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**NANOSTRUCTURED VANADIUM DIOXIDE
THERMOCHROMIC SMART WINDOWS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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NANOSTRUCTURED VANADIUM DIOXIDE THERMOCHROMIC SMART WINDOWS

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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and the Hebrew University of Jerusalem in partial fulfilment
of the requirement for the degree of Doctor of Philosophy
under the agreement for joint doctoral thesis.

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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Date

.....
Liu Chang

Abstract

In the recent years, thermochromic smart windows, as a category of solar control windows, provide the solutions for saving the energy usage in the buildings or vehicles. Vanadium dioxide (VO_2) is considered as a promising smart window material because of its infrared-switchable optical properties, which is led by the intrinsic phase transition at a critical temperature of 68°C . The temperature-stimulated thermochromic effects make VO_2 as the superior candidate of energy-efficient smart windows, but the real application of VO_2 continuous thin films is hindered mainly due to the low luminous transmittance (T_{lum}) and the insufficient solar modulation ability (ΔT_{sol}), which are largely caused by the intrinsically high optical absorption and the unwanted high refractive index (RI). To tackle these issues, the work covered by this thesis utilizes three attempts, namely VO_2 nanocomposites, grid-patterning and RI-tunable anti-reflection coatings (ARC) on the basis of various VO_2 substrates, to achieve largely enhanced both T_{lum} and ΔT_{sol} .

The VO_2 nanoparticles ($\text{VO}_2\text{-NP}$) prepared by mechanical attrition are encapsulated in the polymer matrix, Si-Al gel, to form nanocomposites, which embody the concept of “nanothermochromism”. This method provides a industrial scalable way of fabriating nanoparticles and offer the comparable thermochromic performances of $T_{\text{lum(avg)}} = \text{ca. } 59\%$ and $\Delta T_{\text{sol}} = \text{ca. } 12\%$.

The simulation work using parameter search algorithm illustrates the excellence of VO_2 nanogrids. The “touching-hole” design demonstrates the largest possible T_{lum} of *ca.* 80% with the remarkable ΔT_{sol} of 14%. The proposed VO_2 nanogrids overcome the thickness constraint of continuous thin films from *ca.* 200 nm up to 400 nm theoretically. In practice, $\text{VO}_2\text{-NP}$ are electrochemically deposited (from their suspensions) at the conductive copper grids with controllable line-width, thickness and fill factor to implement the simulated VO_2 grid-patterning

concept. The computed relationship between the energy modulation abilities and fill factor is experimental proved by the experimental results. Furthermore, this work demonstrates a new irreversible “red-ox free” electrodeposition approach, which is induced by altering the ionic strength in the vicinity of the electrode surface. The new deposition method also provides a universal one-step solution for the formation of patterns with other nanomaterials (*e.g.*, gold nanoparticles, carbon nanotubes and graphene oxides). Therefore, besides achieving excellent thermochromic performance, this method provides a versatile approach for the guided growth on a patterned conducting substrate which can be used in different devices.

Based on the understanding of the intrinsic problems of the RI of VO₂, the thermochromic performances of VO₂ nanocomposites and gridded structures can be further improved by applying the RI-tunable ARC. The sol-gel based ARC with tunable RI (from 1.47 to 1.92 at the wavelength of 550 nm) offer more anti-reflection at a lower temperature, thereby maximizing ΔT_{sol} for various VO₂-based films with largely enhanced T_{lum} simultaneously.

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List of Publications

This thesis is based on the following papers, which are referred to in the content by their sequence numbers.

1. C. Liu, X. Cao, A. Kamyshny, J.Y. Law, S. Magdassi, Y. Long, VO₂/Si-Al gel nanocomposite thermochromic smart foils: largely enhanced luminous transmittance and solar modulation., *J. Colloid Interface Sci.* **427** (2014) 49–53.
2. C. Liu, I. Balin, S. Magdassi, I. Abdulhalim, Y. Long, Vanadium dioxide nanogrid films for high transparency smart architectural window applications, *Opt. Express.* **23** (2015) A124–A132.
3. C. Liu, S. Magdassi, Y. Long, D. Mandler, Ionic Strength Induced Electrodeposition: A Universal Approach for Nanomaterials Deposition at Selective Areas, *Nanoscale*. (2016), DOI: 10.1039/C6NR06614C.
4. C. Liu, Q. Lu, H. Yang, C.Y. Tan, D. Mandler, S. Magdassi, T.J. White, F. Boey, Y. Long, Index-tunable Anti-reflection Coatings: Maximizing Solar Modulation Ability for VO₂-based Smart Thermochromic Glazing, *In Manuscript*.
5. C. Liu, N. Wang, Y. J. Ke, Y. Zhou, Y. F. Gao, Y. Long, Progress in VO₂-based Thermochromic Smart Windows (Review), *In Manuscript*.

