 210 nm shows the

enhancement of transmittance over a large wavelength range from 560 to 2500 nm. One worth noting interesting feature for the patterned VO₂ thin films is the shift of transmittance spectra. In detail, for the patterned VO₂ thin film with the period 440 nm, two transmittance peaks emerge below 750 nm and the absorption edge is blue shifted in the spectra, which should be able to improve the T_{lum} due to the reduced visible light scattering. As for the patterned VO₂ thin films with the period 1000 nm, both %T spectra at low and high temperatures are largely red shifted compared with the planar VO₂ thin films, giving rise to the serious decrease of T_{lum} owing to the strong scattering. This blue/red shift of %T spectra with the period should be promising to modulate the thermochromic properties of VO₂ as well as other optical performance in selected wavelength regions for devices.

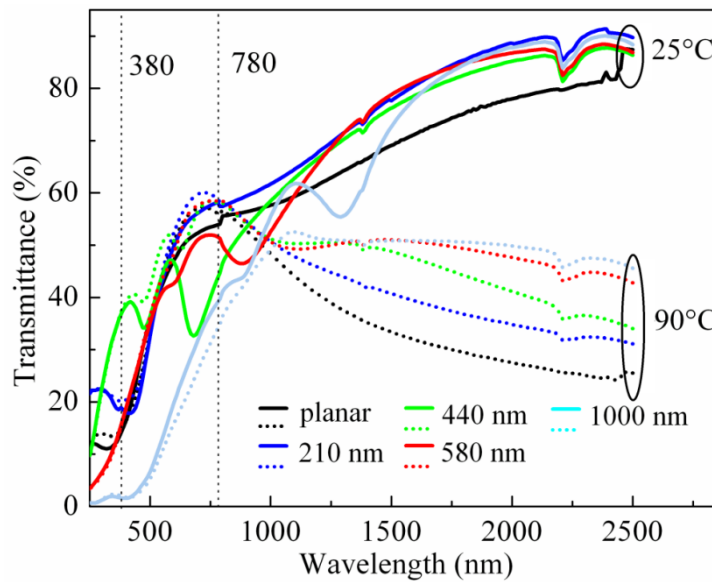


Figure 5.3 UV-Vis-NIR %T spectra measured at 25/90 °C for planar and VO₂@SiO₂ nipple arrays with different periods from 210 to 1000 nm. The thickness of the VO₂ coating is ~140 nm.

[32]

Table 5.1 Calculated thermochromic properties of VO₂@SiO₂ nipple arrays with the period 0, 210, 440, 580 and 1000 nm with ~ 140 nm VO₂ coating. ^[32]

Sample	T_{lum} (25 °C) (%)	T_{lum} (90 °C) (%)	T_{lum} (average) (%)	ΔT_{lum} (%)	T_{IR} (25/90 °C) (%)	T_{IR} (average) (%)	ΔT_{IR} (%)	T_{sol} (25/90 °C) (%)	ΔT_{sol} (%)
Planar surface	39.2	41.7	40.5	-2.5	62.0/44.1	53.1	17.9	46.8/41.1	5.7
$d = 210$ nm	43.6	45.3	44.5	-1.7	67.5/48.1	57.8	19.4	52.1/45.0	7.1
$d = 440$ nm	41.5	48.1	44.8	-6.6	63.2/50.9	57.1	12.3	49.3/48.9	0.32
$d = 580$ nm	40.1	44.2	42.2	-4.1	61.7/51.9	56.8	9.8	48.3/46.1	2.17
$d = 1000$ nm	14.5	11.7	13.1	-2.8	58.5/46.9	52.7	11.6	34.5/27.9	6.6

The thermochromic performance for the planar and the patterned VO₂ thin films in terms of T_{sol} , T_{lum} , T_{IR} and ΔT_{sol} is calculated based on the %T spectra and tabulated in Table 5.1. As a controlled sample, the planar VO₂ thin film shows a relative low visible transmission with $T_{lum}(25/90\text{ °C})=39.2/41.7\%$. For the patterned VO₂ thin films except that with the period 1000 nm, the average T_{lum} is larger than the planar VO₂ thin film, and increases with reducing the period of the pattern as shown in Figure 5.4a, which is in accordance with the theoretical prediction for the antireflection effect of the Moth-eye biomimetic structure. ^[34, 35] Both the patterned VO₂ thin films with the period 210 and 440 nm exhibit ~10% relative increment of average T_{lum} compared with the planar VO₂ thin film (from 40.5% to 44.5%). It is found that the average T_{lum} decreases steadily from 44.5% to 13.1% with increasing the period of the patterns from 210 nm to 1000 nm (Figure 5.4a), consistent with the theoretical calculations ^[34, 35]. The sharp decrease of average T_{lum} at the period 1000 nm should be due to the large red shift as observed in Figure 5.3, arising from the fact that $d=1000$ nm is much larger than the visible wavelength that could result in strong light scattering. ^[28] Apparently, the transmittance for the patterned thin film with the period 1000 nm is not affected so much in IR range compared with that in the visible range, mainly owing to the larger wavelength of IR comparable with 1000 nm (Figure 5.4a). The average T_{IR} for the patterned thin film with the period 1000 nm is close to that of planar thin film (52.7% v.s. 53%). The average T_{IR}

for the patterned thin film with the period 210, 440 and 580 nm is larger than that for the planar thin film, indicating much more obvious antireflection effects compared with 1000 nm-period patterning condition. Furthermore, the T_{IR} declines from 57.8%, 57.1% and 56.8% to 52.7% with increasing the period (Figure 5.4a) whilst the ΔT_{IR} decreases with increasing the period (Figure 5.4b). The ΔT_{lum} and ΔT_{sol} do not exhibit a proportional relationship with the period (Figure 5.4b) as the biomimetic structure could improve the antireflection in both visible and IR range at the temperature 20 and 90 °C while ΔT_{lum} and ΔT_{sol} are calculated as the difference between low and high temperatures. The ΔT_{sol} of 210 nm-period patterned VO₂ thin film is increased from 5.7% to 7.1% while the T_{lum} is relatively increased by ~10% compared with the planar VO₂ thin film, which is mainly attributed to the larger VO₂ content from the bigger surface area of the patterned surface with SiO₂ nipple arrays.^[28] The reduction of light scattering may be also another reason for the enhanced ΔT_{sol} and the improved T_{lum} . Moreover, the ΔT_{sol} of 440 and 580 nm-period patterning sample drops dramatically. It should be ascribed to the increased light scattering with the increased period (Figure 5.4b). The average T_{lum} =44.5% and ΔT_{sol} =7.1% for the 210 nm-period patterning VO₂ thin film as highlighted in Table 5.1 is much less than that of theoretical calculations, where the ΔT_{sol} could be up to 15.5% while the T_{lum} could reach ~70% simultaneously for the Moth-eye biomimetic VO₂@SiO₂ nipple array with the period 180 nm.^[28] The main discrepancies should be mainly due to the period difference as it is difficult to reduce the period to 180 nm under the experimental conditions. Whatever, the improved thermochromic performance compared with the planar VO₂ thin films does confirm the antireflection effect of the Moth-eye biomimetic VO₂@SiO₂ nipple arrays in experiment.

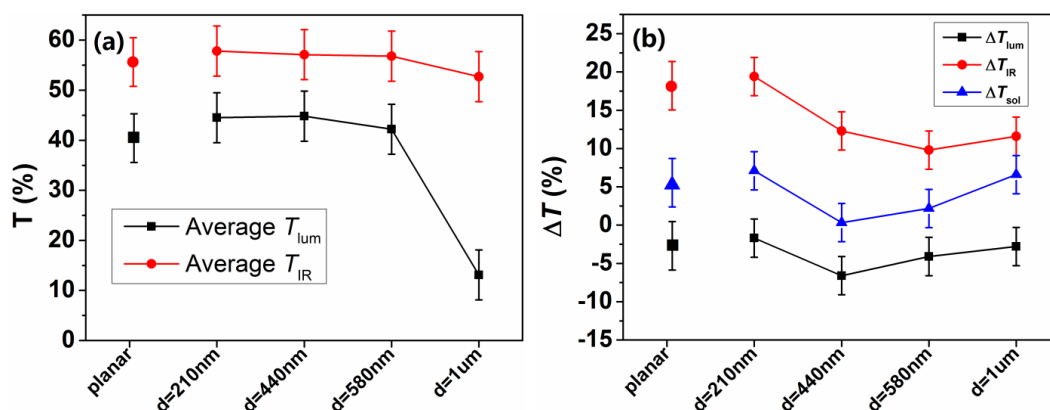


Figure 5.4 Period Effect of VO₂@SiO₂ nipple arrays on its T_{lum} and T_{IR} (a) and (b) ΔT_{lum} , ΔT_{IR} and ΔT_{sol} . [32]

Table 5.2 Calculated thermochromic properties and measured contact angle for the planar VO₂ (~40 nm thickness), the VO₂@SiO₂ nipple array with the period 210 nm and for the VO₂@SiO₂ nipple array with FOS overcoat ($p=210$ nm). [32]

Sample	T_{lum} (25 °C)/%	T_{lum} (90 °C)/%	$\Delta T_{sol}/\%$	Contact angle/°
Planar VO ₂	63.8	60.1	3.0	26
210nm patterned VO ₂	66.8	68.4	3.2	58
210nm patterned VO ₂ /FOS	65.9	68.0	3.1	118

In order to improve the anti-oxidation ability and assign the hydrophobic property to the biomimetic patterned VO₂ thin films, a FOS overcoat with 2 vol.% FOS mixed with methanol / H₂O/ TEOS/Ethanol [19] is added onto the VO₂@SiO₂ nipple array with the period 210 nm and the VO₂ thickness ~40 nm. The UV-Vis-NIR %T spectra and the contact angle of the planar and 210 nm-period patterned VO₂ thin films with and without FOS overcoats are shown in Figure 5.5a. As depicted in the inset of Figure 5.5, the patterned VO₂ thin film shows the larger contact angle than the planar VO₂ thin film due to the increase of surface roughness along with the patterning. [26] With additional FOS overcoats, the contact angle is found to be largely improved to 118° as shown in Figure 5.5 (inset) and Table 5.2, which should be due to the low surface energy of the FOS overcoats. [19] The morphology of the VO₂@SiO₂ patterned thin film is further characterized by TEM. Figure 5.5b is a bright-field cross-section TEM image of a single VO₂@SiO₂ nipple. The thickness of the VO₂ coated on the nipple and on the flat surface is observed to be ~40 nm. The material around the VO₂@SiO₂ nipple is the platinum (Pt)

nanoparticles coated during the lift-out process for enhancing the surface conductivity and eliminating the drift during cutting the surface with ion beam.

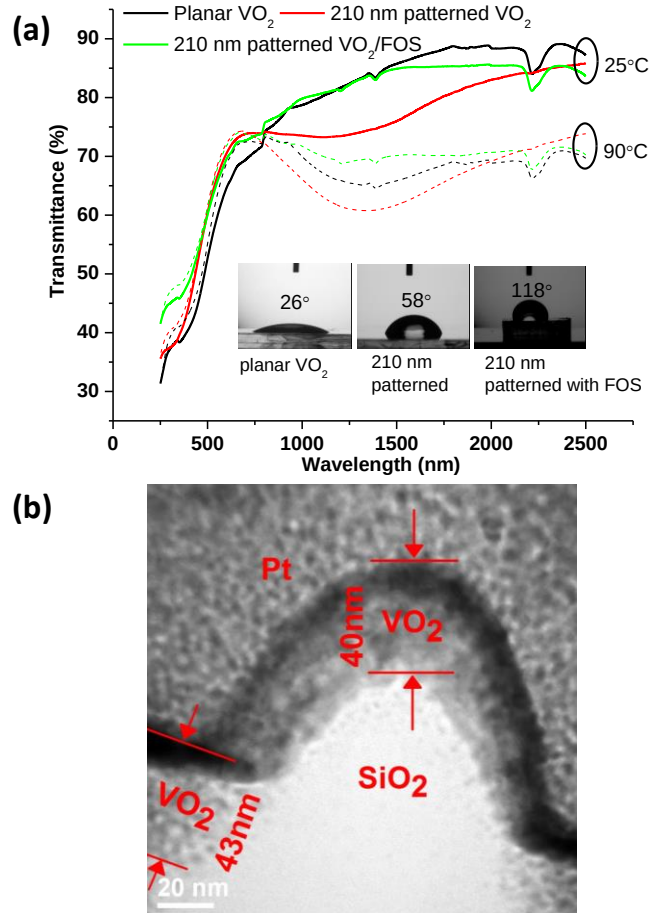


Figure 5.5 (a) UV-Vis-NIR transmittance spectra recorded at 25/90 °C for planar VO₂, 210 nm patterned VO₂ with ~40 nm thickness and 210 nm patterned VO₂ with FOS overcoat. The inset is the corresponding measured contact angles. (b) Cross-section bright-field TEM image to show the VO₂ coating on SiO₂ nipple with a thickness ~40 nm. ^[32]

Compared with the 210 nm-period patterned VO₂ thin film with 140 nm VO₂ thickness (Table 5.1), the 210 nm-period patterned sample with ~40 nm VO₂ thickness (Table 5.2) shows the increased T_{lum} (44.5% v.s. 66.8%) and the decreased ΔT_{sol} (7.1% v.s. 3.2%), which is just owing to the reduced VO₂ content. As shown in Table 5.2, similar to the planar and patterned VO₂ thin films with ~140 nm VO₂ thickness, amongst the thin films with ~40 nm VO₂ thickness, the nipple-array patterning also exhibits the effective

antireflection effect with a relative $\sim 10\%$ enhancement of T_{lum} and a slightly increased ΔT_{sol} from 3.0% to 3.2%. The T_{lum} and ΔT_{sol} are nearly unaffected by the FOS overcoat, but the contact angle is greatly enlarged from 58° to 118° with the FOS overcoat, which could provide self-cleaning as well as anti-oxidation properties for the patterned VO₂ thin films. ^[19]

5.3.2 Bottom-up assembly of patterned VO₂ surface

5.3.2.1 Patterned VO₂ thin film synthesized by one-step vacuum annealing

Precursor characterization. The crystal structure of the precursor V/V₂O₅-H₂O₂ is determined by the XRD technique using 2 theta scanning mode with a grazing angle of 1°. As shown in Figure 5.6, both of the XRD patterns for V -H₂O₂ and V₂O₅-H₂O₂ precursor gels can be indexed with V₂O₅·nH₂O (n $\approx$ 2), characterized with pre-oriented (003)/(004)/(005) peaks from the layered structure with an orthorhombic crystal system (JCPDS #40-1296, a=3.56 Å, b=4.37 Å, c=11.55 Å, $\alpha=\beta=\gamma=90^\circ$).^[36-37]

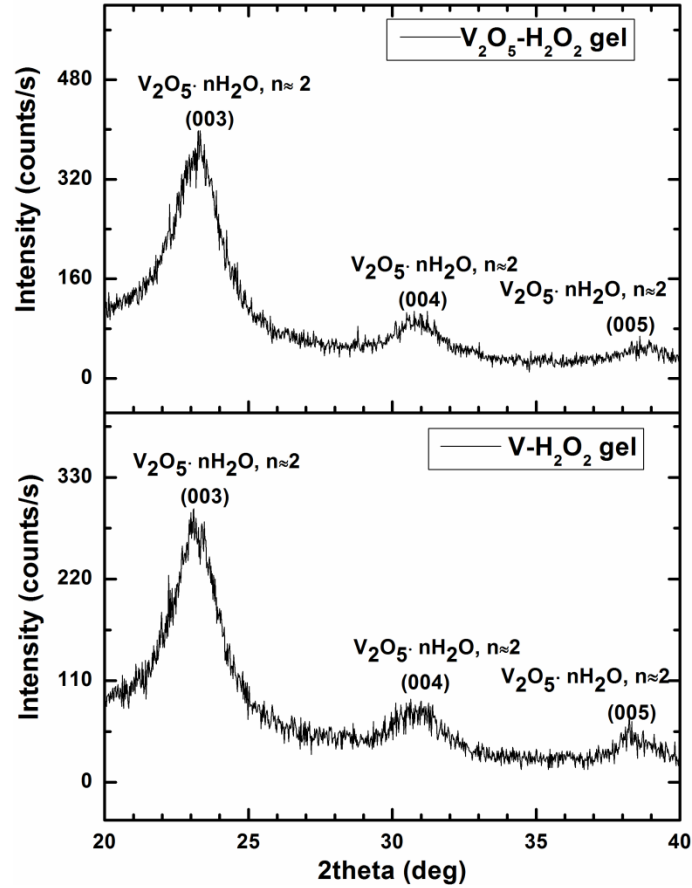


Figure 5.6 XRD patterns of the V-H₂O₂ and V₂O₅-H₂O₂ precursor gels with a grazing angle 1 ° using the 2 theta scanning mode in the 2 theta range 20-40 °.^[38]

The number of lattice water molecules, n , is further determined by a TGA method. As shown in Figure 5.7, the weight loss 18.12% for the V-H₂O₂ dried gel and 15.35% for the V₂O₅-H₂O₂ dried gel have been observed in the heating process. According to the weight loss expression:

$$weight\ loss\% = \frac{n \cdot 18}{n \cdot 18 + 182} \times 100 \quad (5.1)$$

The ' n ' could be calculated to be 2.2 (V₂O₅ · 2.2H₂O) and 1.8 (V₂O₅ · 1.8H₂O) for V-H₂O₂ and V₂O₅-H₂O₂ dried gels, respectively. The further weight loss above 700 °C should be ascribed to the thermolysis of V₂O₅. The less lattice water molecules may benefit V₂O₅-H₂O₂ dried gel with less deformation in the next annealing process.

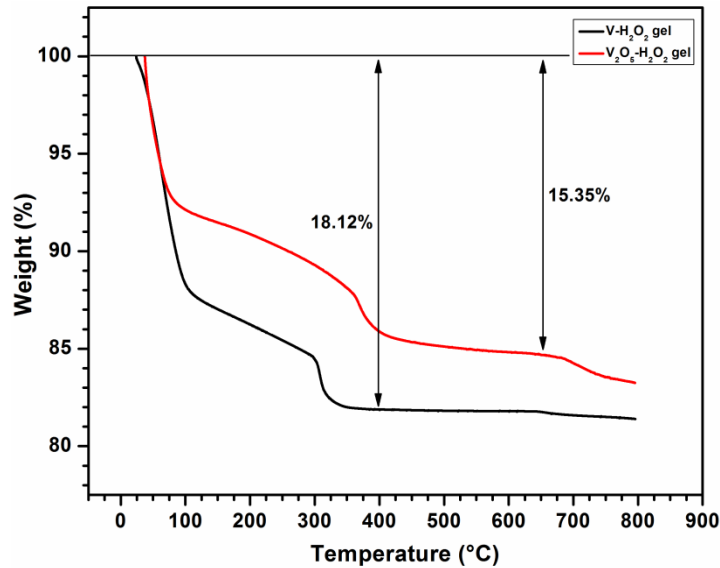


Figure 5.7 TGA curves of the V-H₂O₂ and V₂O₅-H₂O₂ dried precursor gels under N₂ flow.^[38]

One-step annealing. As described above, the V/V₂O₅-H₂O₂ dried gels are the vanadium pentoxide hydrate (V₂O₅·nH₂O), which is unstable above 500 °C:



Therefore, it is reasonable to apply additional annealing process to get VO₂ thin films from the V/V₂O₅-H₂O₂ dried gels. As shown in Figure 5.8, after annealing at 750 °C for 2 hours with a heating rate 1 °C/min under vacuum (1.2 × 10⁻³ Pa) and cooling to room temperature in vacuum, the XRD patterns of the annealed V/V₂O₅-H₂O₂ dried gels show the (201) peak from crystallized fused silica substrate and (011)/(-202)/(-112)/(012)/(112)/(220) peaks from the crystalline VO₂(Monoclinic *P* 2₁/c, JCPDS #82-661), which indicates the high phase purity of the obtained VO₂(M) phase. According to the literature, the V₂O₅ thin film can be transformed to VO₂(M) with vacuum annealing at 480 °C, but there also exists metastable VO₂(B) phase in the annealed film under this process,^[39] and the metastable VO₂(B) phase can be further transformed to VO₂(M) after additional annealing at 750 °C in N₂ flow.^[40] Therefore, we make progress in getting pure VO₂(M) through one-step vacuum annealing at 750 °C. The morphology of the thin films is characterized by FESEM. As shown in Figure 5.9, the VO₂ thin films attained from the V/V₂O₅-H₂O₂ precursors both exhibit continuous nano-grain dense packed nanostructures.

Both of the thin films show a wide grain size distribution from 100 to 500 nm, where the VO₂ grains around 500 nm may give rise to strong scattering, and lead to a negative effect on the thermochromic performance as concluded from the literatures about the scattering effect.^[41]

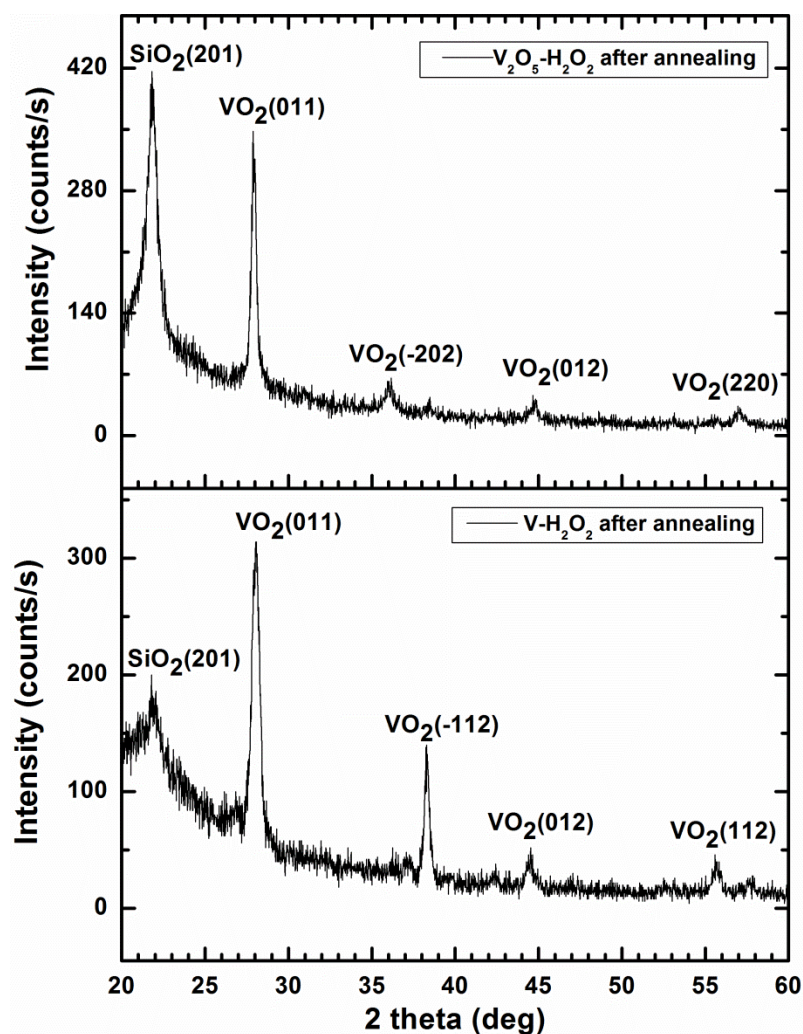


Figure 5.8 XRD patterns of the obtained VO₂ thin films on fused silica substrate from annealed V-H₂O₂ and V₂O₅-H₂O₂ dried gels with a grazing angle 1° using the 2 theta scanning mode in the 2 theta range 20-60°.^[38]

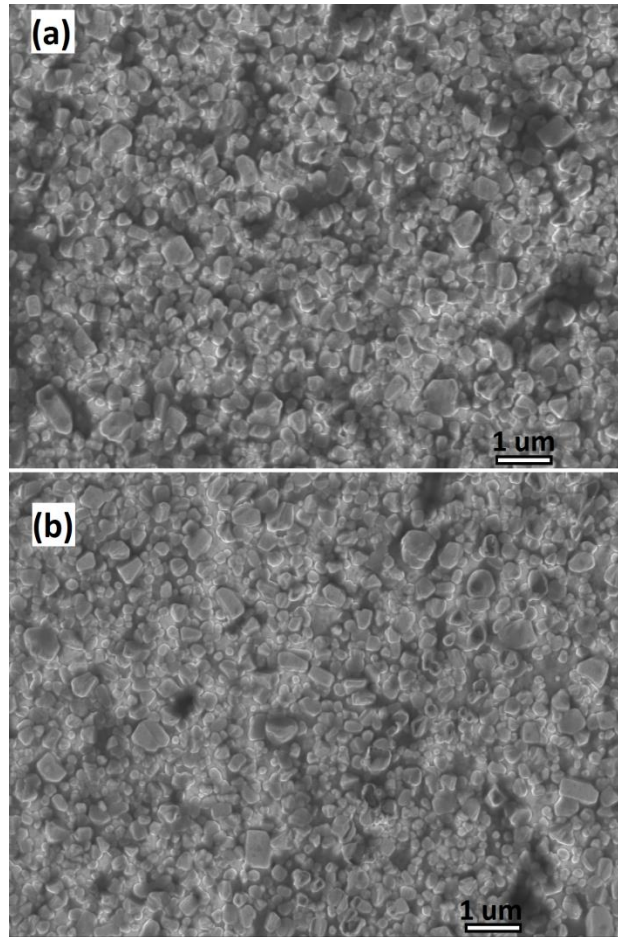


Figure 5.9 FESEM images of VO₂ thin films starting from V-H₂O₂(a) and V₂O₅-H₂O₂(b) precursors after annealing at 750 °C.^[38]

Thermochromic properties. The temperature dependent transmittance spectra for the VO₂ thin films are measured in a wavelength range 250-2500 nm at the temperature 20 and 90 °C. As shown in Figure 5.10, both films starting from the V/V₂O₅-H₂O₂ precursors exhibited characteristic high %T at low (20 °C) temperature and low %T at high (90 °C) temperature for VO₂ thin films.^[42, 43] The transmittance contrast 40% and 45% across the MIT for the two samples in the IR region ($\lambda=2000$ nm, Figure 5.10a-b) is comparable to the reported values for continuous VO₂ thin films,^[44] revealing the acceptable crystallinity of the thin films. The integrated visible transmittance (T_{lum}) and the solar modulating ability (ΔT_{sol}) are calculated based on the temperature-dependent %T spectra, and have been tabulated in Table 5.3. The calculated T_{lum} for VO₂ thin film from V₂O₅-H₂O₂ gel is slightly larger than that from V-H₂O₂ gel (16.18%(20

°C)/ 23.32%(90 °C) v.s. 10.06%(20 °C)/ 14.13%(90 °C)), but also with a larger ΔT_{lum} (7.14% v.s.4.07%), which results in a smaller ΔT_{sol} than that annealed from V₂O₅-H₂O₂ gel (1.91% v.s.4.54%). The larger ΔT_{lum} and the smaller ΔT_{sol} of the VO₂ thin film should be owing to the serious scattering from the nanograins larger than 200 nm, whose concentration in the VO₂ thin film starting from V₂O₅-H₂O₂ gel is larger than that from V-H₂O₂ gel (92.3% v.s.46.2%).

The %T hysteresis loop (Figure 5.10 c, d) is measured at the temperature range 20-100 °C under the wavelength 2500 nm. As shown in Figure 5.10 c, d, both VO₂ thin films exhibit the sharp MIT, in accord with the nature of the first-order transition of VO₂(M) materials. The first-order derivate of %T hysteresis loops (inset in Figure 5.10 c, d) indicate the phase transition temperature τ_c =63.3, 61.6 °C and loop width $\Delta\tau_c$ =5.6, 3.2 °C for the VO₂ thin films annealed from the V-H₂O₂ and V₂O₅-H₂O₂ precursors, respectively. The smaller $\Delta\tau_c$ for the latter should be ascribed to the larger mean grain size in terms of grain size effect as suggested in the literatures.^[45, 46] The value of τ_c for both of the thin films is lower than 68 °C estimated for VO₂ bulk materials, which should be due to the grain size effect,^[45, 46] non-stoichiometry^[47] and/or other parameters.^[48]

Although the synthesis of VO₂ thin films through sol-gel technique and a following reducing and annealing process based on V-H₂O₂ precursor has been reported in literatures,^[49, 50] the presented one-step annealing in vacuum is still of great importance, since the additional intermediate reducing step with flammable H₂, CO and/or other reducing gases can be totally eliminated in this new method. Moreover, the V₂O₅-H₂O₂ precursor is much easier to prepare owing to the higher solubility of V₂O₅, and V₂O₅ is much cheaper than V powder, both of which give rise to the advantage of V₂O₅-H₂O₂ precursor. In addition, this method also offers a great flexibility for cations doping.

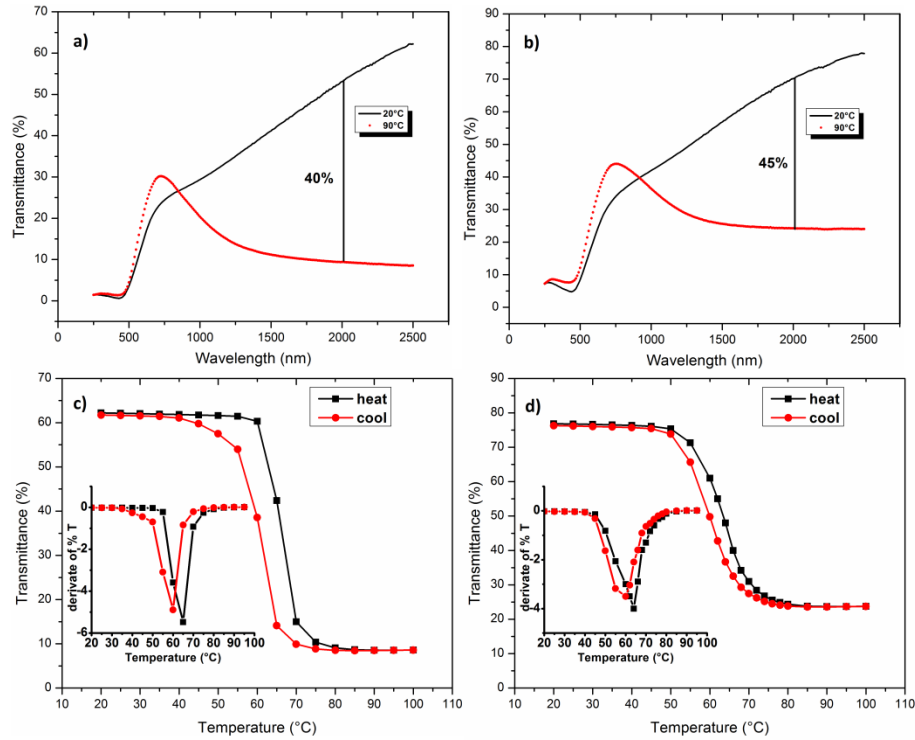


Figure 5.10 Transmittance spectra in the wavelength range of 250-2500 nm and the recorded %T hysteresis loop in the range of 20 to 100 °C for VO₂ thin films starting from V-H₂O₂(a, c) and V₂O₅-H₂O₂(b, d) precursors after annealing at 750 °C. The inset in c) and d) is the first-order derivate of the %T. ^[38]

Table 5.3 Calculated luminous/solar transmittance and metal insulator transition temperatures for V-H₂O₂ and V₂O₅-H₂O₂ annealed samples. ^[38]

	$T_{lum}(20^{\circ}C)$	$T_{lum}(90^{\circ}C)$	$T_{sol}(20^{\circ}C)$	$T_{sol}(90^{\circ}C)$	ΔT_{sol}	$\tau_c(heat)$	$\tau_c(cool)$	τ_c
V-H ₂ O ₂ annealed sample	10.06%	14.13%	21.03%	16.49%	4.54%	66.1°C	60.5°C	63.3°C
V ₂ O ₅ -H ₂ O ₂ annealed sample	16.18%	23.32%	30.40%	28.49%	1.91%	63.2°C	60.0°C	61.6°C

In summary, pure crystalline VO₂ thin films have been synthesized through a facile sol-gel technique with a following one-step annealing in vacuum starting from two inorganic precursors V-H₂O₂ (V₂O₅ · 2.2H₂O) and V₂O₅-H₂O₂ (V₂O₅ · 1.8H₂O). The obtained VO₂ films show comparable thermochromic performance to the reported in literatures, and exhibit lower phase transition temperatures than the typical 68 °C for VO₂ bulk materials owing to the nanosize effect and/or other physical reasons. This facile sol-gel technique

as well as the one-step annealing without additional reducing manipulations supplies an alternative approach for the preparation of high crystalline VO₂ thin films with good thermochromic properties. The low-cost and easy-to-handle advantages of the V₂O₅-H₂O₂ precursor make it a promising candidate for sol-gel preparation of VO₂, although the annealing temperature 750 °C seems to be too high for practical applications.

5.3.2.2 Island-like/nanoporous patterned VO₂ thin film with CO₂ annealing

Synthesis of VO₂ thin films. The VO₂ thin films are prepared using the sol-gel technique with the layered V₂O₅-H₂O₂ (V₂O₅ · 1.8H₂O) precursor gel^[36-38] under different annealing temperatures. As shown in Figure 5.11, only V₃O₇ phase (JCPDS #71-454) could be obtained below the annealing temperature 450 °C, and the pure VO₂(M) phase (JCPDS #82-661) could be attained above the annealing temperature 550 °C. Therefore, the VO_x phase evolution on fused silica substrate during the annealing process under CO₂ inert atmosphere could be concluded as V₂O₅ · 1.8H₂O → V₃O₇ → VO₂(M). In addition, no other XRD peaks above 30 ° could be observed in the characterization, and the XRD patterns above 30 ° are omitted in the Figure 5.11.

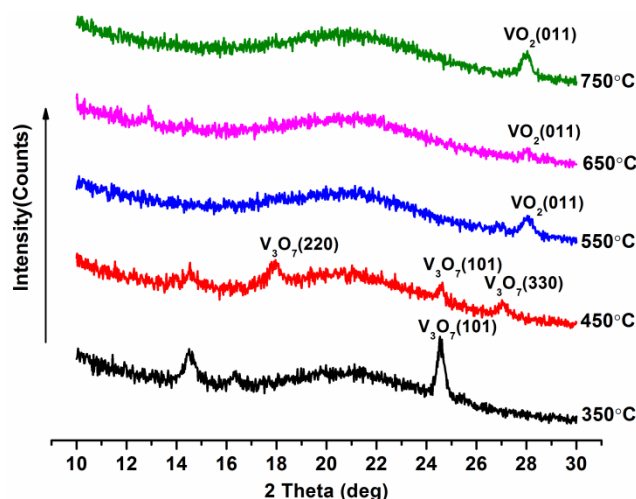


Figure 5.11 XRD patterns for the VO_x thin films grown on fused silica substrates under different annealing temperatures from 350 to 750 °C in CO₂ flow.^[51]

It was also tried to grow VO₂ thin films on normal soda glass instead of fused silica substrate, however, only the XRD peaks (001)/(101)/(301)/(002) from compound NaV₂O₄F (JCPDS #85-581) could be observed after annealing at 550 °C as shown in Figure 5.12a. This is mainly ascribed to the element diffusion of Na and F from the soda glass to the vanadium oxide films.^[52] In comparison, after applying an ITO buffer layer (~500 nm) between the soda glass and the vanadium oxide thin film, the pure VO₂(M) phase could be obtained again with the characteristic (011) XRD peak (Figure 5.12b). The additional (211)/(222)/(321)/(400)/(411) peaks in Figure 5.12b should be ascribed to the In₂O₃ diffraction (JCPDS #73-1809) from the buffer layer. Therefore, without a buffer layer prohibiting the Na/F diffusion, the normal soda glass is not applicable for the growth of crystalline VO₂(M) thin films.