Papers partially mentioned in the thesis:

6. C. Liu, N. Wang, Y. Long, Multifunctional overcoats on vanadium dioxide thermochromic thin films with enhanced luminous transmission and solar modulation, hydrophobicity and anti-oxidation, *Appl. Surf. Sci.* **283** (2013) 222–226.
7. Q. Lu, C. Liu, N. Wang, S. Magdassi, D. Mandler, Y. Long, Periodic micro-patterned VO₂ thermochromic films by mesh printing, *J. Mater. Chem. C.* **4** (2016) 8385–8391.

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Abbreviations

V	Vanadium
Si	Silicon
Al	Aluminum
VO ₂	Vanadium Dioxide
VO ₂ (M)	Monoclinic Phase VO ₂ (at low temperature)
VO ₂ (R)	Rutile Phase VO ₂ (at high temperature)
VO ₂ -NP	VO ₂ nanoparticles
AuNP	Gold Nanoparticles
CNT	Carbon Nanotubes
MWCNT	Multi-walled Carbon Nanotubes
GO	Graphene Oxides
IR	Infrared
NIR	Near-infrared
UV	Ultra-violet
Vis	Visible Light
RI	Refractive Index
ARC	Anti-reflection Coatings
AR	Anti-reflection
Si-Al	Silica-alumina
TEOS	Tetraethylorthosilicate
MTMS	Trimethoxysilane
ASB	Aluminum Tri(secbutoxide)
HCl	Hydrochloric Acid
CTAV	Cetyltrimethylammonium Vanadate
CTAB	Cetyltrimethylammonium Bromide
NMP	N-methyl-2-pyrrolidone
PVP	Polyvinylpyrrolidone
PET	Polyethylene Terephthalate

PS	Polystyrene
PU	Polyurethane
PDMS	Polydimethylsioxane
DPM	Dipropylene Glycol Methyl Ether
EDX	Energy Dispersive X-ray Spectroscopy
EBS	Electron Backscatter Diffraction
EM	Electron Microscopy
SEM	Scanning Electron Microscopy
XHR-SEM	Extremely High Resolution Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
HRTEM	High Resolution Transmission Electron Microscopy
BF	Bright Field
DF	Dark Field
HAADF	High Angle Annular Dark Field
DP	Diffraction Pattern
SAED	Selected Area Electron Diffraction
UHV	Ultra-high Vacuum
SE	Secondary Electron
BSE	Backscattered Electron
ESI	Energy Spectroscopic Images
CCD	Charge Coupled Device
XRD	X-ray Diffraction
FWHM	Full Width at Half Maximum
AFM	Atomic Force Microscopy
XPS	X-ray Photoelectron Spectroscopy
DLS	Dynamic Light Scattering
FDTD	Finite Difference Time Domain
EPD	Electrophoretic Deposition
WE	Working Electrode
RE	Reference Electrode
CE	Counter Electrode

S	Sense
QRE	Quasi-reference Electrode
PML	Perfectly Matched Layer
EDL	Electrical Double Layer
CCC	Critical Coagulation Concentration
DLVO	Derjaguin-Landau-Verwey-Overbeek
VDW	Van der Waals
Red-ox	Reduction-oxidation
ASTM	American Standard Testing Method
0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
RT	Room Temperature
DI	Deionized

Frequently Used Symbols

τ_c	Critical Phase Transition Temperature
λ	Wavelength
$T(\lambda)$	Measured Spectral Transmittance
$R(\lambda)$	Measured Spectral Reflectance
$A(\lambda)$	Measured Spectral Absorbance
$T_{lum/IR/sol}$	Integrated Luminous/IR/Solar Transmittance
$T_{lum/IR/sol(avg)}$	Average Integrated Luminous/IR/Solar Transmittance
$T_{lum/IR/sol(low)}$	Integrated Luminous/IR/Solar Transmittance (at Low Temperature)
$T_{lum/IR/sol(high)}$	Integrated Luminous/IR/Solar Transmittance (at High Temperature)
$R_{lum/IR/sol}$	Integrated Luminous/IR/Solar Reflectance
$R_{lum/IR/sol(avg)}$	Average Integrated Luminous/IR/Solar Reflectance
$R_{lum/IR/sol(low)}$	Integrated Luminous/IR/Solar Reflectance (at Low Temperature)
$R_{lum/IR/sol(high)}$	Integrated Luminous/IR/Solar Reflectance (at High Temperature)
ΔT_{lum}	Energy Modulation Ability of Luminous Transmittance