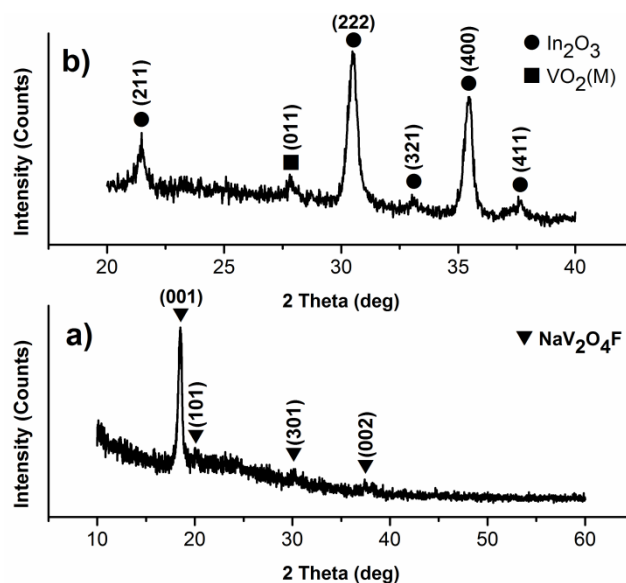


Figure 5.12 XRD patterns for the thin films grown on (a) bare soda glass and (b) soda glass with ITO buffer layer at 550°C in CO₂ flow.^[51]

The morphology of VO_x thin films is characterized by FESEM. As shown in Figure 5.13a-b, the V₃O₇ thin film obtained at the annealing temperature below 450 °C exhibits a morphology composed of dense-packed and elongated nanograins. When the annealing temperature is increased to 550 °C (Figure 5.13c), an interesting nanoporous structure with elongated and interconnected platelet VO₂ nanograins is formed. The formation temperature of pure crystalline VO₂(M) thin film under CO₂ annealing is decreased from

750 to 550°C compared with the vacuum annealing method.^[52] Moreover, CO₂ is believed to have great influence on the morphology evolution of the VO₂ thin films due to its less gas solubility around the VO₂ grain boundaries, leading to the formation of porous structures. With further increasing the annealing temperature from 550 to 650/750 °C, the VO₂ grains begin to isolate from each other owing to the Ostwald ripening on the grain boundary^[53], and zero dimensional island-like nanostructure is formed with increased island size as well as the island-island distance along with the annealing temperature. The thin film growth mode transition from layer by layer to island growth is mainly ascribed to increased thermal stress with increasing the annealing temperature. Furthermore, the porous structure of the VO₂ (M) thin film formed with annealing temperature 550°C should be meaningful in enhancing the thermochromic performance.^[54] Finally, the mean grain size of VO₂ thin films formed at 650 and 750 °C is ~320 and ~400 nm, respectively, which is not in accord with the scattering domain size derived by the Scherrer equation (Equation 5.3) from the XRD patterns (~200nm), mainly owing to the hemispherical rather than spherical grain shape.

$$D = \frac{k\lambda}{B\cos\theta} \quad (5.3)$$

Where, D is the mean grain size, k is a dimensionless shape factor (~0.9) and B is the line broadening (full width) at half the maximum intensity (FWHM).

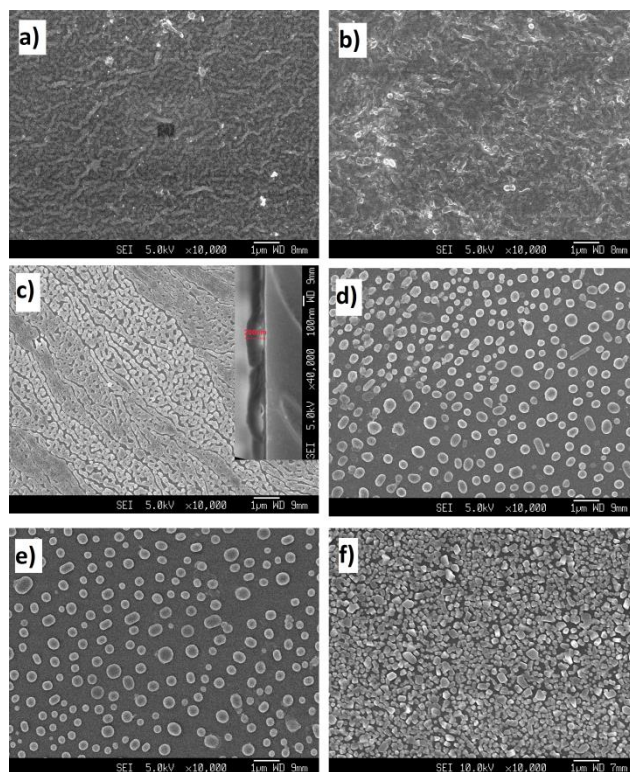


Figure 5.13 FESEM images for the thin films grown on fused silica substrates under CO₂ atmosphere at different annealing temperatures: a) 350°C; b) 450°C; c) 550°C; d) 650°C; e) 750°C, and for the VO₂ thin film formed via vacuum annealing at 750°C (f).^[51]

The porous structure of VO₂ thin films is further studied by TEM analysis. A cross-section TEM sample is prepared by cutting from the porous VO₂ thin film and lifting out with a tip assisted by Pt adhesion in a focused ion beam (FIB) system.^[55] As shown in Figure 5.14a, the nanopores within the cross-section sample is filled up with Pt nanograins and the pore size is in a range of 50-100 nm, which is consistent with the FESEM result (Figure 5.13c). The corresponding selected area electron diffraction (SAED) pattern (Figure 5.14b) of a selected VO₂ grain as marked in Figure 5.14a by a red circle shows a characteristic VO₂(M) diffraction array along the zone axis [1, 0, 2], indicating the crystalline nature of the obtained VO₂ thin films. The appearance of extra diffraction spots in the SAED should be ascribed to the diffractions from the adjacent VO₂ nanograins along other zone axis.

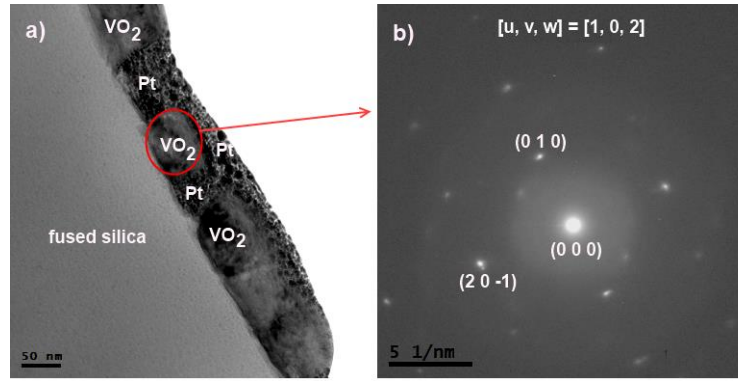


Figure 5.14 Bright-field cross-section TEM view of the VO₂ thin film on fused silica substrate with annealing temperature 550 °C (a) and corresponding SAED pattern of one single VO₂ grain (b).^[51]

Thermochromic properties. The transmittance spectra in the wavelength range 250-2500 nm is measured at the temperature 20 and 90 °C, and the %T hysteresis loop at the wavelength 2500 nm is recorded in a temperature range 20 to 100 °C. The calculated thermochromic properties based on the %T spectra are tabulated in Table 5.4.

As shown in Figure 5.15a, the VO₂ thin film with the annealing temperature 550 °C exhibits the largest transmittance contrast, 50.12% at 2500 nm, and then the %T contrast at 2500 nm is steadily decreased to 12.94% and 7.51% with increasing the annealing temperature to 650 and 750 °C, respectively. As depicted in Table 5.4, the T_{lum} is steadily increased from 33.1% to 61.3% when increasing the annealing temperature from 550 to 750 °C, which may be ascribed to the antireflection effects of the island array formed above 650 °C in terms of gradient refractive index along the height direction.^[56] As shown in Figure 5.15b, the %T hysteresis loop width is gradually widened from 10 to 30 °C when the annealing temperature is increased from 550 to 750 °C, leading to a supercooling effect. As reported in literatures,^[45, 46, 57] the %T loop width could be obviously affected by the grain size that is less than 100 nm. However, the grain size for the VO₂ thin films annealed at 650 and 750 °C, is nearly 300 nm, which may not be applicable for this effect. Notably, the large supercooling effect ($\Delta\tau_c=30$ °C) is comparable to the most recently reported highly-order patterned VO₂ nanotubes.^[58] With respect to the solar modulating ability, the ΔT_{sol} is steadily depressed from 2.2 to -2.3%

upon increasing the annealing temperature from 550 to 750 °C, which should be ascribed to the morphology evolution from nanoporous to zero dimensional island structure, since the large grain size in the island structures could result in serious scattering, and lowering the ΔT_{sol} down in a fast rate. Furthermore, compared with the reference sample formed at 750 °C under vacuum, the nanoporous sample formed at 550 °C in CO₂ gives slightly higher solar modulating ability $\Delta T_{\text{sol}}=2.17\%$ v.s. $\Delta T_{\text{sol}}=1.91\%$, but supplies much higher luminous transmittance $T_{\text{lum}}=35.9\%$ v.s. $T_{\text{lum}}=19.8\%$, which should be ascribed to its nanoporous morphology with lower refractive index.

In order to evaluate the effect of ITO buffer layer on the thermochromic performance of VO₂ thin films, a nanoporous VO₂(M) thin film is grown on the soda glass with ITO buffer layer (inset in Figure 5.16 a). The obtained thin film shows a depressed transmittance contrast 24.39% at 2500 nm (Figure 5.16a) and a small %T hysteresis loop width $\Delta\tau_c=5$ °C (Figure 5.16b). The visible transmittance is reduced to $T_{\text{lum}}=34.5\%$ (20 °C)/39.16%(90 °C), and the solar modulating ability is slightly lower than that grown on fused silica substrate (1.64% v.s. 2.17%), which should be owing to the light absorption from the extra ITO buffer layer.

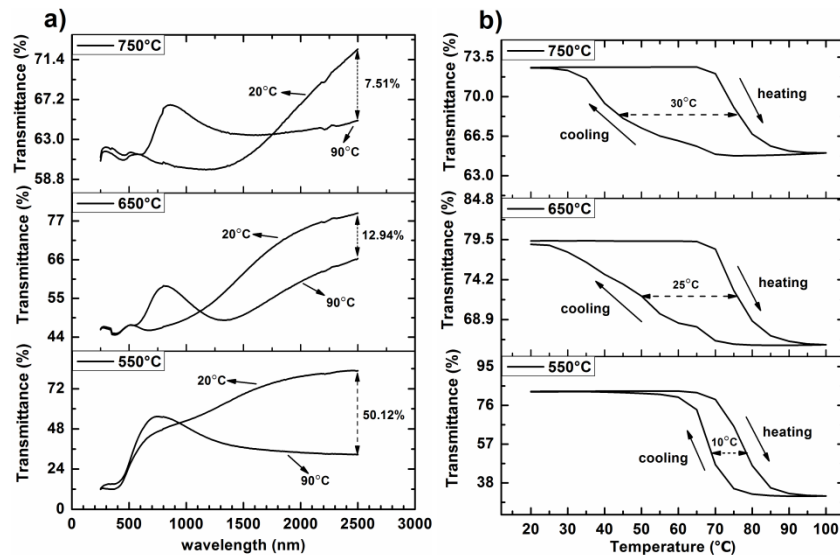


Figure 5.15 Recorded %T spectra in the wavelength range of 250 to 2500 nm at 20 and 90 °C (a) and the %T hysteresis loop at 2500 nm at a temperature range of 20 to 100 °C (b) for the VO₂(M)

thin films grown on fused silica substrates under different annealing temperatures from 550 to 750 °C. ^[51]

Table 5.4 Calculated thermochromic performance for obtained VO₂ thin films under different annealing temperatures. ^[55]

T/°C	Thickness/nm	$T_{lum}(20/90^{\circ}\text{C})/\%$	$\Delta T_{sol}/\%$	$\tau_c(\text{heat/cool})/^{\circ}\text{C}$
550 (CO ₂)	200	33.1/38.7	2.2	75/65
650 (CO ₂)	198	47.0/47.9	-2.0	70/45
750 (CO ₂)	197	61.3/61.5	-2.3	70/40
750 (Vac.) ^[38]	198	16.2/23.3	1.9	65/60

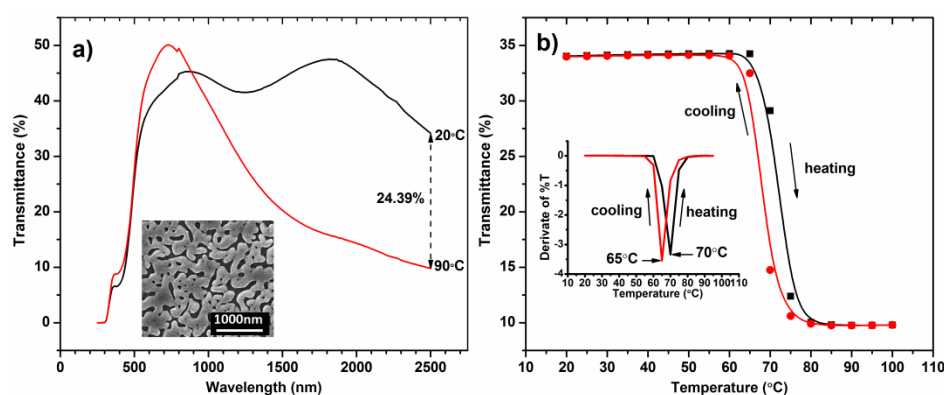


Figure 5.16 Recorded %T spectra in the wavelength range 250 to 2500 nm at 20 and 90 °C(a) and the %T hysteresis loop at 2500 nm at the temperature range 20 to 100 °C(b) for the VO₂(M) thin film grown on soda glass with ITO buffer layer with the annealing temperature 550 °C. The inset in a) is the corresponding FESEM image, and the inset in b) is the first-order derivate of the %T. ^[51]

In summary, a facile sol-gel method is proposed to synthesize the crystalline VO₂ thin films with various nanostructures from nanoporous to zero dimensional island morphologies. The crystalline VO₂ thin films can be obtained on both fused silica and ITO glass substrates with annealing under CO₂ atmosphere at 550 °C. The annealing temperature is below the glass transition temperature of normal soda glass (~570 °C), which is critical for practical applications. The phase evolution of VO_x in the annealing process is found to be V₂O₅ · nH₂O (n ≈ 2) → V₃O₇ → VO₂(M). Compared with the thin films annealed under vacuum, the obtained nanoporous VO₂ thin films annealed at 550 °C in CO₂ flow exhibited the increased T_{lum} = 35.9% as well as the enlarged ΔT_{sol} = 2.17%.

In addition, it also opens an alternative way to promote interesting zero dimensional island-like VO₂ nanostructures with large super-cooling effect (30 °C). Moreover, the CO₂ annealing process may be useful for the development of green chemistry in industrial production.

5.3 Conclusions

In this chapter, the top-down and bottom-up methods are utilized to prepare the patterned VO₂ thin films with modulated thermochromic performances. The outcomes can be summarized in the following:

i) A series of Moth-eye biomimetic top-down VO₂@SiO₂ nipple arrays have been fabricated using RIE method to enhance the thermochromic performance of VO₂ for smart window applications. The patterning with the period $d=210, 440$ and 580 nm, smaller than the visible light wavelength is found to be able to increase the T_{lum} and T_{IR} whilst the 1000 nm-period patterning has no antireflection effect owing to the strong scattering as well as the obvious %T spectra red shift from the large period that is resolved by the incident light. The average T_{lum} , T_{IR} as well as the ΔT_{IR} increases with decreasing the period of the patterning as the d is inversely proportional to the light scattering. Therefore, the VO₂@SiO₂ nipple array with the period $d=210$ nm and the VO₂ thickness ~ 140 nm exhibits the best combination of $T_{lum}=44.5\%$ and $\Delta T_{sol}=7.1\%$. As far as we know, it is the first case to get the antireflection effects of the Moth-eye biomimetic VO₂@SiO₂ nipple array in experiment. In addition, the patterning also increases the hydrophobicity of the VO₂ thin film by enhancing the contact angle. The hydrophobic property could be further improved by applying an additional FOS hydrophobic coating with an increased contact angle up to $\sim 120^\circ$, which is meaningful to promote the self-cleaning application of VO₂ thin films. It is reasonable to predict that after continuous reducing the period $d < 200$ nm, the T_{lum} and ΔT_{sol} should be further increased accordingly. This Moth-eye biomimetic VO₂@SiO₂ nipple array with additional hydrophobic coating

suggests an alternative approach to get the multifunctional VO₂ thin films with enhanced thermochromic performance and other chemical/physical properties.

ii) The bottom-up patterned VO₂ thin films are prepared with one-step vacuum annealing starting from two inorganic precursors V-H₂O₂ (V₂O₅·2.2H₂O) and V₂O₅-H₂O₂ (V₂O₅·1.8H₂O). The phase transition temperature τ_c for the obtained VO₂ thin films is found to be slightly lower than the reported bulk VO₂ materials owing to the grain-size effect, and the thermochromic performance of the thin films is comparable to the reported VO₂ thin films. The one-step annealing without additional reducing manipulations as well as the easy-to-control sol-gel technique open an alternative way for the synthesis of crystalline VO₂ thin films. In addition, the V₂O₅-H₂O₂ precursor is found to be a promising candidate for the sol-gel preparation of pristine and doped VO₂ thin films due to its cost effective and easy-to-handle advantages.

iii) In light of the high annealing temperature of the vacuum synthesis, a series of bottom-up patterned crystalline VO₂ thin films are synthesized through a modified bottom-up approach, i.e. CO₂ annealing, where a morphology evolution from nanoporous structure to zero dimensional VO₂ islands is observed under different annealing temperatures. It is found that the pure VO₂ thin films cannot be grown directly on normal soda glass, since the elemental diffusion of Na and Cl during the annealing at 550 °C in CO₂ flow from the soda glass to the thin film could inhibit the formation of VO₂(M) phase, and ITO is found to be an efficient buffer layer to eliminate such elemental diffusions. The utilized annealing temperature 550 °C is below the normal glass transition temperature around 570 °C, which is very important for its application in windows. With respect to the phase formation, a phase evolution V₂O₅·nH₂O (n≈2) → V₃O₇ → VO₂(M) under different annealing temperatures could be induced through the XRD analysis. The nanoporous VO₂ thin films annealed at 550 °C under CO₂ inert atmosphere exhibits an increased T_{lum} =35.9% and an enlarged ΔT_{sol} =2.17% compared with the vacuum annealed VO₂ thin films. Additionally, the zero dimensional VO₂ islands attained with annealing above 650 °C in CO₂ shows interesting large super-cooling effect (30 °C), which may be useful for the

functional devices. Furthermore, the fully utilization of CO₂ in the annealing process should be meaningful for the concept of green chemistry in the environmental protection.

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Chapter 6*

Hydrothermal Synthesis of VO₂ Nanostructures

The free standing VO₂ nanostructures, including the VO₂ nanopowders and nanobeams were synthesized by systematically hydrothermal designing. The phase of the hydrothermal products could be tuned by the hydrazine reducing reagents and the morphology evolution from starting layered structure to nanowire, nanobeam and nanoparticles could be observed during the hydrothermal synthesis, which could be demonstrated by a proposed rolling mechanism. The addition of ammonium hydroxide was found to be effective to control the product morphologies from nanobeam to nanoparticles. The obtained W-doped VO₂ nanobeams showed the interesting dual SPR signals and the giant electrical resistance modulation with 4-order of magnitude, which has surpassed the reported values in literatures.

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6.1 Introduction

As a smart material, vanadium dioxide (VO₂) has been widely studied as its reversible phase transition from the low-temperature monoclinic insulating phase (M phase, $P 2_1/c$) to the rutile (tetragonal) metallic phase (R phase, $P 4_2/mnm$) occurring around 68 °C.^[1-6] Across the phase transition or MIT of VO₂, a dramatic decline of infrared (IR) transmission when heating through the phase transition temperature (τ_c) could take place and facilitate the application in thermochromic smart windows in terms of solar modulating abilities.^[7-11] With respect to the nanostructured VO₂ materials, there have been some recently reported VO₂ nanostructures for smart window applications, e.g. W-doped VO₂@SiO₂ nanoparticles,^[11b] VO₂ nanonets^[11c] and TiO₂(R)/VO₂(M)/TiO₂(A) multilayer thin film^[11d], where the nanoparticles, nanonets and multilayer thin films exhibited the thermochromic performance $T_{lum}/\Delta T_{sol}=50.6\%/14.7\%$, $46.3\%/10.7\%$, $29.0\%/10.2\%$, respectively. In addition, VO₂ nanostructures could also be applied in smart sensor and smart device applications, e.g. single domain switches,^[12] flexible strain sensors,^[13] field-effect transistors (FET),^[14] solid-state thermal memories^[15] and batteries.^[16] Regarding to the cost control and the large-scale fabrication, it is necessary to develop the low-temperature synthesis technique for crystalline VO₂ nanostructures, which is especially important for smart window applications. Moreover, the τ_c is too high for pure VO₂ to be used in smart sensor or devices as it should always be utilized at room temperature. As is well known, an efficient way to reduce the τ_c of VO₂ is doping with high valence and/or large-in-radius metal cations,^[17-21] among which the tungsten cation (W⁶⁺) was found to exhibit the largest τ_c reducing rate of $\sim 20\text{-}28\text{ K/at.}\%$.^[22]

As reported in literatures, nanostructured VO₂ materials could be fabricated with the technologies e.g. the high temperature evaporation,^[23-26] sol-gel methods^[27] and magnetron sputtering^[28] which always need complicated and expensive equipment. Comparatively, hydrothermal assembly is an alternative low-temperature ($< 300\text{ }^\circ\text{C}$) and facile approach for preparing the nanostructured metal oxide materials, since the supercritical solubility of metal oxide materials under a high autogenous vapour pressure from hot water can greatly facilitate the low-temperature crystallization.^[29] In recent

years, VO₂ nanomaterials, e.g. nanopowders^[30,31] and nano-asterisks,^[33] have been synthesized below 300 °C under hydrothermal conditions, which always exhibit the polycrystalline characteristics, and are not the best candidate for the single-domain research on MIT of VO₂, as the grain boundary effect on the MIT cannot be eliminated in the polycrystalline products. In addition, the VO₂ nanorods^[32] were also synthesized under hydrothermal conditions, but the micro-scale width and length restrict their application in smart applications due to the discontinuous dispersion. As far as we know, the hydrothermal assembly of single-crystalline W-doped uniform VO₂ nanobeams with the width below 100 nm and the length below 500 nm has not been reported yet, although such similar structures have been attained under high temperature evaporation conditions.^[34]

In this chapter, a facile hydrothermal approach was proposed to synthesize single-crystalline W-doped VO₂ nanobeams, and the structural evolution of the products was found to start from the 2D V₂O₅-H₂O₂ starting layered structure to vanadium oxide nanowires, nanobeams and nanopowders, which has been explained by a proposed rolling formation mechanism. The controllable uniform single-crystalline VO₂ nanobeams were obtained by carefully controlling the molar ratio of the starting materials, and exhibit a high W doping efficiency as well as a unique Surface Plasmon Resonance (SPR) performance arising from the uniform distribution of W dopants in the VO₂ lattice. The generated SPR is meaningful for the thermochromic smart window applications as it can result in the enhancement of solar modulation ability ΔT_{sol} through reducing the transmission at the metallic state around the SPR positions.

6.2 Materials and methods

All the chemicals utilized in the experiment, including V₂O₅ (99.6%, Alfa Aesar), H₂WO₄ (99.9%, Alfa Aesar), H₂O₂ (30 wt.%, Sigma-Aldrich) and N₂H₄ · H₂O (99.9%, Alfa Aesar) were used as received without any further purification.

Hydrothermal synthesis of vanadium oxide materials. 182 mg V₂O₅ and 10 mg H₂WO₄ powder were added into preheated 5 mL H₂O₂ (30 wt.%, 90 °C) solution with vigorous stirring. After a strong evaporation, a W-doped V₂O₅-H₂O₂ sol coloured in dark brown was obtained. And 15 mL deionized (DI) water was added into the sol subsequently. The V⁵⁺ sol was then reduced by N₂H₄ H₂O (25/30/35/50/100 µL), and was quickly sealed in a 100 mL Teflon-lined stainless steel autoclave. The autoclave was then put in an oven and heated at 260 °C for 24 hours. After cooling to room temperature in the air, copious amounts of acetone were used to clean and collect the hydrothermal products by centrifuging with a speed 10000 rpm for at least 3 times. Finally, an additional overnight vacuum drying was applied to the cleaned products for characterization.

Characterization. A Shimadzu XRD-6000 X-ray diffractometer (Cu-Kα, λ = 0.15406 nm) was used to determine the crystalline phases of the hydrothermal products with a voltage 40 kV, a current 30 mA and an X-ray grazing angle of 1.0°. A field emission scanning electron microscope (FESEM, JSM-7600F, JEOL, Japan) was used to characterize the morphology of the products with an accelerating voltage of 5 kV and a probe current 7 µA. In the conventional transmission electron microscopy (TEM) characterization, including the selected area electron diffraction (SAED), dark field (DF) and bright field (BF) imaging, a TEM set FEI Tecnai G2 (FEI Company, Eindhoven, The Netherlands) with an accelerating voltage of 200 kV was used to determine the morphology and crystalline phase of the products. For HAADF (high-resolution high angle annular dark field) STEM (scanning transmission electron microscopy) and energy-dispersive X-ray (EDX) characterizations, an FEI Titan probe-aberration-corrected STEM (FEI Company, Eindhoven, The Netherlands) with an accelerating voltage of 200 kV was used to carry out the corresponding investigations. A four quadrant EDX was equipped to the STEM and the probe forming aberration coefficients were corrected to fourth order. The elemental analysis for the chemical composition of the hydrothermal products was performed with a X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra, UK) with an Al Kα (1486.6 eV) monochromatic X-ray source, used with an anode high voltage 15 kV and an emission current 10 mA. The XPS peak calibration was performed with the standard C 1s position *B.E*=284.5 eV. A differential scanning calorimeter (DSC Q10, TA

Instruments, USA) was used to collect the cycling DSC data in a temperature range 5-60 °C under a N₂ atmosphere. A UV-Vis-NIR spectrophotometer (Cary 5000, Agilent Ltd, USA) equipped with a Linkam PE120 system Peltier heating & cooling stage was used to record the UV-Vis-NIR transmittance spectra in the wavelength range 250-2500 nm at the temperature below and above the phase transition temperature. The T_{lum} (integrated visible transmittance, 380< λ <780 nm) and the $T_{sol/IR}$ (integrated solar/IR transmittance, 280< λ <2500 nm/780< λ <2500 nm) were calculated based on the measured transmittance spectra using the Equation 3.20:

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

where $T(\lambda)$ is the transmittance from the %T spectra, ϕ_{lum} is the standard luminous efficiency function for the photopic vision of human eyes^[44] and $\phi_{sol/IR}$ is the solar/IR irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon).^[45] The %T hysteresis loop at a fixed wavelength of 2500 nm was measured at a temperature range 10 to 40 °C. With respect to the phase transition temperature τ_0 , the heating and cooling %T(τ) cycles were fitted with a sigmoidal function of the form (Equation 4.2):

$$\%T(\tau) = A2 + (A1 - A2) / [1 + \exp(\tau - \tau_c) / B]$$

where τ is the temperature in °C and A1, A2, τ_c and B are the fitting parameters. The $\tau_{c,h}$ and $\tau_{c,c}$ represent the fitted phase transition temperatures for heating and cooling cycles, respectively and the average phase transition temperature is defined as $\tau_c = (\tau_{c,h} + \tau_{c,c}) / 2$. The loop width can be calculated as $\Delta\tau_c = \tau_{c,h} - \tau_{c,c}$.^[46] The integrated transmittance variation ($\Delta T_{lum/sol/IR}$) compared to the corresponding integrated transmittance at 10 °C is calculated with $\Delta T_{lum/sol/IR} = T_{lum/sol/IR}(10\text{ °C}) - T_{lum/sol/IR}(\tau)$.

6.3 Results and discussion

Hydrothermal synthesis. The hydrazine hydrate (N₂H₄·H₂O) is an effective reducing reagent for reducing the V₂O₅ starting material to VO₂ ($2\text{V}_2\text{O}_5 + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} \rightarrow 4\text{VO}_2 + \text{N}_2 + 3\text{H}_2\text{O}$).^[35] In the V₂O₅-H₂O₂ precursor, the residual H₂O₂ can also react with the N₂H₄·H₂O ($2\text{H}_2\text{O}_2 + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} \rightarrow \text{N}_2 + 5\text{H}_2\text{O}$), making it difficult to predict the amount the N₂H₄·H₂O that should be used to reduce the V⁵⁺ to V⁴⁺ in the precursor. Therefore, controlling of the amount of N₂H₄·H₂O used in the hydrothermal reaction is essential for attaining the pure VO₂ phase in the ultimate hydrothermal products. Figure 6.1a illustrates the X-ray diffraction (XRD) patterns for the hydrothermal products under different contents of N₂H₄·H₂O in the starting materials, indicating the phase evolution for the hydrothermal synthesis of W-doped VO₂. As shown in the XRD patterns (Figure 6.1a), below 30 μL for the addition of N₂H₄·H₂O, a mixture phase of V₆O₁₃ and VO₂(R) was formed, indicating the partial reduction of the V⁵⁺ precursor. With increasing the content of N₂H₄·H₂O up to 35 μL, the pure and well crystallized VO₂(R) (JCPDS #79-1655) phase was successfully synthesized. When it is further increased to 50 and 100 μL, the corresponding products become V₆O₁₁ and V₂O₃, indicating the reduction of VO₂ ($\text{V}_6\text{O}_{12} \rightarrow \text{V}_6\text{O}_{11} \rightarrow \text{V}_6\text{O}_9$). It should be noted that without the W doping, only the VO₂(A) intermediate phase, crystallizing in the tetragonal system with the *P*4₂/ncm space group (JCPDS #42-876), could be synthesized under the same conditions for VO₂(R) synthesis, suggesting that the formation energy barrier for VO₂(R) phase could be reduced by W doping. Such doping effect on the VO₂ phase formation has also been observed in the previously reported Mo-doped VO₂(M) nanorods synthesis, where only the VO₂(B) phase crystallized in monoclinic *C*2/m (JCPDS #81-2392) rather than pure VO₂(M) could be attained without the Mo doping.^[36]

The morphology of the hydrothermal products has been characterized by FESEM as shown in Figures 6.1 (b-f). The morphology is gradually changed with the phase evolution ($\text{V}_6\text{O}_{13} \rightarrow \text{VO}_2 \rightarrow \text{V}_6\text{O}_{11} \rightarrow \text{V}_2\text{O}_3$) from V₆O₁₃ nanowire to VO₂ nanobeam and to V₆O₁₁/V₂O₃ nanoparticle, where a continuous reduction of aspect ratio is observed in the morphology evolution. As shown in Figure 6.1b, at the content 25 μL of N₂H₄·H₂O, the V₆O₁₃ nanowires exhibited the size ~50 nm in average width and micrometre in average length (aspect ratio > 50), on which there existed VO₂ nanobeams. With increasing

N₂H₄·H₂O content to 30 μL, the length of V₆O₁₃ nanowires was decreased and the content of VO₂ nanobeams became larger (Figure 6.1c). When the content of N₂H₄·H₂O was further increased to 35 μL, the product was fully composed of VO₂(R) nanobeams, which exhibited the aspect ratio in a range of 4-8, where the corresponding width and length of the VO₂ nanobeams fell into the range 90-100 nm and 400-800 nm, respectively (Figure 6.1d). When the content of N₂H₄·H₂O was finally increased to 50 and 100 μL, the V₆O₁₁ and V₂O₃ nanoparticles were attained as observed in Figure 6.1e and f, respectively with the average grain size of ~50 nm. In addition, it is interesting to find that the W doping level could be used to tune the morphology of the VO₂ nanobeams. As shown in Figure 6.2, when the W doping level was lowered from 2 at.% to 1.5 at.% and 1 at.%, the morphology of VO₂ product was subsequently changed from the nanobeams to the mixture of nanobeam and nanoparticles.

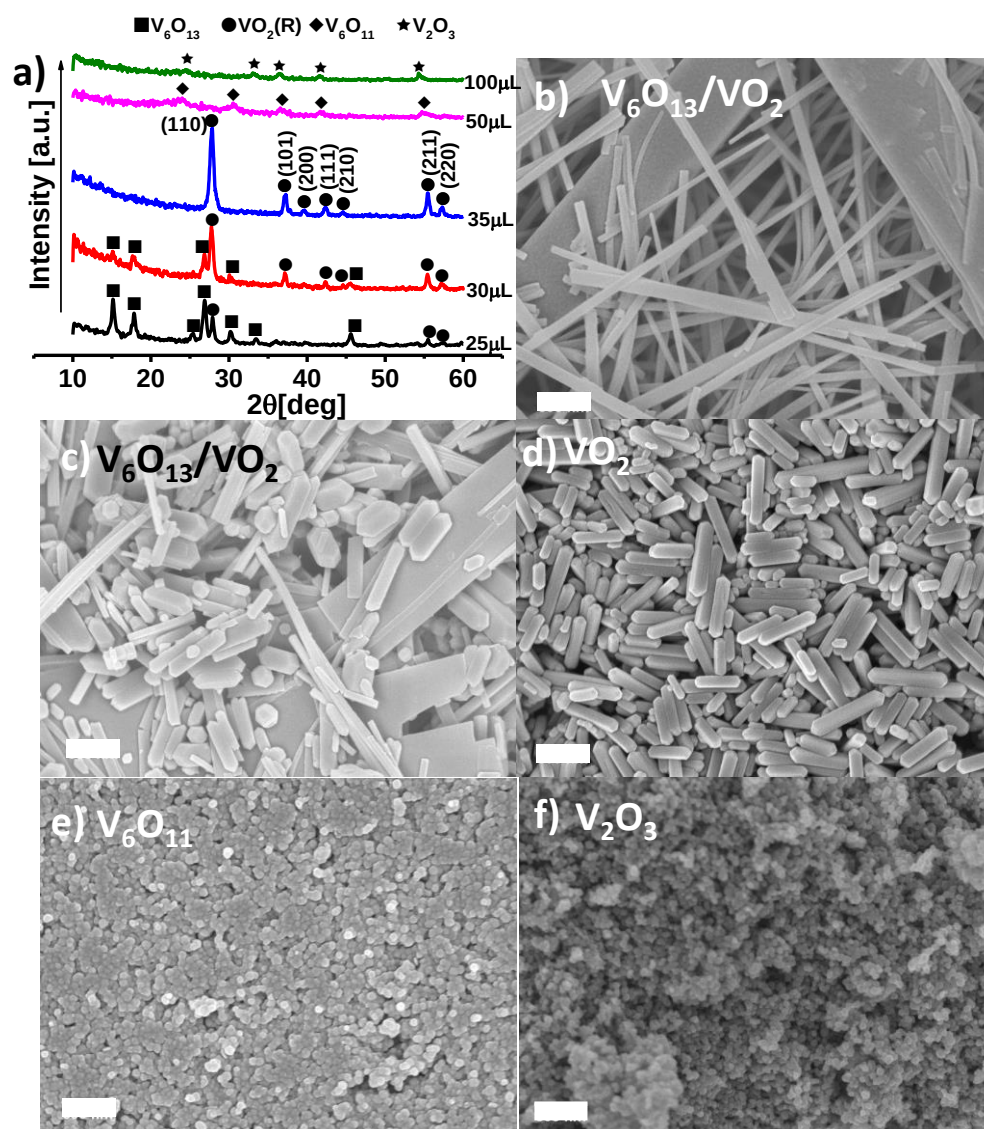


Figure 6.1 (a) XRD patterns of the hydrothermal products under different amounts of N₂H₄·H₂O addition. (b) Corresponding FESEM images for the hydrothermal products. The N₂H₄·H₂O content is: b, 25 μL; c, 30 μL; d, 35 μL; e, 50 μL; f, 100 μL. In (b) and (c), the phase for nanowires is V₆O₁₃, and the phase for nanobeams is VO₂. The scale bar in b-f is 500 nm in length.^[47]

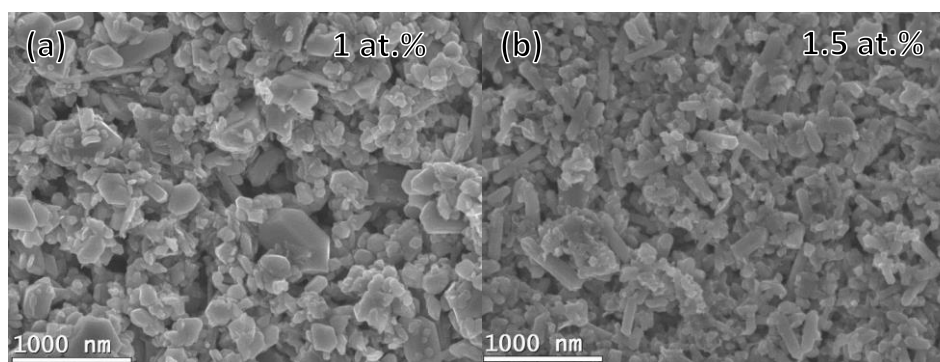


Figure 6.2 FESEM images for the W-doped VO₂ products under the doping level 1 at.% (a) and 1.5 at.% (b).^[47]

With respect to the mechanism for the phase and morphology evolution in the hydrothermal process, a rolling hypothesis starting from the layered V₂O₅-H₂O₂ precursor is proposed to explain the formation of the subsequent V₆O₁₃ nanowires, VO₂ nanobeams and the V₆O₁₁/V₂O₃ nanopowders.^[37] As shown in Figure 6.3a and Figure 6.4, the V₂O₅-H₂O₂ precursor exhibits a two-dimensional layered structure that should have a chemical composition of V₂O₅ · nH₂O (n ≈ 2, JCPDS #40-1296), consistent with the previously experimental results,³⁸ as confirmed by the selected area electron diffraction (SAED) that can be indexed with the (001) planes. With increasing the content of reducing reagent N₂H₄ · H₂O ([N₂H₅]⁺ OH⁻) in the starting materials, the hydrothermal product is gradually reduced with a phase evolution process V₆O₁₃ → VO₂ → V₆O₁₁ → V₂O₃. Along with the phase evolution, the morphology of the hydrothermal products is also changed steadily. In detail, with increasing the reaction temperature as well as the autogenous pressure during the hydrothermal process, the lamellar structure of the V₂O₅ · nH₂O (n ≈ 2) is chemically reduced and tends to curl into one-dimensional tubular structures, partial of which continue to grow and extend to solid V₆O₁₃ nanowires by continuous lateral growth (Figure 6.4b). As VO₂, V₆O₁₁ and V₂O₃ have less solubility than V₆O₁₃, they should show less growth rate via Oswald ripening that allows mass transfer from smaller nanocrystals to larger ones to facilitate the crystal growth. Therefore, the VO₂ nanobeams were formed with relative low aspect ratios (Figure 6.3c and 6.1d), and the V₆O₁₁/V₂O₃ that have the lowest solubility were attained in the form of nanopowders from the collapse of nanowires/nanobeams. To summarize in Figure 6.3c, starting from a 2-D layered V₂O₅-H₂O₂ precursor, the 1-D nanotubes/nanowires/nanobeams were obtained in the

hydrothermal process through a rolling mechanism and the 0-D nanoparticles were finally attained via collapse of the 1-D nanostructures, whilst the phase evolution $V_2O_5 \rightarrow V_6O_{13} \rightarrow VO_2 \rightarrow V_6O_{11} \rightarrow V_2O_3$ takes place across the hydrothermal process accordingly.