ΔT_{IR}	Energy Modulation Ability of IR Transmittance
ΔT_{sol}	Energy Modulation Ability of Solar Transmittance
ΔR_{lum}	Energy Modulation Ability of Luminous Reflectance
ΔR_{IR}	Energy Modulation Ability of IR Reflectance
ΔR_{sol}	Energy Modulation Ability of Solar Reflectance
T% contrast	Transmittance Contrast between low and high temperature
n	Refractive Index
k	Extinction Coefficient
I	Ionic Strength
c_i	Ionic Concentration
z_i	Ionic Valence
z	Charge Number
ζ -potential	Zeta Potential
wt%	Weight Percentage
vol%	Volume Percentage
FF	Fill Factor
FF _{free}	Fill Factor of Free Area

Chapter 1

Introduction

Thermochromic smart windows, as a category of solar control windows, provide the solutions for enhancing the energy efficiency of the buildings or vehicles. Vanadium dioxide (VO_2) is considered as a promising smart window material because of its infrared-switchable optical properties, which is led by the intrinsic phase transition at a critical temperature of 68 °C. The temperature-stimulated thermochromic effects make VO_2 as the superior candidate of energy-efficient smart windows, but the practical applications of VO_2 continuous thin films are hindered mainly due to the low luminous transmittance (T_{lum}) and the insufficient solar modulation ability (ΔT_{sol}). To tackle these issues, the work covered by this thesis utilizes three attempts, namely VO_2 nanocomposites, grid-patterning and RI-tunable anti-reflection coatings (ARC) on the basis of various VO_2 substrates, to achieve largely enhanced both T_{lum} and ΔT_{sol} . The motivation and hypothesis of each attempt are illustrated in this chapter with the specific objectives and scopes. The brief introduction of each chapter is outlined as a preview of the entire thesis, and the key findings from each attempt are highlighted to reveal the novelty of the overall research studies.

1.1 Hypothesis/Problem Statement

1.1.1 Overview

In the industry-intensive countries, the rapid development of economy mostly results in the overwhelming energy consumption. For instance, nowadays, about 80-90% of working time is spent indoor, *i.e.* in building or in the vehicle.^[1] 30-40% of the world's primary energy is consumed to maintain the comfortable indoor temperature.^[2,3] Especially in the tropical countries, *e.g.*, Singapore, almost every building or transportation is air-conditioned to 21-26 °C all year long by utilizing the energy-consuming air cooling systems, which increase the electricity bills and indirectly incur the inconvenient truth—global warming. Therefore, a need has raised to investigate the “green” nanotechnology for improving the indoor energy-efficiency and reducing the unwanted consequences caused by the cooling systems.

Solar control windows incorporating with chromogenic coatings provide the novel solutions to physically embody the “green” concept in real life applications. The multifunctional windows not only provide the daylighting and visual contacts, but also regulate the solar energy in/out-flow through the glass based on the intrinsic light-switchable properties. The stimuli for different chromogenic materials reveal a great deal of variety, such as charging/discharging for electrochromic materials,^[4-7] illuminating/dimming for photochromic polymers,^[8-10] heating/cooling for thermochromic coatings,^[11-13] *etc.* Among all the chromogenic materials, the thermochromic coating is one of the most cost-effective and promising choices for “smart-window” applications, because the light-switchable properties are naturally triggered by solar heat/irradiation without the installation of external stimulation systems.