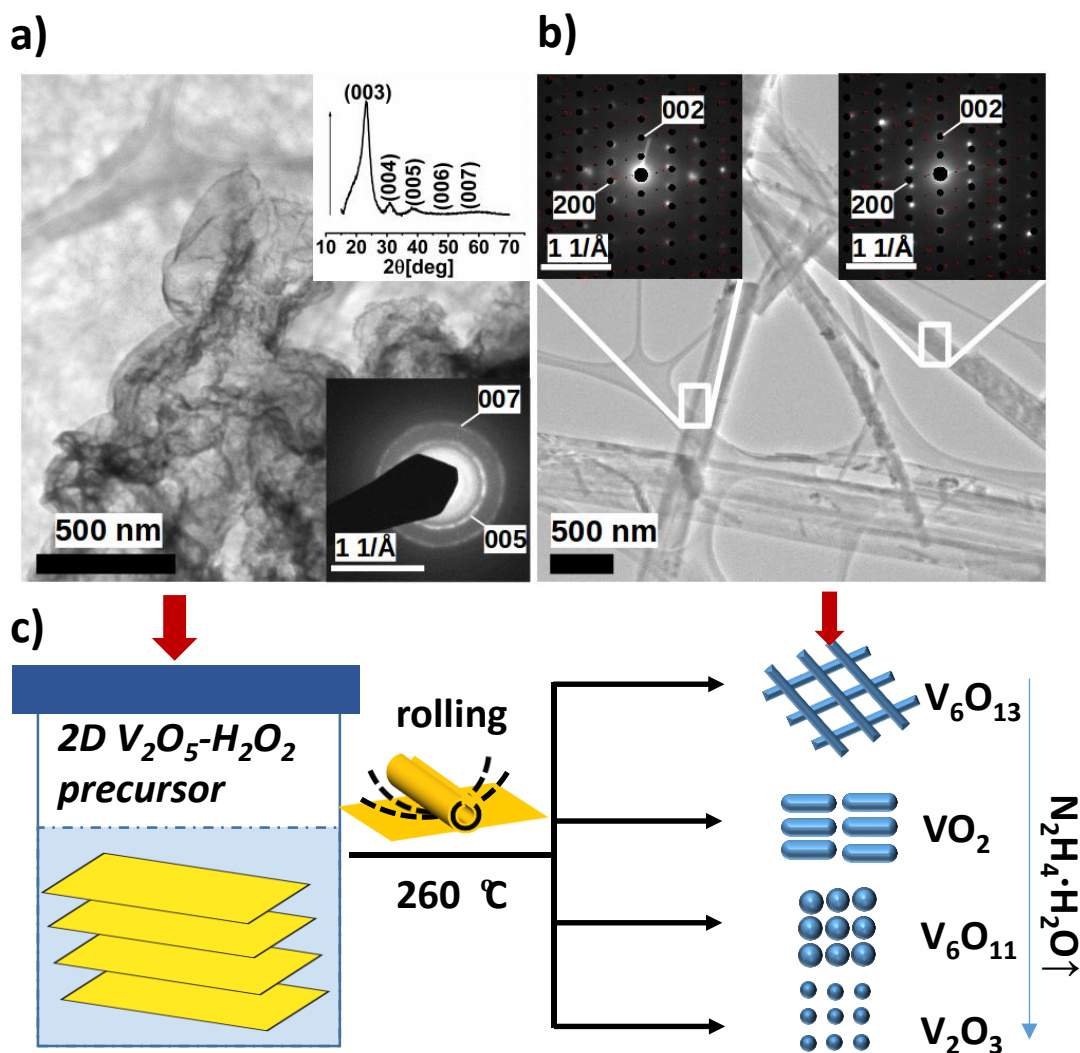


Figure 6.3 a) Bright-field TEM image of a layered $V_2O_5 \cdot H_2O_2$ precursor, with SAED and XRD patterns inset. b) Bright-field TEM image of a V_6O_{13} tube and wires, with SAED patterns inset. c)

Schematic diagram describing the formation of vanadium oxide nanostructures by a rolling mechanism.^[47]

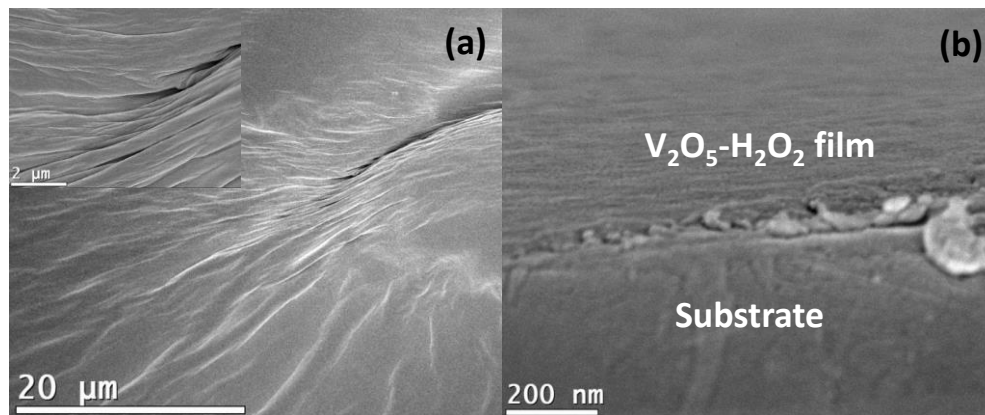


Figure 6.4 FESEM images for the top view (a) and side view (b) of the V₂O₅-H₂O₂ precursor film with layered structure.^[47]

The high resolution XPS (X-ray photoelectron spectroscopy) V 2p and W 4f scan of the W-doped VO₂ nanobeams have been shown in Figure 6.5a and 6.5b, respectively. The V 2p_{3/2} peak locates at the binding energy 516.3 eV, in accordance with the valence state of V⁴⁺, which further proves the phase purity of the VO₂. The W 4f_{5/2} and W 4f_{7/2} peaks could be clearly observed in the binding energy range of 40-35 eV, indicating the W dopants in the VO₂ nanobeams. The W⁶⁺ doping level could be calculated based on the V 2p and W 4f peaks, and the measured value is 2.45 at.%. On the other hand, the EDX elemental analysis of the W-doped VO₂ nanobeams as shown in Figure 6.5d reveals a W doping level of ~2 at.%, which is similar to the value of XPS analysis and is consistent with the molar ratio of W : V in the precursor. In order to get the τ_c of the W-doped VO₂ nanobeams, a differential scanning calorimeter (DSC) curve was recorded for the 2 at.% W-doped VO₂ nanobeams in the temperature range 5-60 °C under N₂ flow with heating and cooling cycles as shown in Figure 6.5c. The corresponding endothermic and exothermic peaks in the heating and cooling cycles show the latent heat $\Delta H=15.14/18.97$ J/g, nearly half of the commercial product ($\Delta H=38.7/41.87$ J/g),^[35] which should be ascribed to the reduced crystallinity resulted from the lattice distortion from the W⁶⁺ doping in the VO₂ lattice, since the MIT energy barrier is closely related to strain concentration in the VO₂ crystal structure. As observed in Figure 6.5c, the phase transition temperature for heating and cooling cycles is $\tau_{c,h}=23.1$ °C and $\tau_{c,c}=14.9$ °C, respectively, leading to an average value $\tau_c =19$ °C, in accord with the reported τ_c reducing rate of W⁶⁺ (20-28 °C/at.%). At lower W doping levels, the τ_c was found to also

obey the τ_c reducing rate, and it could be tuned to 42.5/34.4 °C at the W doping level 1/1.5 at.% as shown in Figure 6.6. The W doping levels can be controlled through changing the H₂WO₄ content in the precursor preparations.

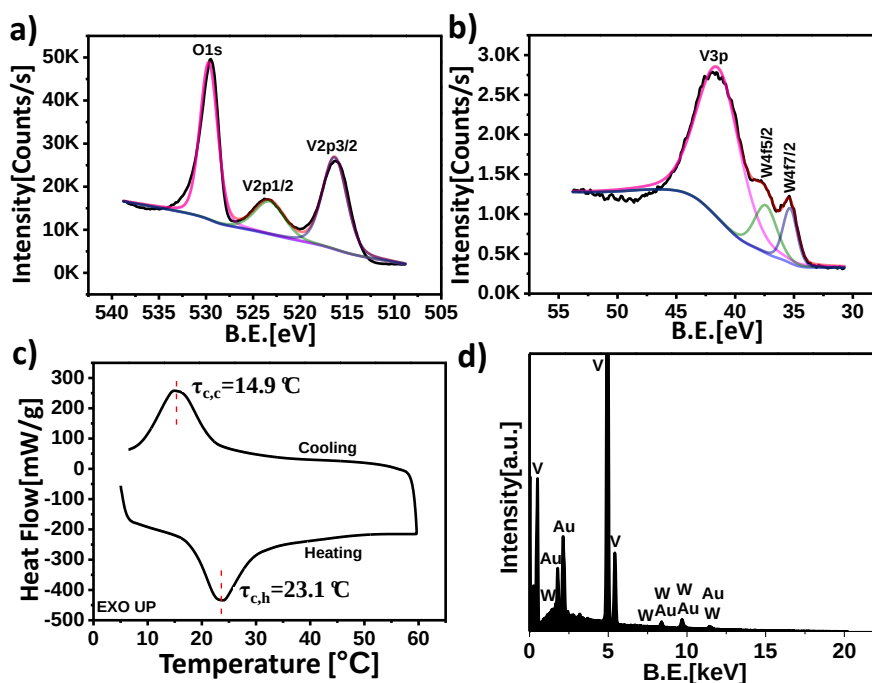


Figure 6.5 High resolution XPS scan of (a) O1s and V2p and (b) V3p and W4f. (c) DSC curve for the 2.45at.% W doped VO₂ nanobeams. (d) EDX spectrum recorded from a W-doped VO₂(R) nanobeam.^[47]

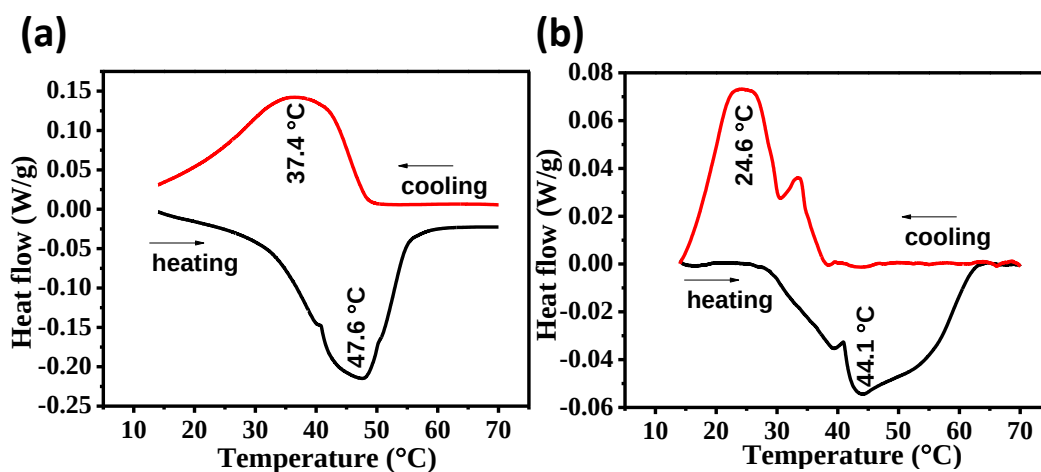


Figure 6.6 DSC curves of the 1 at.% W doped (a) and 1.5 at.% W doped VO₂ products.^[47]

The morphology and the crystalline phase of the W-doped VO₂ nanobeams were also characterized with the TEM and STEM. As shown in Figure 6.7a, the electron diffraction of one single W-doped VO₂ nanobeam was recorded as a SAED pattern. Two sets of diffraction spots as the VO₂(R) and VO₂(M) phases are identified in the SAED pattern, which are specified using black and red indices. Figure 6.7b shows the corresponding bright-field transmission electron microscope (BF-TEM) image, where the growth direction [001] is observed for the W-doped VO₂ nanobeam, in accordance with the (110)/(200)/(210)/(220) planes observed in the XRD pattern. Figure 6.7c and d show the corresponding dark-field (DF) TEM images along the [001] and [010] directions, respectively. Within the DF-TEM image, the brighter layers with the width of few nanometers, as shown in Figure 6.7c, should be ascribed to the slight misorientation of the (020) planes in the lateral direction. In addition, compared to the BF and DF (100) TEM images, the DF-TEM image tilted to the [010] direction shows a smaller outer contour, figuring out that the (010) planes are not diffracting strongly, owing to a similar reason as the misorientation observed in the DF (100) TEM image. Moreover, there is no change of the SAED pattern when moving the electron beam along each nanobeam, which reveals the single crystalline nature of the nanobeams. The W-doped VO₂ nanobeams were also investigated with the high-angle annular DF scanning TEM (HAADF STEM) and EDX STEM mapping as shown in Figure 6.8. Figure 6.8a shows a low magnification HAADF STEM image for the W-doped VO₂ nanobeams, where the whiter areas can be ascribed to the overlap of the nanobeams. Within the HAADF image, the nanobeams exhibit the width around 100 nm and the length below 800 nm, which is consistent with the FESEM result. As shown in the high resolution HAADF STEM image (Figure 6.8b), the atom replacement of V by W in the VO₂ lattice could be clearly observed as marked by arrows in the image, indicating the successful doping of W⁶⁺. The W atom with larger atomic number ($Z=74$) should be brighter in the high resolution HAADF STEM image than the V atom ($Z=23$), since their contribution to the elastic scattering signals collected by the detector is proportional to the atomic number ($\propto Z^{3/2}$). Furthermore, as shown in the EDX-STEM elemental (V, W, O) mapping (Figure 6.8d-e) for the VO₂ nanobeam, the W atoms are doped into the VO₂ nanobeams uniformly,

revealing the good doping efficiency of the hydrothermal technique presented in this chapter.

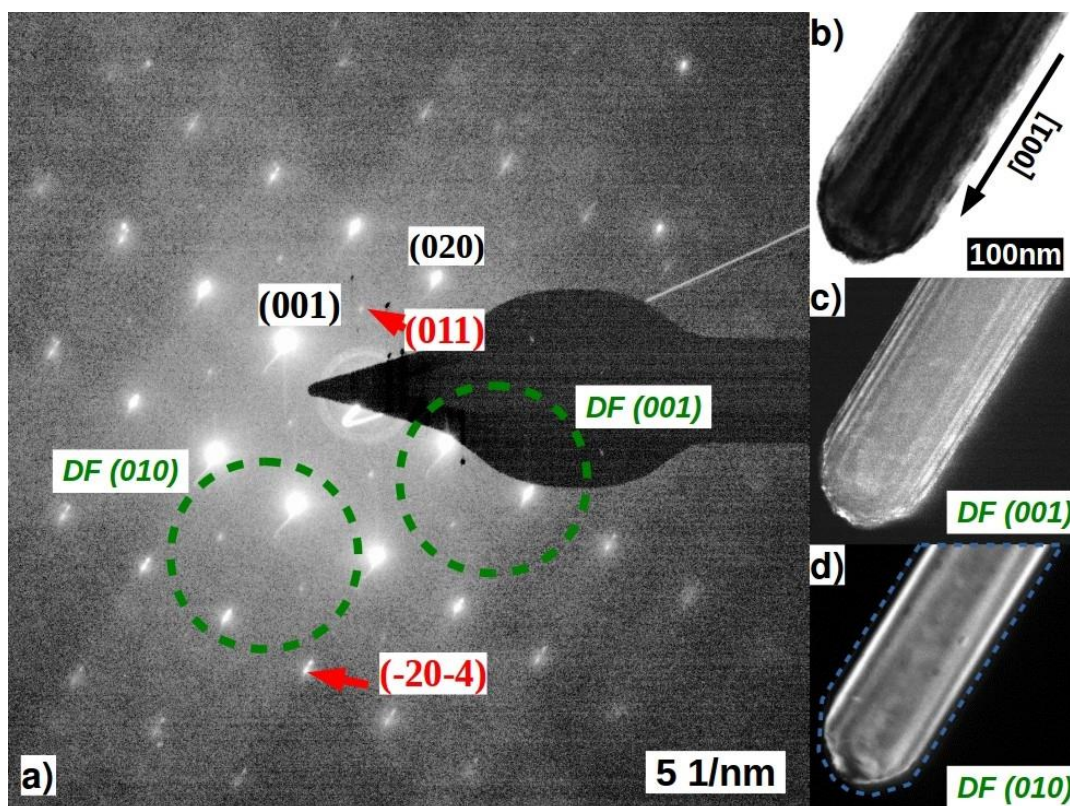


Figure 6.7 (a) SAED pattern recorded for a selected W-doped VO₂ nanobeam. The black and red indices correspond to the VO₂(R) and VO₂(M) phases, respectively. (b) BF-TEM and (c-d) DF-TEM images for the corresponding W-doped VO₂ nanobeam in (a). The DF-TEM images are recorded along [001] (c) and [010] (d) directions. The outer contour of the DF (001) TEM image is reproduced using dashed lines in (d). The dash circles in (a) indicate the positions of the objective aperture used to record images (c-d). The scale bars for the DF-TEM images are given in (b).^[47]