Vanadium dioxide (VO₂) is a leading thermochromic material, which exhibits a highly reversible temperature-responsive optical behavior at a critical

phase transition temperature (τ_c) of 341 K (68 °C).^[14] VO₂ transits from an infrared (IR)-transmitting semiconducting state at low temperature ($T < \tau_c$) to an IR-reflecting metallic state at high temperature ($T > \tau_c$), while it maintains the visible transmittance almost unchanged.^[15,16] VO₂ can be considered as an excellent candidate for smart window applications (the working mechanisms refer to **Figure 1.1**), due to two facts: 1) The intrinsic thermochromic features show the competency for regulating the in-flow of solar heat brought by IR,^[14] which carries about 50% of the total solar heating on Earth;^[17] 2) The extensive researches have evidenced that the τ_c can be reduced to room temperature by doping with metal ions of high valence.^[18–22] However, VO₂-based thermochromic smart windows have not yet been commercialized because of low luminous transmittance (T_{lum}) and insufficient solar modulation ability (ΔT_{sol}), which are caused by the inherently high refractive index (RI or ‘ n ’) of the semiconducting VO₂ at low temperature; and also it is challenging to enhance T_{lum} and ΔT_{sol} simultaneously. Hereby, to tackle the above-mentioned issues, the works covered by this thesis utilize either computational optical designs or experimental characterizations to exercise three distinct approaches, namely 1) *VO₂/Si-Al nanocomposites*, 2) *VO₂ grid-patterning: simulations and experiments*, and 3) *RI-tunable anti-reflection coatings (ARC)*. The motivation and hypothesis of each approach is illustrated in details in the following sections, and the thermochromic performances of different VO₂-based nanostructures will be analyzed in-depth in Chapter 4-6.

Figure 1.1 Schematic illustrations of the working mechanism of VO₂-based thermochromic smart windows (VO₂ coatings on glass). Adapted from Reference [23].

1.1.2 Hypothesis #1 – VO₂/Si-Al nanocomposites

The simulations results reported by S. Li *et al.* suggest that the VO₂-based continuous thin films suffer from the limitation of ΔT_{sol} ($<10\%$)^[24] as indicated in **Figure 1.2(b)**, depressing the solar modulation efficiency of the smart windows. In order to obtain a noticeable magnitude of ΔT_{sol} in VO₂ thin films, the film thickness has to increase with the deterioration of T_{lum} ($<40\%$) (**Figure 1.2(a)**),^[24] which is too low to ensure the sufficient daylighting in buildings.^[25] To solve this issue, S. Li *et al.* propose a new concept, called “nanothermochromism”,^[24] and use the computational data to evidence that VO₂ nanoparticles (VO₂-NP) dispersed in a dielectric host are more advantageous than VO₂ continuous thin films if used for smart window applications, because VO₂-NP offer much higher T_{lum} (**Figure 1.2(c)**) together with largely enhanced ΔT_{sol} (**Figure 1.2(d)**). Although previous investigations have produced the pure crystallized VO₂-NP by solid-state annealing or thermolysis and embedded them as nanofillers in the polymer matrix,^[26,27] none of these nanocomposites could provide the experimentally acceptable T_{lum} ($>60\%$) together with large ΔT_{sol} ($>10\%$).^[28] Also, the thermolysis synthesis method requires the complex control of annealing conditions and has a low yield-to-cost ratio.

Figure 1.2 Simulated results of (a) T_{lum} and (b) T_{sol} based on the VO₂ continuous thin films with different film thickness, and (c) T_{lum} and (d) T_{sol} based on the VO₂ nanocomposites with a different aspect ratio of VO₂-NP. Reprinted with permission from Reference [24]. Copyright 2010, American Institute of Physics.

Hereby, in Chapter 4, an alternative straightforward implementation of “nanothermochromism” is considered to simplify the preparation method of nano-size VO₂ particles and to improve the contemporary results of pure VO₂-NP based nanocomposites. The cost-effective mechanical attrition is taken into account for reducing the size of the crystallized VO₂ particles from micro to nano-size, so as to be well-dispersed in a transparent silica-alumina (Si-Al) gel. During the optimization of VO₂ nanocomposites, both the effect of VO₂ solid content and foil thickness should be systematically investigated to obtain the balanced amount of VO₂-NP in the polymer matrix. The target is to concurrently prompt T_{lum} to around 60% with the comparable ΔT_{sol} to the best reported pure VO₂-NP based nanocomposites.

1.1.3 Hypothesis #2 – VO₂ grid-patterning: simulations and experiments

Besides the applications of “nanothermochromism”, the nano-patterning of VO₂ is also of interest. For example, the biomimetic “moth-eye” nanostructure, which usually takes advantage of the shape of paraboloid cone to engender a continuous gradient of refractive index (RI), inducing the anti-reflection (AR) functionality and leading to the improved T_{lum} .^[29] However, to acquire the highest T_{lum} (*ca.* 70%) with ΔT_{sol} (15.5%), the high aspect ratio (e.g. height= 500 nm and base-width=135 nm) is a must.^[30] This is due to the fact that: 1) the pitch size (*ca.* 130 nm) restricts the base-width in order to keep the nanostructure be unresolved by the incident light; 2) the height has to be high enough to ensure the sufficient amount of VO₂ overlay on the tapered template.^[30] This challenges the modern nano-fabrication techniques and makes the entire nanostructures less durable due to the sharp tips.

As inspired by the biomimetic “moth-eye” structuring, a new idea of VO₂ “nanogrids” is initiated to tackle the above-mentioned issue of high aspect ratio. Chapter 5 demonstrates the systematic optical modeling with three densely-packed structural models, explicitly 1) square holes in the VO₂ square lattices, 2) circular holes in the VO₂ square lattices, and 3) circular holes in VO₂ hexagonal lattices. Theoretically, the size of holes could be precisely controlled to offer the physical pathway for the visible light, thus increasing T_{lum} . Meanwhile, with the optimization of the thickness, a high volume of VO₂ could be contained in the abundant ridge area, so as to potentially retain a significant ΔT_{sol} . The size and shape of the nanogrids, the cell periodicity and the thickness of the nanostructure should be systematically investigated by employing the Finite Difference Time Domain (FDTD) simulation. Ideally, the optimized VO₂-based grid-patterning nanostructures will exhibit a large enhancement of T_{lum} with a good maintenance of ΔT_{sol} as compared to the continuous thin films, and open up a new avenue towards the applications of thermochromic smart windows.

Furthermore, prior to the author's studies, the previous implementation of VO₂ grid-patterning is inspired by the nanoporous structuring, utilizing post-annealing to remove the polystyrene (PS) template as well as crystallize the monoclinic phase of VO₂ (denotes as VO₂(M)) from V⁴⁺ precursors.^[31] However, the concentration of the precursors has to be carefully monitored in order to obtain the fine crystallized VO₂ nanostructures, and also this method can be applied only on the quartz glass substrates because of the existence of the high-temperature annealing process. Since the thickness of a monolayer is passively governed by the dimension of PS spheres, the deposition process has to be repeated for three times or more to increase the spatial amount of VO₂; nevertheless, the ΔT_{sol} obtained by the three-layer nanostructure is still hardly greater than 10%.

In order to actively control the line-width, thickness, fill factor (FF), *etc.* of the VO₂ grid-patterning, the electrochemical deposition of the crystallized VO₂-NP is of interest due to the fine-tunable applied potential and deposition time. However, the electrodeposited nanomaterials or VO₂ thin films^[32–34] are usually formed upon deposition with involving the reduction-oxidation (red-ox) reactions, which may deteriorate the intrinsic properties of VO₂-NP and produces the non-thermochromic impurities of V₂O₅ or V₆O₁₃, thus becoming undesirable for smart window applications. To get rid of the red-ox reactions on the VO₂-NP deposits, a new electrodeposition concept induced by ionic strength is raised in Chapter 5 to physically implement the VO₂ grid-patterning concept. Specially, a copper electrode is electrochemically oxidized under well-controlled conditions to generate a flux of copper ions. The latter is used to increase the ionic strength in the vicinity of the working electrode and therefore reduce the repulsion forces between the particles (**Figure 1.3**) based on the well-known Derjaguin-Landau-Verwey-Overbeek (DLVO) theory. Since the fine crystallized VO₂-NP are directly deposited (not formed upon deposition) from their aqueous solutions, the post-annealing process is substantially removed and hence the PET foils with the conductive Cu grids can be used as the working electrodes to physical embody the VO₂ grid-patterning concept on the flexible substrates. The experimental results

can be compared with the simulated “nanogrid” outcomes by monitoring the relationship between FF and thermochromic properties. The optimizations of the electrochemical conditions exercise to obtain the optimal combinations of T_{lum} and ΔT_{sol} for the thermochromic smart windows.

Figure 1.3 Diagram of the concept of the ionic-strength induced electrodeposition. Reproduced with permission from Reference [35]. Copyright 2016, The Royal Society of Chemistry.