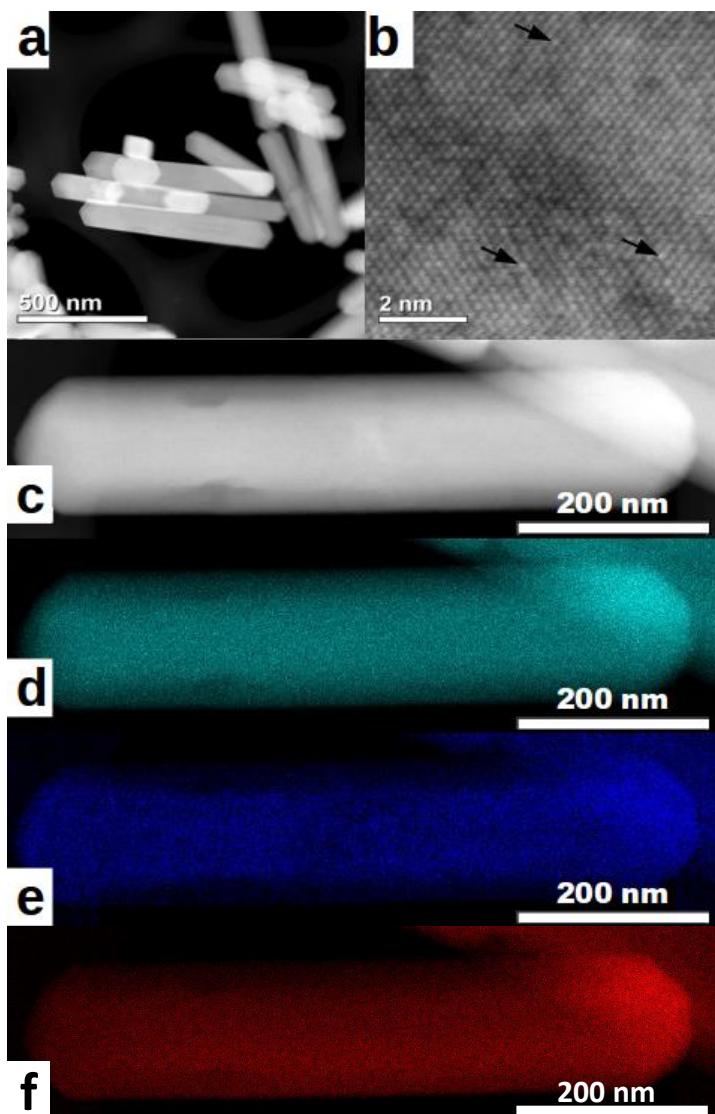


Figure 6.8 (a) Low magnification HAADF STEM image for a selected W-doped VO₂ nanobeam. (b) High resolution HAADF STEM image of a selected area on the edge of the nanobeam. Black arrows indicate atomic columns with higher contrast. (c-e) Simultaneously recorded HAADF STEM image (c) and EDX mapping of V (d), W (e) and O (f) across the nanobeam.^[47]

Optical properties. As shown in Figure 6.9a, the temperature-dependent UV-Vis-NIR spectra for the thin film composed of W-doped VO₂ nanobeams were measured in the wavelength range of 250-2500 nm at the temperature 10 - 40 °C as plots of %T (transmission) vs λ . Regarding to the SPR of metal materials, as reported in the literature,^[39] metal nanobeams can exhibit SPR pairs owing to the polarization along the

transverse and longitudinal axes. Upon heating from 20 to 40 °C, a pair of %T valleys at the wavelength 619 and 1344 nm was observed in the UV-Vis-NIR spectra, which should be assigned to the transverse ($\lambda_{\text{SPR,T}}=619$ nm) and longitudinal ($\lambda_{\text{SPR,L}}=1344$ nm) SPR peaks of metallic VO₂, and is quite different from the spectra of VO₂ nanoparticles with a single SPR peak around 600 nm.^[40] As the incidence in the NIR region with short-wavelength carries more energy, the increased %T contrast arising from the SPR %T valley in this region should result in a large enlargement of ΔT_{sol} according to the Equation 3.20. Such similar SPR enhanced ΔT_{sol} has also been found and investigated in the VO₂@SiO₂ nanostructures.^[41] Owing to the widely distributed length of the W-doped VO₂ nanobeams, a large FWHM (full width at half maximum, 567.9 nm) of the longitudinal SPR locating at 1344 nm could be attained, which is much wider than that of the transverse SPR locating at 619 nm (FWHM= 278.3 nm) (Figure 6.9b). To the best of our knowledge, it is the first case to observe the temperature-dependent dual SPR peaks in the VO₂ nanostructures. The dual SPR peaks may offer the possibility to tune the %T/%R contrast at the required wavelength region, which should be promising for many smart applications.^[12b-12d] When lowering the temperature from 40 to 20 °C, the largely decreased SPR intensity (4.0 % to 2.8 % and 2.7 % to 1.3 %) for corresponding transverse and longitudinal SPR could be observed, which suggests a progressive MIT process in this temperature range above the $\tau_c=19$ °C. With further cooling the W-doped VO₂ nanobeams, the SPR disappeared at 15 °C, owing to the finished MIT below the $\tau_c=19$ °C. In addition, when reducing the W doping level from 2 at.% to 1.5 and 1.0 at.%, the positions of the SPR valleys were blue shifted from 1344, 619 nm to 1290, 530 nm (Figure 6.10), mainly due to the morphology evolution from the nanobeams to the mixture of nanobeam and nanopowders. As shown in Figure 6.9c, under the fixed wavelength of 2500 nm, the IR %T contrast ($\%T_{\tau=10\text{ °C}}-\%T_{\tau>10\text{ °C}}$) is firstly increased rapidly upon heating when the temperature is below 20 °C, and then reached a stable value at the temperature above 30 °C, which also uncovers the MIT transition below 20 °C. In order to confirm the phase transition temperature, the %T hysteresis loop in a temperature range 10 to 40 °C at a fixed wavelength of 2500 nm was measured. As depicted in Figure 6.9d, the phase transition in the heating/cooling process gradually proceeds in the temperature range from 15 to 30 °C/30 to 10 °C, and the sharpest

transition occurs around 22/15 °C. The best least-square fitting for the heating/cooling %T data gives $\tau_{c,h}=21.6$ °C, $\tau_{c,c}=14.4$ °C and $\tau_c=(\tau_{c,h}+\tau_{c,c})/2=18$ °C, which is consistent with the DSC result. The $\Delta\tau_c=7.3$ °C is comparable to the reported results for 2 at.% W doped VO₂. As described in the literature, the τ_c reduction along with the W doping should be ascribed to the free electron carriers^[4] as well as the extra strains^[42] arising from the cation replacement of V⁴⁺ by W⁶⁺ in the VO₂ lattice.

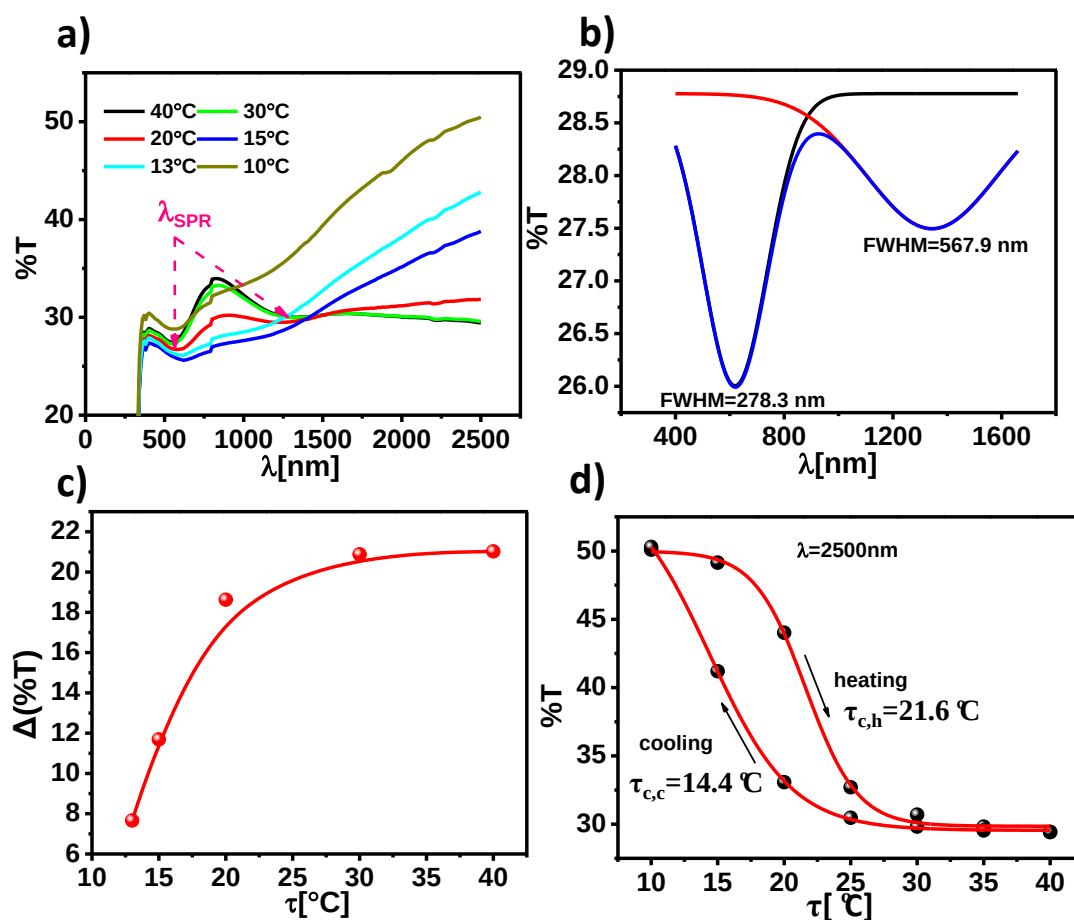


Figure 6.9 (a) UV-Vis-NIR %T spectra recorded in the temperature range 10 to 40 °C. (b) Base line subtracted SPR valleys of the %T spectra at 20 °C (blue line) with Gauss fitting (black and red lines). (c) %T contrast ($\%T_{\tau=10^\circ\text{C}} - \%T_{\tau>10^\circ\text{C}}$) at 2500 nm at different temperatures. (d) Temperature-dependent %T hysteresis loop recorded at a fixed wavelength of 2500 nm. The solid line represents the best least-square fitting result.^[47]

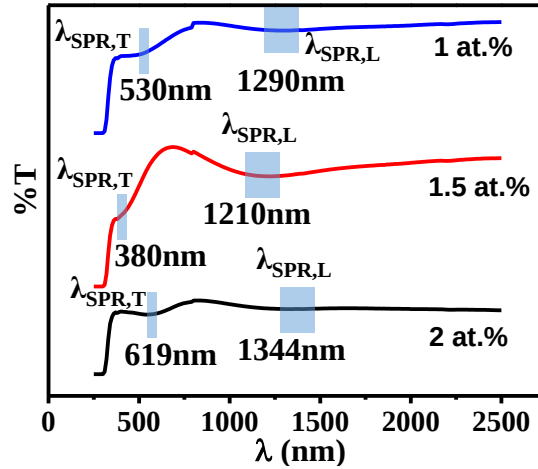


Figure 6.10 Doping level dependent %T spectra of VO₂ products at the temperature $>\tau_c$ and their SPR valleys.^[47]

With respect to the thermochromic properties, the temperature-dependent T_{lum} and ΔT_{sol} for the VO₂ nanobeams are calculated according to the corresponding UV-Vis-NIR %T spectra. As shown in Figure 6.11a, with cooling from 40 to 13 °C, the T_{lum} increases slightly from 26.3% to 27.8%, meanwhile the ΔT_{sol} increases gradually from 2.1% to a peak value of 5.0% at 15 °C, and then decreases to 4.0% at 13 °C. The sharp decrease of ΔT_{sol} above the temperature 15 °C should be attributed to the bump of the %T spectra around 800 nm, arising from the dual SPR valleys at the metallic states. As shown in Figure 6.11b, the ΔT_{IR} exhibits a changing trend similar to the ΔT_{sol} , where a peak value 6.8% at 15 °C could be observed, which should be also due to pairs of SPR valleys of the W-doped VO₂ nanobeams. The best thermochromic properties (T_{lum} =26.0%, ΔT_{sol} =5.0%) for the W-doped VO₂ nanobeams cannot reach the reported value (T_{lum} =56.0%, ΔT_{sol} =8.7%) for the reported W-doped VO₂ nanoparticles.^[11b] After additional 30 μ L NH₃ H₂O (30 wt.%) was added into the precursor, it was found that the hydrothermal product VO₂ nanobeams could be transformed to VO₂ nanoparticles with average grain size $\sim$ 30 nm, and the VO₂ nanoparticles exhibited a better thermochromic performance with T_{lum} =31.2%, ΔT_{sol} =6.4% (Figure 6.12), which is still less than the reported W-doped VO₂ nanopowders, mainly owing to the larger grain size of the obtained nanoparticles (30 v.s. 18.9 nm).

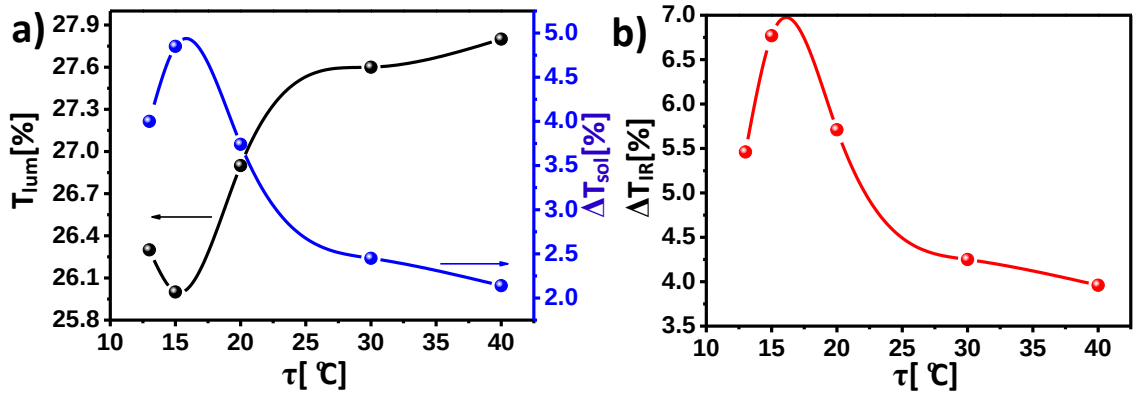


Figure 6.11 (a) Temperature dependent thermochromic properties (T_{lum} , ΔT_{sol}) and (b) IR modulating ability (ΔT_{IR}) for a thin film deposited on a glass substrate with 2 at.% W-doped VO₂ nanobeams at the temperature from 13 to 40 °C. $\Delta T_{sol/IR}$ was calculated as $\Delta T_{sol/IR}(T) = T_{sol/IR}(10\text{ °C}) - T_{sol/IR}(T)$.^[47]

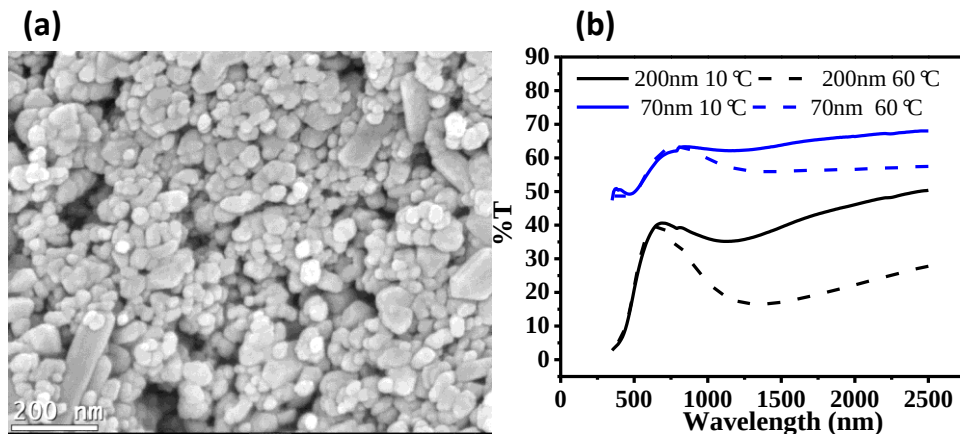


Figure 6.12 (a) FESEM image of the W-doped VO₂ nanoparticles after adding additional 30 μ L NH₃ H₂O (30 wt.%) in the precursor. (b) UV-Vis-NIR %T spectra for the 200/70 nm-thick VO₂ thin film fabricated with the products in (a). The calculated T_{lum} and ΔT_{sol} are 31.2%, 6.4% for 200 nm-thick sample and 53.4%, 1.7% for 70 nm-thick sample.^[47]

Electrical properties. In light of the sharp phase transition as well as the low τ_c for the W-doped VO₂ nanobeams, we are motivated to fabricate the Mott field-effect transistors (FETs) to induce the phase transition by applying a gate voltage. As shown in Figure 6.13a, the temperature-dependent electrical resistance was measured for the film composed of 2 at.% W-doped VO₂ nanobeams. The phase transition temperature can be deduced from the hysteresis loop of the resistance, and the $\tau_c = 19\text{ °C}$ is consistent with the

optical and DSC measurements. The MIT of the W-doped VO₂ nanobeams is similar to that reported for pure VO₂ nanobeams in the literature,^[43] which exhibits a resistance reduction larger than 3 orders of magnitude, much sharper than that for the previously reported W-doped VO₂ nanobeams with the resistance reduction by 2 orders of magnitude. The large electrical resistance reduction across the MIT of the W-doped VO₂ nanobeams obtained in this chapter should be due to the single crystalline nature of the nanobeams as well as the uniform distribution of W dopants in the VO₂ lattice. The inset in Figure 6.13d shows the geometry of the FET device used in this study, where the VO₂ nanobeams dispersed in ethanol were coated onto a SiO₂(~120 nm)/Si substrate. Figures 6.13b-d show the field emission of the FET device with a channel of the W-doped VO₂ nanobeams. By applying a gate voltage of 2V at the temperature below 11 °C, the drain current increases slowly along with the drain voltage (Figure 6.13b). As for the I v.s. V_G curves as shown in Figure 6.13c, the drain current starts to increase dramatically above the temperature 12 °C. Moreover, under the voltage $V_D=1V$ and $V_G=2V$, the temperature-dependent drain current also begins to be sharply improved at the temperatures above 12 °C (Fig. 6.13d). All of the above observation reveals the transition temperature $\tau_c=12$ °C for the MIT of VO₂. The decrease of drain current when increasing the gate bias above 12 °C should be owing to the gate-source leakage, resulted from the transition from insulator to metal of the nanobeams at this temperature. Since the measurement presented here was carried out at low temperatures, the extra strain induced by the thermal mismatch between the nanobeams and the substrate should not be taken into consideration for the τ_c reduction. The τ_c reduction from 19 to 12 °C compared with the optical measurement should be attributed to the applied electric field. Therefore, it can be concluded that the FET device fabricated from the W-doped VO₂ nanobeams synthesized here shows the advantages of a large-magnitude resistance modulation across the MIT, as well as a further τ_c reduction induced by the electric field.

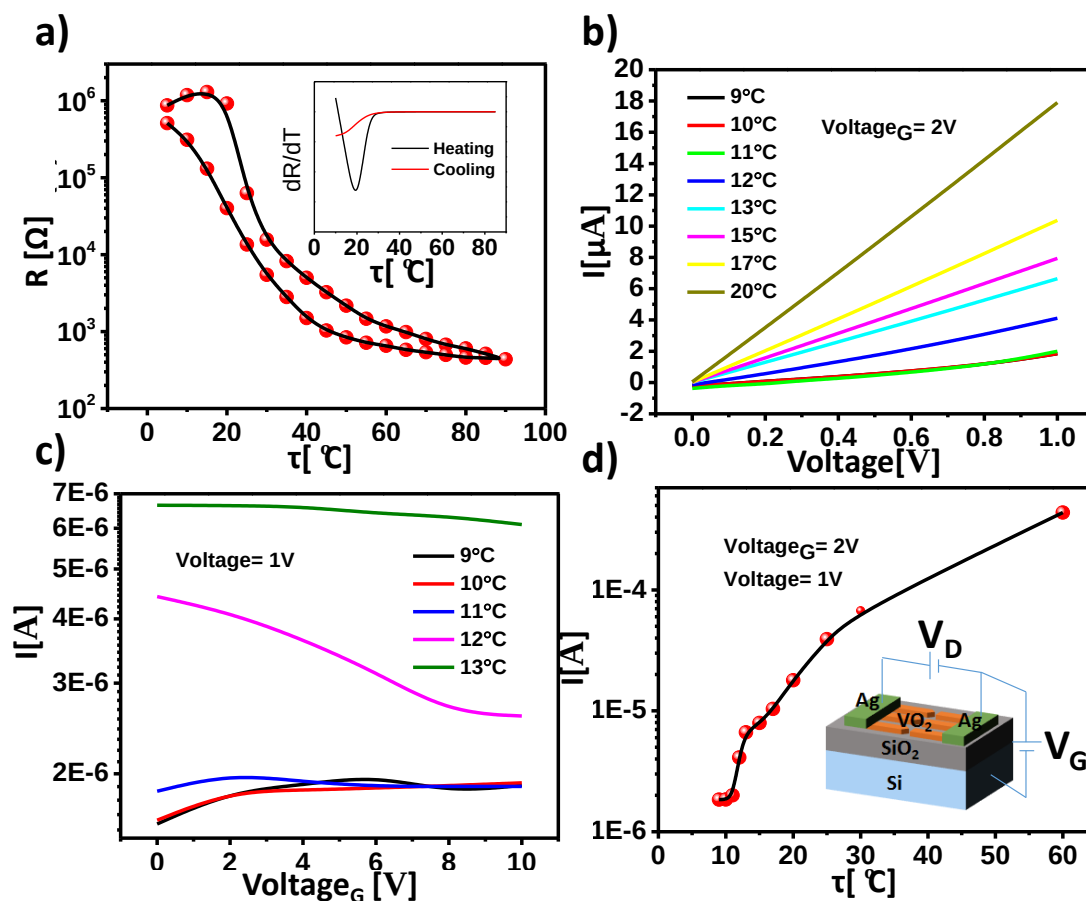


Figure 6.13 (a) Resistance hysteresis loop of the film composed of W-doped VO₂ nanobeams. (b) Temperature-dependent I/V curve measured at a gate voltage of 2 V. (c) Temperature-dependent I/V_G curve measured at a drain voltage of 1 V. (d) Temperature-dependent drain current measured at a gate voltage of 2 V and a drain voltage of 1 V.^[47]

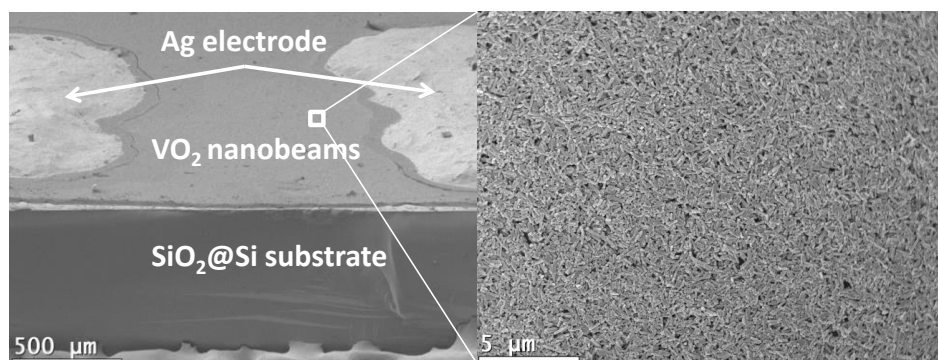


Figure 6.14 Side-view FESEM images for the FET device.^[47]

6.4 Conclusions

In summary, a hydrothermal process starting from a layered V₂O₅-H₂O₂ gel was proposed for the synthesis of nanostructured W-doped vanadium oxide materials for application. The phase and morphology of the hydrothermal products could be controlled by adjusting the content of reducing agent N₂H₄ H₂O in the precursor, where a phase and morphology evolution of the products V₆O₁₃ (nanotubes/nanowires) → VO₂ (nanobeams) → V₆O₁₁ (nanopowders) → V₂O₃ (nanopowders) could be observed in the hydrothermal process. A rolling formation mechanism was proposed to explain such phase and morphology evolution for the hydrothermal synthesis starting from the 2D layered precursor. It is noticed that W doping plays a critical role in the formation of the pure VO₂(R) phase, and only the intermediate VO₂(A) could be obtained without W doping under the same conditions for VO₂(R) synthesis, suggesting the energy barrier reduction for the formation of VO₂(R) under the W doping. The uniform single-crystalline VO₂ nanobeams showed a pair of SPR valleys ascribed to the polarization along the transverse and longitudinal axes at the metallic state, which has not been found for the previously reported VO₂ nanostructures. In addition, the single-crystalline 2 at.% W-doped VO₂ nanobeams show a large electrical conductivity contrast (3-4 orders of magnitude) across the MIT, which is 1-2 orders of magnitude higher than the reported values. The easy-to-control hydrothermal synthesis for the uniform single crystalline W-doped VO₂ nanobeams should be meaningful for the ambient applications in various areas, such as thermochromic windows, FET devices and smart sensors.

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Chapter 7

Conclusion and future works

The threads of the thesis are drawn together to show the implications of this research. The contribution of this research to the development of thermochromic VO_2 nanomaterial and its applications will be addressed in the following fields: doping mechanisms proposed for single Rare Earth (Eu, Tb, La) doping and the Mg/W-codoping that modulating the thermochromic properties of VO_2 ; top-down fabrication of Moth-eye mimic VO_2 antireflection structures with enhanced thermochromic properties as well as the bottom-up assembly of patterned VO_2 surface by controlling the annealing temperature and atmosphere with interesting properties; the controllable hydrothermal synthesis of free standing single-crystalline VO_2 nanobeams with important potential applications. In the end, the future work will be illustrated with opportunities and strategies.

7.1 The effect of Single RE doping and Mg/W-codoping on modulating thermochromic properties

To begin with, in chapter 4 section 4.3.1, the doping effects of Rare Earth Eu, La and Tb on the thermochromic performance modulations were systematically investigated. Especially, the Eu/La/Tb doping was firstly fully studied in terms of doping mechanism, and the La doping was found to be able to enhance the T_{lum} and ΔT_{sol} simultaneously with $T_{lum} > 50\%$ and $\Delta T_{sol} > 10\%$, representing the best value for continuous VO₂ thin films.

In detail, the Eu-doped VO₂ thin films were prepared with the V₂O₅-H₂O₂ precursor through the inorganic sol-gel method. With fully characterizing, the rare earth Eu³⁺ doping was found to be able to reduce the phase transition temperature effectively and improve the thermochromic properties of VO₂ thin films by increasing the T_{lum} and enlarging the ΔT_{sol} . The 4 at.% Eu-doped VO₂ thin film provides a best combination of high visible transmission $T_{lum} = 53.8\%$, large solar modulating ability $\Delta T_{sol} = 6.7\%$ and a reduced $\tau_c = 47.5$ °C, which shows obvious advantages compared with the pristine undoped VO₂ thin film. Below the 5 at.% doping level, the Eu doping could effectively reduce the τ_c of VO₂, and follows a τ_c reducing rate of 6.5 °C/at% which should mainly owing to the relatively large ionic radius of Eu³⁺. However, at the high doping level 5 at.%, the Eu doping could only increase the τ_c of VO₂, which should be due to the competition between the introduced h⁺ charge carrier from charge balance and the increased strain energy from the lattice deformation. The enhanced thermochromic performance with reduced τ_c , increased T_{lum} and enlarged ΔT_{sol} shows a better doping effect of Eu³⁺ than the normal W or Mg doping, opening an alternative door for improving the thermochromic properties of VO₂ smart window.

The Tb³⁺ doping in the VO₂ lattice was investigated to explore its effect on enhancing the thermochromic properties by reducing τ_c and increasing the T_{lum} . With increasing the doping level of Tb³⁺ from 0 at.% to 5 at.%, the T_{lum} was found to be largely improved from 45.8% at the doping level of 0 at.% to 73.2% at the Tb doping level of 5 at.% whilst

the τ_c was found to be marginally reduced from 67.5 °C at the doping level of 0 at.% to 60 °C at the Tb doping level of 5 at.% accordingly. However, with further improving the doping level from 6 at.% to 10 at.%, the T_{lum} was found to be slightly depressed to 62.8% and the τ_c recovered to 67.5 °C, which should be mainly due to the competition between the increased strain from lattice distortion and the introduced free h^+ carrier from the charge balance after the cation substitution of V^{4+} by Tb^{3+} . As for the smart window applications, the future investigation on Tb/M (M=W, Mg, F, Zr)-codoped VO_2 thin films would be performed to explore the opportunity to obtain the combination of high T_{lum} , large ΔT_{sol} and a low τ_c . No matter the low ΔT_{sol} , the high T_{lum} up to 80% should be of great interest for the smart window applications.

Starting from a facile sol-gel synthesis method, the La-doped VO_2 thin films were fully characterized to investigate its effect on enhancing the thermochromic properties of VO_2 thin films. Interestingly, the high visible transmission as well as large solar modulating abilities was observed for the obtained La-doped VO_2 thin films, which could definitely promote the smart window applications. It should be noted that under the 4 at.% La doping, a remarkable combination $T_{lum}=50.1\%$, $\Delta T_{sol}=10.3\%$ could be obtained, which should be the best thermochromic performance for the continuous VO_2 thin films, including the calculated and experimental cases. Furthermore, a simultaneously increment of T_{lum} and ΔT_{sol} could be found for the 5 at.% La doped VO_2 thin film, different from the trade-off for normal VO_2 continuous thin films. A further investigation on the comparison between the La and the Eu/Tb doping effect on the thermochromic performance of VO_2 thin films has been carried out subsequently, and the T_{lum} is found to be inverse proportional to the ionic radius of the RE dopants, which should be ascribed to the lattice distortion arising from the RE doping, and is related to the band gap changing. In addition, the ability of the La doping to reduce the τ_c as suggested by the DFT calculation was firstly proved by the experiment, and a τ_c reducing rate -1.1 °C/at.% was deduced through the least-square fitting of the temperature dependent τ_c data below the doping level of 4 at.%. Nevertheless, the recovering of τ_c to that of normal VO_2 was found when further increasing the La doping level to 5 at.%, which should be due to the competition between the increased strain from lattice distortion and the improved h^+

carrier density from the charge balance during the doping that are coexistent in the La-doped VO₂ thin films. The last but not the least, a band gap narrowing down phenomenon below the La doping level of 3 at.% was observed, which should be due to the band structure changes caused by the La doping, just like the W doping. The investigation of RE doping presented in the thesis should be meaningful for rationally analysis of the doping with the cations occupying the large ionic radius and the low valence state as well. Especially, the τ_c reducing capability of Eu doping, the largely enhanced T_{lum} of Tb doping and the highly improved ΔT_{sol} of La doping should be of great importance for the smart window applications of VO₂ materials.

In chapter 4 section 4.3.2, the Mg/W codoping effects on the enhancement of thermochromic properties of VO₂ thin films were firstly studied concerning the band gap widening, T_{lum} enhancing and the codoping mechanism.

In detail, a novel solution method based on V⁴⁺ precursor was utilized to synthesize the first Mg/W-codoped VO₂ thin film with enhanced thermochromic properties. The VO₂ thin films were supposed to be benefitted with the reduced τ_c from the W dopant and the enhanced T_{lum} from the Mg dopant by the Mg/W codoping. Different from the τ_c reduction in the single Mg or W doped VO₂ thin films, a slight increase of the τ_c with a rate of 1.6 °C/at.% Mg was observed for the Mg/W-codoping under a fixed 2 at.% W doping level. Interestingly, the τ_c increasing rate (1.6 °C/at.%) under Mg/W-codoping was found to be close to the τ_c reducing rate (-1.4 °C/at.%) for single Mg doping cases, which should be due to the similar equilibrium carrier density (ECD) between two doping conditions after the counteraction between the h⁺ and e⁻ carriers arising from the Mg²⁺ and W⁶⁺ doping, respectively. It also indicates the critical roles that ECD plays in modulating the τ_c of VO₂. Similar to the band gap widening of single Mg doping in the VO₂ thin films, the band gap E_g widening effect was also found in the Mg/W codoping conditions, which led to the enhancement of T_{lum} . The best thermochromic performance for Mg/W-codoped VO₂ thin films was found to be the combination of T_{lum} = 81.3%, ΔT_{sol} = 4.3% and τ_c = 35.05 °C with the formula V_{0.94}W_{0.02}Mg_{0.04}O₂. The low τ_c as well as the high T_{lum} should be promising for the practical smart window applications of VO₂.

7.2 Top-down fabrication of Moth-eye mimic VO₂ antireflection structure and the bottom-up assembly of patterned VO₂ surface

In chapter 5 section 5.3.1, the Moth-eye biomimetic VO₂@SiO₂ antireflection structures were fabricated with top-down method for improving the VO₂ thermochromic properties.

The VO₂@SiO₂ nipple arrays with the period $d=210, 440$ and 580 nm were found to be able to increase the T_{lum} and T_{IR} since the periods are small enough not to be resolved by the visible light wavelength whilst the 1000 nm-period patterning has no antireflection effect owing to the interference and the strong scattering. Since the d is inversely proportional to the light scattering, the continuous decrease of d was found to increase the average T_{lum} , T_{IR} and the ΔT_{IR} . The pattern with the period $d=210$ nm and the VO₂ thickness ~ 140 nm was found to exhibit the best thermochromic performance with $T_{\text{lum}}=44.5\%$ and $\Delta T_{\text{sol}}=7.1\%$. To our knowledge, it is the first time to observe the thermochromic performance enhancement with Moth-eye biomimetic VO₂@SiO₂ nipple arrays in experiment. Moreover, the hydrophobicity of the patterns were also investigated, and the additional FOS hydrophobic overcoat could further improve the hydrophobicity, which is meaningful for developing self-cleaning applications of VO₂. It is rational to predict that the T_{lum} and ΔT_{sol} could be further increased with continuously lowering the period of the patterns. The design and fabrication of the Moth-eye biomimetic VO₂@SiO₂ nipple array suggests an alternative approach for enhancing the thermochromic properties of VO₂ materials.

In section 5.3.2, the bottom-up method with different annealing atmospheres and annealing temperatures was used to prepare patterned VO₂ surfaces.

A one-step vacuum annealing and two inorganic precursors V-H₂O₂ (V₂O₅ 2.2H₂O) and V₂O₅-H₂O₂ (V₂O₅ 1.8H₂O) were introduced into the sol-gel synthesis for dense packed VO₂ thin films. The obtained VO₂ thin films showed comparable thermochromic performance with the literatures, and exhibited lower phase transition temperature than

the typical 68 °C reported for VO₂ bulk materials, may be owing to the nanosize effect and/or other physical reasons. This facile sol-gel technique with one-step annealing without additional reducing process provides a cost-effective and controllable approach for the preparation of dense packed VO₂ thin films with good thermochromic properties. The low-cost and easy-to-handle characteristics of the V₂O₅-H₂O₂ precursor make it promising for the inorganic sol-gel synthesis of VO₂ thin films, nevertheless the annealing temperature 750 °C seems to be too high to be applied in the practical applications.

In order to get patterned VO₂ thin films, the atmosphere was changed to CO₂ and the annealing temperature was designed systematically. In detail, the CO₂ atmosphere was introduced into the sol-gel and annealing process for the synthesis of crystalline VO₂ thin films with controllable nanostructures from nanoporous to zero dimensional island morphologies. The annealing under CO₂ atmosphere at 550 °C was found to be effective for attaining the crystalline porous VO₂ thin films on both fused silica and ITO glass substrates rather than on the normal soda glass substrate, since the Na/F elemental diffusion could occur on the VO_x/glass interface that could inhibit the formation of the correct VO₂ phase. The proposed VO₂ synthesis procedure should be useful for practical applications as the annealing temperature 550 °C is below the glass transition temperature of normal soda glass (~570 °C). The phase evolution of vanadium oxides in the annealing process was found to be V₂O₅ · nH₂O (n≈2) → V₃O₇ → VO₂(M), and the morphology evolution from nanoporous to zero-dimension island structure upon increasing the annealing temperature from 550 to 750 °C was also found in the systematic investigation. Compared with the dense packed nanograins under vacuum annealing for VO₂ synthesis, the obtained nanoporous VO₂ thin films annealed with CO₂ flow exhibited the increased T_{lum} =35.9% as well as the enlarged ΔT_{sol} =2.17%. In addition, the obtained interesting zero dimensional island-like VO₂ nanostructures at the annealing temperature above 650 °C showed a large super-cooling effect with $\Delta\tau_c$ =30 °C, which should be meaningful for the magnetocaloric applications. Furthermore, the developed CO₂ annealing process should also be useful for the green chemistry concept in the industrial production.