1.1.4 Hypothesis #3 – RI-tunable anti-reflection coatings applied on various VO₂-based substrates

The intrinsically low T_{lum} and ΔT_{sol} are due to the fact that VO₂ has much higher RI from 500 nm to 2200 nm wavelength at a lower temperature in the wavelength (λ) range of *ca.* 500-2000 nm (**Figure 1.4(a)**).^[30] The high-RI in the semiconducting phase of VO₂ causes the unwanted high reflection (**Figure 1.4(b)**) and suppresses T_{lum} at low temperature ($T_{lum(low)}$) (**Figure 1.4(c)**), thereby resulting in small ΔT_{sol} . Based on Fresnel equation, high reflection may be theoretically reduced to the minimum by adopting a specific ARC layer on top of the VO₂ substrates, if n_{ARC} could be tuned to the vicinity of $\sqrt{n_{VO_2(low)}}$ rather than $\sqrt{n_{VO_2(high)}}$.^[35] Hereby, this reveals the possibility to further improve the thermochromic properties of the VO₂ nanocomposites. However, by far, only fixed-

RI ARC were applied on the continuous VO₂ thin films, [12,36–42] and all the previous studies have experienced the ARC materials selection process to meet the different RI requirements. Also, most of them indicated an inevitable decrease of the transmittance contrast (T% contrast) in the IR region, while none of them focused on enhancing ΔT_{sol} through tackling the intrinsic RI-limitation of VO₂ substrates. Therefore, in Chapter 6, the sol-gel based RI-tunable ARC are designed to preferentially offer more anti-reflection (AR) to the cold state as compared with the hot state, ultimately enhancing the ΔT_{sol} due to the fact of $\Delta T_{\text{sol}} = T_{\text{sol}(\text{low})} - T_{\text{sol}(\text{high})}$. This design is preliminarily tested on the substrates of VO₂ nanocomposites by heating the Si-Al based ARC at different temperature. To understand the relationship between n_{ARC} and ΔT_{sol} , another sol-gel based ARC, prepared by TEOS solutions, are also employed to extend the tunability of n_{ARC} , and VO₂ continuous thin films are used as the thermochromic substrates due to the given spectral RI (**Figure 1.4(a)**) in the previous literature.^[30] Subsequently, the compositions of sol-gel based ARC and heating temperature should be optimized in order to maximize the “nanothermochromic” properties of VO₂ nanocomposites in the aspects of both T_{lum} and ΔT_{sol} . Moreover, the RI-tunable ARC also attempt to apply on the grid-patterned VO₂ films to check the general applicability of this concept.

Figure 1.4 (a) Spectral RI of VO₂ at both low-temperature state (dashed blue line) and high-temperature state (solid red line). Reprinted with permission from Reference [30]. Copyright 2013, Optical Society of America. (b) Spectral reflectance and (c) spectral

transmittance from 250 to 2500 nm at both low- (solid blue lines) and high-temperature (dotted red lines) states. Reprinted with permission from Reference ^[43]. Copyright 2011, Elsevier B.V.

1.2 Objective and Scope

The objective of this thesis is to adopt various VO₂-based nanostructures in the applications of thermochromic smart windows for obtaining the simultaneous enhancement of T_{lum} and ΔT_{sol} .

To accomplish the objective mentioned above, the scope of this thesis attempts to apply the following strategies and the relationship between the three approaches is demonstrated in **Figure 1.5**.

- a) Introducing a simple and scalable approach to prepare thermochromic nanocomposites with mechanically attrited VO₂-NP dispersed in a transparent Si-Al gel matrix (**Figure 1.5(a)**) – the physical implementation of “nanothermochromism”;
- b) Initiating a new idea of VO₂ “nanogrids” based on the FDTD simulations to favorably transmit visible light dramatically through the orderly-patterned nanoholes but retain large NIR modulation due to the abundant ridge area formed by VO₂; Also, physically embodying the grid-patterning concept by utilizing the new ionic-strength induced electrodeposition of the intact “red-ox free” VO₂-NP from their aqueous suspensions onto the conductive Cu-grid/PET substrates under the well-controlled deposition conditions (**Figure 1.5(b)**);
- c) Applying the sol-gel based ARC with tunable RI to offer more AR at a lower temperature, thereby maximizing ΔT_{sol} for not only VO₂ nanocomposites but

also VO₂ periodic grid-patterning films (and continuous thin films) (**Figure 1.5(c)**).

Figure 1.5 (a) Scope a): dispersing VO₂-NP in the Si-Al matrix to form nanocomposites; (b) Scope b): simulation of “nanogrids” concept and experimental implementation of VO₂ grid-patterning by using ionic strength induced electrodeposition; (c) Scope c): applying the RI-tunable ARC on the various VO₂ substrates to offer more AR effect at low temperature as compared to that at high temperature.