7.3 Mechanism of doping effect

Based on the systematic investigation on single Mg, W, Eu, Tb and La doping effects as well as the Mg/W codoping effects on the thermochromic performance of VO₂ thin films, the mechanism for thermochromic property modulation by doping in the VO₂ lattice could be roughly deduced as the following: the hole (h^+) carriers that induced by doping with M^{n+} ($n < 4$) cations will increase the τ_c , e.g. Al³⁺; the free electron (e^-) carrier that induced by doping with M^{n+} ($n > 4$) cations will reduce the τ_c , e.g. W⁶⁺; the counteraction between the h^+ and e^- carriers under the codoping conditions (M_1^{n+} ($n < 4$) and M_2^{n+} ($n > 4$)) will result in a larger τ_c than the single M_2^{n+} ($n > 4$) doping; the induced strain though doping with cations with larger ionic radius than the V⁴⁺ will decrease the τ_c ; the M^{n+} doping with $n < 4$ but ionic radius larger than V⁴⁺ will give rise to a decrease of τ_c at low doping levels, but will result in an increase of τ_c at high doping levels, e.g. RE³⁺, which is due to the competition between the induced strain energy from the lattice distortion and the free e^- carrier from the charge balance; and the M^{n+} doping with $n > 4$ and ionic radius larger than V⁴⁺ should give rise to the most efficient τ_c reduction, e.g. W⁶⁺.

With regard to the T_{lum} and ΔT_{sol} , they could be affected by too many factors, e.g. band gap, porosity, microroughness, antireflection coatings, antireflection patterns and SPR. The doping in the VO₂ could influence the band gap, porosity and SPR that could be used to modulate the T_{lum} and ΔT_{sol} for VO₂ thin films. As discussed in this thesis, the Mg/W codoping, single Eu/Tb/La doping could result in the band gap widening that could reduce the absorption and thus improve the T_{lum} . The La doping could result in the SPR %T valley, which benefits the VO₂ thin films with enhanced T_{lum} and enlarged ΔT_{sol} simultaneously.

7.4 Controllable hydrothermal synthesis of free standing single-crystalline VO₂ nanomaterials

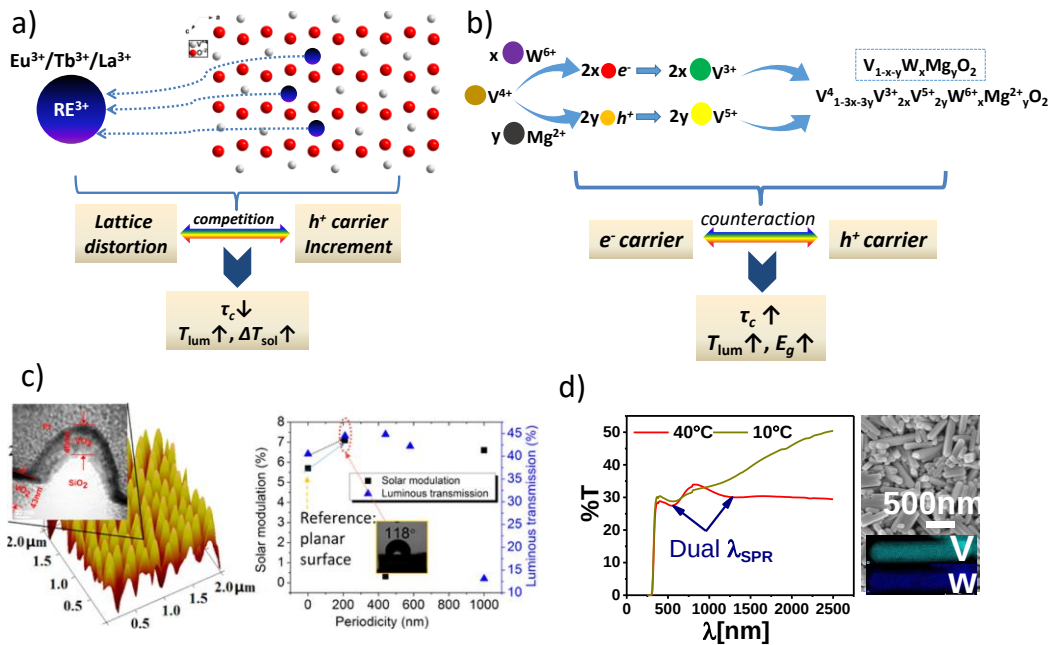
In chapter 6, the single crystalline W-doped VO₂ nanobeams and nanopowders were synthesized using a controllable hydrothermal method starting from the V₂O₅-H₂O₂

inorganic precursor. The W-doped VO₂ nanobeams show an interesting dual SPR in the %T spectra, which is of great importance for optical modulation on selected wavelength regions, and is meaningful for smart window applications.

In detail, nanostructured W-doped vanadium oxide materials were hydrothermally synthesized starting from a layered V₂O₅-H₂O₂ gel with a phase evolution from V₆O₁₃ to V₂O₃ and the corresponding morphology evolution from nanotubes to nanoparticles. In the hydrothermal process, the content of reducing agent N₂H₄ · H₂O in the precursor could be used to control the phase and morphology evolution of the hydrothermal products. The phase and morphology evolution of the products was found to be V₆O₁₃ (nanotubes/nanowires) → VO₂ (nanobeams) → V₆O₁₁ (nanopowders) → V₂O₃ (nanopowders). Such phase and morphology evolution starting from the 2D layered precursor was proposed to be explained by a rolling formation mechanism, where starting from a 2-D layered V₂O₅-H₂O₂ precursor, the 1-D nanotubes (V₆O₁₃)/nanowires (V₆O₁₃)/nanobeams (VO₂) were obtained in the hydrothermal process through a rolling mechanism and the 0-D nanoparticles (V₆O₁₁/V₂O₃) were finally attained via collapse of the 1-D nanostructures. The W doping was found to play a critical role in the pure VO₂(R) phase synthesis, since only the intermediate VO₂(A) could be obtained without W doping under the same conditions for VO₂(R), which suggests the energy barrier reduction for the formation of VO₂(R) after the W doping in the VO₂ lattice. An interesting pair of SPR valleys for the uniform single-crystalline VO₂ nanobeams was found in the %T spectra, which could be ascribed to the polarization along the transverse and longitudinal axes at the metallic state, never been found for the previously reported VO₂ nanostructures. In addition, the 2 at.% W-doped single-crystalline VO₂ nanobeams show an electrical conductivity contrast (3-4 orders of magnitude) across the MIT, which is 1-2 orders of magnitude larger than the reported W-doped VO₂ materials. The controllable hydrothermal synthesis as well as the uniform single crystalline W-doped VO₂ nanobeams should be of interest for the ambient applications in thermochromic windows, FET devices and smart sensors.

In summary, in this thesis, our contributions to the VO₂ thermochromic materials are the

proposed doping mechanism for Rare Earth doping in VO_2 in terms of competition between the extra strain and the hole carriers, which results in the best thermochromic properties for continuous VO_2 thin films; the suggested codoping mechanism for Mg/W-codoped VO_2 thin films, where the charge carrier counteraction gives rise to the improvement of visible transmission; the Moth-eye biomimetic VO_2 nanostructure with enhanced thermochromic performance and the free standing W-doped VO_2 nanobeams with intriguing dual SPR, providing tunable solar modulation at selected wavelength (Scheme 7.1).



Scheme 7.1 Our contribution in this thesis to the thermochromic VO_2 nanomaterials. a) and b): doping and codoping mechanisms for the corresponding Rare Earth (Eu/Tb/La) and Mg/W-codoped VO_2 thin films. c): Moth-eye biomimetic patterned VO_2 with enhanced thermochromic performance. d) Dual-SPR free standing VO_2 nanobeams with intriguing optical and electrical properties.

7.5 Future works

Currently, in this thesis, the facile inorganic sol-gel synthesis of pristine and doped VO_2 thin films and the controllable hydrothermal assembly of VO_2 nanostructures have been systematically investigated for thermochromic applications. The proposed inorganic sol-

gel method exhibits the advantages with cost-effective and easy-to-control features. The top-down fabricated Moth-eye biomimetic VO₂ structures show obvious improved thermochromic properties though the efficient antireflection. The obtained Mg/W-codoped VO₂ thin films show the increased T_{lum} and the ambient phase transition temperature. The La doping exhibits the efficiency in enhancing the thermochromic performance with increased T_{lum} and enlarged ΔT_{sol} . The controllable hydrothermal method shows the advantages in low-temperature synthesis and large-scale fabrication for the thermochromic VO₂ nanomaterials. In light of the progress presented in the thesis, it can be predicted to get the further development to optimize or further increase the thermochromic properties of VO₂ nanomaterials. Especially, some recommendations for the future studies have been listed in the following.

7.5.1 Modification of the bottom-up method to improve the performance of the patterned VO₂ surface

The top-down patterning method using in this thesis was to coat the VO₂ onto the patterned fused silica substrate. It has the limit in further lowering the period and reducing the cost in RIE process. At the same time, the used bottom-up patterning method has no obvious advantage in improving the performance. Therefore, the future research on patterning the VO₂ thin films will be focused on the efficient and cost-effective bottom-up nanoscale patterning fabrications. Changing the precursor and/or optimizing the bottom-up annealing process may be the choice for increasing the efficiency.

7.5.2 Metal cations co-doped VO₂ nanostructures

The Mg/W-codoped VO₂ thin films have been illustrated in this thesis, which exhibit the enhanced T_{lum} >80% as well as the reduced τ_c , and the single La doping as discussed in the thesis shows the ability to enhance the thermochromic properties with increased T_{lum} >50% and the large ΔT_{sol} >10%. The enhancement of thermochromic properties via doping is based on optimizing the influence of carrier density and the strain energy from

charge balance and lattice distortion, respectively. Therefore, the metal cations codoping with optimized formula for proper charge carrier density and introduced strain energy should be an alternative rational way to further increase the thermochromic performance of VO₂ nanostructures, no matter synthesized through the sol-gel or hydrothermal synthesis methods. The La-Mg, Eu-Mg and Tb-W codoping should be the potential candidates for optimizing the thermochromic performance of VO₂ products.

7.5.3 Numerical prediction of the doping effects on τ_c modulation

In this thesis, the codoping effect and RE doping effect on modulating the thermochromic performance of VO₂ nanomaterials have been discussed qualitatively with respect to the counteraction between the free electron and the free hole carriers as well the competition between the free hole carriers and the strain energy, respectively. However, the fabrication of doped VO₂ product with exactly designed τ_c needs the precise prediction for the doping effects. Therefore, the numerical prediction of the doping effects on τ_c modulation will be a promising direction for designing the VO₂ smart window wisely. The first principle or the DFT calculations as well as the empirical equations should be possible approaches for the numerical calculations of the doping effects.

List of publication

First-author publications

1. N. Wang, M. Duchampb, Can Xue, R. Dunin-Borkowski, G. Liu, Y. Long. Single-crystalline W-doped VO₂ nanobeams with highly reversible electrical and plasmonic responses near room temperature, *Adv. Mater. Interfaces*, 3: 1600164 (2016).
2. Wang, N.; Tan Chew Shun, N.; Duchamp, M.; Dunin-Borkowski, R. E.; Li, Z.; Long, Y. Effect of Lanthanum Doping on Modulating Thermochromic Properties of VO₂ Thin Films. *RSC Adv.* 6: 48455-48461(2016).
3. N. Wang, S. Liu, X. T. Zeng, S. Magdassi, Y. Long, Mg/W-codoped vanadium dioxide thin films with enhanced visible transmittance and low phase transition temperature, *J. Mater. Chem. C* 3:6771-6777(2015).
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First-coauthor publications

1. X. Qian, N. Wang, Y. Li, J. Zhang, Z. Xu, Y. Long, Bioinspired Multifunctional Vanadium Dioxide: Improved Thermochromism and Hydrophobicity, *Langmuir* 30: 10766-10771(2014).

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3. X. Cao, N. Wang, S. Magdassi, D. Mandler, Y. Long, Europium Doped Vanadium Dioxide Material: Reduced Phase Transition Temperature, Enhanced Luminous Transmittance and Solar Modulation, *Sci. Adv. Mater.* 6:558-561(2014).
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APPENDIX

Table A.1 Crystal data for VO₂(M) and VO₂(R) phases.

	VO ₂ (M)	VO ₂ (R)
Formula	VO ₂	VO ₂
Formula mass	82.9	82.9
Cryst. Syst.	<i>P</i> 2 ₁ /c	<i>P</i> 4 ₂ /mnm
<i>a</i> /Å	5.755	4.598
<i>b</i> /Å	4.525	4.598
<i>c</i> /Å	5.386	2.851
α /°	90	90
β /°	122.6	90
γ /°	90	90
<i>V</i> /Å ³	118.15	60.29
<i>Z</i>	4	2

Table A.2 Detailed crystal structure of VO₂(M).

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data_602360-ICSD
_database_code_ICSD 602360
_audit_creation_date 2011-02-01
_audit_update_record 2012-02-01
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_chemical_formula_structural 'V O2'
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_exptl_crystal_density_diffn 4.66
_cell_measurement_temperature 294.
_publ_section_title

;
The thermochromic vanadium dioxide: I. Role of stresses and substitution on
switching properties
;
loop_
_citation_id
_citation_journal_full
_citation_year
_citation_journal_volume
_citation_page_first
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_citation_journal_id ASTM
primary 'Journal of Solid State Chemistry' 1993 103 81 94 JSSCBI
loop_
_publ_author_name
'Rakotoniaina, J.C.'
'Mokrani-Tamellin, R.'
'Gavarri, J.R.'
'Vacquier, G.'
'Casalot, A.'
'Calvarin, G.'
_cell_length_a 5.755(3)
_cell_length_b 4.525(1)
_cell_length_c 5.386(3)
_cell_angle_alpha 90.
_cell_angle_beta 122.61(3)
_cell_angle_gamma 90.
_cell_volume 118.15
_cell_formula_units_Z 4
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_symmetry_Int_Tables_number 14
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_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 'x, -y+1/2, z+1/2'
2 '-x, -y, -z'
3 '-x, y+1/2, -z+1/2'
4 'x, y, z'
loop_
_atom_type_symbol
_atom_type_oxidation_number
V4+ 4
O2- -2
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_symmetry_multiplicity
_atom_site_Wyckoff_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_B_iso_or_equiv
_atom_site_occupancy
_atom_site_attached_hydrogens
V1 V4+ 4 e 0.239 0.979 0.026 . 1. 0
O1 O2- 4 e 0.106 0.212 0.209 . 1. 0
O2 O2- 4 e 0.401 0.703 0.299 . 1. 0
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Table A.3 Detailed crystal structure of VO₂(R).

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data_237337-ICSD

_database_code_ICSD 237337

_audit_creation_date 2015-02-01

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_chemical_formula_structural 'V O2'

_chemical_formula_sum 'O2 V1'

_chemical_name_structure_type Rutile

_exptl_crystal_density_diffn 4.57

_cell_measurement_temperature 298.

_publ_section_title

'Slow spin dynamics between ferromagnetic chains in a pure-inorganic framework'

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_citation_id

_citation_journal_full

_citation_year

_citation_journal_volume

_citation_page_first

_citation_page_last

_citation_journal_id ASTM

primary 'Inorganic Chemistry' 2013 52 13742 13750 INOCAJ

loop_

_publ_author_name

'David, Renald'

'Kabbour, Houria'

'Colis, Silviu'

'Mentre, Olivier'

_cell_length_a 4.5983

_cell_length_b 4.5983

_cell_length_c 2.8514(5)

_cell_angle_alpha 90.

_cell_angle_beta 90.

_cell_angle_gamma 90.

_cell_volume 60.29

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_symmetry_space_group_name_H-M 'P 42/m n m'

_symmetry_Int_Tables_number 136

_refine_ls_R_factor_all 0.0077

loop_

_symmetry_equiv_pos_site_id

_symmetry_equiv_pos_as_xyz

1 '-y+1/2, x+1/2, -z+1/2'

2 'y+1/2, -x+1/2, -z+1/2'

3 'y, x, -z'

4 '-y, -x, -z'

5 'y+1/2, -x+1/2, z+1/2'

6 '-y+1/2, x+1/2, z+1/2'

7 '-y, -x, z'

8 'y, x, z'

9 'x+1/2, -y+1/2, -z+1/2'

```
10 '-x+1/2, y+1/2, -z+1/2'
11 'x, y, -z'
12 '-x, -y, -z'
13 '-x+1/2, y+1/2, z+1/2'
14 'x+1/2, -y+1/2, z+1/2'
15 '-x, -y, z'
16 'x, y, z'
loop_
  _atom_type_symbol
  _atom_type_oxidation_number
V4+ 4
O2- -2
loop_
  _atom_site_label
  _atom_site_type_symbol
  _atom_site_symmetry_multiplicity
  _atom_site_Wyckoff_symbol
  _atom_site_fract_x
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_B_iso_or_equiv
  _atom_site_occupancy
  _atom_site_attached_hydrogens
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O1 O2- 4 f 0.6999 0.6999 0. 0.025 1. 0
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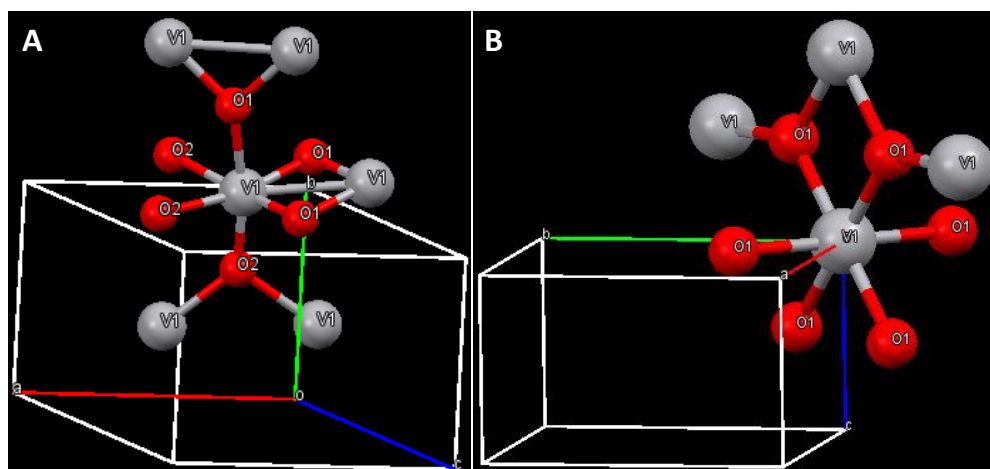


Figure A.1 Unit crystal structure for the VO_2 (M) (a) and the VO_2 (R) (b).