1.3 Dissertation Overview

The thesis addresses the intrinsic problems of VO₂ thermochromic materials based on the contemporary literature review and develops four VO₂-based nanostructures to enhance both T_{lum} and ΔT_{sol} of thermochromic smart windows *via* the applications of various experimental methods and optical simulations.

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

Chapter 2 reviews the literature concerning the basic knowledge of thermochromic smart windows, revealing the current challenges of VO₂-based smart windows in real-life applications, and discussing the achievements and shortcomings in the contemporary developments of enhancing both T_{lum} and ΔT_{sol} .

Chapter 3 explains the rationale for selecting different materials and synthesis/characterization/modeling techniques, and also discusses the principles underlying the particular methods.

Chapter 4 elaborates the synthesis and characterizations of VO₂/Si-Al gel nanocomposite thermochromic smart foils casted on soda glass for achieving largely enhanced T_{lum} and ΔT_{sol} .

Chapter 5 elaborates an original idea of VO₂ “nanogrid” based on the systematic simulations, and implements the grid-patterning idea by developing a novel “red-ox free” electrodeposition of VO₂-NP based on altering the ionic strength in the proximity of the electrode surface.

Chapter 6 introduces the RI-tunable sol-gel based ARC for maximizing the ΔT_{sol} of various VO₂-based nanostructures with improved thermal stability.

Chapter 7 demonstrates how the thesis hypothesis is proven with the evidence from either simulations or experiments, and how the project objectives are met and addressed. It also elaborates the prospects for future developments of thermochromic smart windows.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

- a) Establishing a facile approach to synthesize VO₂-NP with a dimension of

approximately 20 nm *via* simple mechanical bead-milling method, which are well-dispersed in a transparent Si-Al gel matrix to attain high T_{lum} ($T_{\text{lum}(20\text{ }^{\circ}\text{C})}=63.7\%$ and $T_{\text{lum}(90\text{ }^{\circ}\text{C})}=54.4\%$) and large $\Delta T_{\text{sol}}=12\%$.

- b) i) Acquiring the largest simulated T_{lum} of *ca.* 80% when increasing FF of the touching holes configuration in the hexagonal cells with circular hole design; Extending the upper-limit of thickness on enhancing ΔT_{sol} from *ca.* 200 nm for VO₂ continuous thin films to 400 nm for VO₂ nanogrids.
- ii) Developing a novel electrochemical approach of the ionic-strength induced electrodeposition of VO₂-NP without involving the red-ox reactions on the nanomaterials; Realizing the VO₂-NP grid-patterning on the flexible foils with the excellent thermochromic combinations of $T_{\text{lum(avg)}}=38.4\%$ and $\Delta T_{\text{sol}}=13.9\%$, or $T_{\text{lum(avg)}}=57.7\%$ and $\Delta T_{\text{sol}}=10.5\%$ under different deposition conditions.
- c) Further improving the ΔT_{sol} of not only VO₂-based nanocomposites (from 15.7% to 18.9%) but also VO₂ continuous thin films (from 4.3% to 6.3%) and periodic micro-patterning films (from 3.6% to 10.5%) *via* applying a single-layer of RI-tunable ARC, which tackle the intrinsically high-RI issue of the low-temperature semiconducting VO₂.

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Chapter 2

Literature Review

Solar control windows are of great interest for the energy-efficient buildings or vehicles in the recent decade. Vanadium dioxide (VO_2) has been intensively studied as a promising candidate for the thermochromic smart windows, since it reveals a reversible infrared (IR)-switching properties based on the intrinsic phase transition at a critical temperature (68°C). However, due to the inherently high refractive index (RI) at the low-temperature state, VO_2 thin films suffer from both low luminous transmittance (T_{lum}) and insufficient solar modulation ability (ΔT_{sol}), which obstacle the way for practical applications of VO_2 -based smart windows. To tackle these issues, the different nanostructures of VO_2 , namely i) nanocomposites, ii) nanoporous films, iii) nano-patterning structures and iv) anti-reflection coatings, were considered in the contemporary investigations in order to achieve the improvement of both T_{lum} and ΔT_{sol} . Meanwhile, some questions are also raised from the former literature and those issues are addressed in the context of the Ph.D. studies to close the gap in the current developments.

2.1 The Basics of Solar Control Windows

The glazing is commonly utilized in the architectures or vehicles to provide visual contact through the glass, allow the daylight to illuminate the space and offer heat control to some extent. These functions can be brought in practice by transmitting or blocking the certain wavelength (λ) range of solar spectra. For instance, according to the human eye sensitivity, the visible light, in the range of $0.4 < \lambda < 0.7 \mu\text{m}$, is usually permitted to pass through the windows, contributing to the daylighting and visual contact. Both the ultra-violet (UV) ($\lambda < 0.4 \mu\text{m}$) and the near-infrared (NIR) ($\lambda > 0.7 \mu\text{m}$) light are insensitive to human eyes, while the later contributes *ca.* 49% of the solar heating on Earth.^[1] Hence, the control of energy-flow in the NIR region becomes vital.

Solar control windows are typically the applications of the single-layer or multi-layer thin films on the suitable window substrates, *e.g.*, glass. They are usually designed for a warm climate to block the solar heat in the hot season with a good maintenance of visible transmittance. The ideal case for solar control coatings is described as below.^[2]

$$\text{solar control} \begin{cases} \text{Transmittance } (\lambda) = 1 & \text{when } 0.4 < \lambda < 0.7 \mu\text{m} \\ \text{Reflectance } (\lambda) = 1 & \text{when } 0.7 < \lambda < 50 \mu\text{m} \end{cases}$$

In practice, solar control coatings hinder part of the transmission in the NIR region in the hot season and offer high transparency in the visible region all year long, thereby largely reducing the solar heat gain through the windows and saving the energy for cooling the space (*e.g.*, the utilization of air-conditioners).

The concept of solar control windows can be realized in real life by employing the chromogenic materials,^[3] which are able to alter their own optical behaviors when experiencing different external stimulus, *e.g.*, UV irradiation (light) for photochromic coatings^[4,5] and polymers,^[6–8] ambient temperature changes (heat)

for thermochromic coatings,^[9–11] and inserting or extracting charges (electricity) for electrochromic coatings.^[12–15] There are also other categories of chromogenisms, such as solvatochromism (due to the changes of solvent polarity), ionochromism (induced by ion variations), halochromism (stimulated by pH alternations), tribochromism (stimulus from friction) and piezochromism (caused by pressure).^[16] Among the chromogenic materials, the thermochromic coatings are one of the most promising candidates for energy efficient building fenestration, because their reversible optical behaviors are stimulated naturally from solar heat/irradiation, which means no need of extra energy supply and no additional facilitator system required. Therefore, thermochromic smart windows are widely investigated for implementing the energy-efficiency idea in the modern architectures or transportations.

2.2 The Performance Evaluations of Thermochromic Smart Windows

To quantify the amount of visible light useful for human vision under normal conditions, the integrated luminous transmittance (T_{lum}) and reflectance (R_{lum}) have been defined based on the photopically averaged transmittance (**Equation 2.1**) and reflectance (**Equation 2.2**), respectively. The λ range for calculating T_{lum} and R_{lum} is selected from 380 nm to 780 nm according to the photopic luminous efficiency of the human eyes (red curve in **Figure 2.1**). As indicated in the blue curve of Figure 2.1, λ from 250 to 2500 nm carries 99.2% terrestrial solar energy. Thus, in order to evaluate the averaged transmittance and reflectance in the NIR region and the entire solar spectrum, the λ range of 780–2500 nm and 250–2500 nm are used to calculate the integrated infrared (IR) transmittance (T_{IR}) and reflectance (R_{IR}), as well as the integrated solar transmittance (T_{sol}) and reflectance (R_{sol}), respectively. Moreover, another set of key evaluation factors for thermochromic smart windows are the energy modulation abilities in the different parts of solar spectrum. They represent the differences of the transmitted and reflected energy when the thermochromic coatings exhibit different optical properties at low and high ambient temperature.

The symbols are $\Delta T_{lum/IR/sol}$ and $\Delta R_{lum/IR/sol}$, and the values can be calculated according to **Equation 2.3** and **Equation 2.4**, respectively.

$$T_{lum/IR/sol} = \frac{\int \phi_{lum/IR/sol}(\lambda) T(\lambda) d\lambda}{\int \phi_{lum/IR/sol}(\lambda) d\lambda} \quad (2.1)$$

$$R_{lum/IR/sol} = \frac{\int \phi_{lum/IR/sol}(\lambda) R(\lambda) d\lambda}{\int \phi_{lum/IR/sol}(\lambda) d\lambda} \quad (2.2)$$

$$\Delta T_{lum/IR/sol} = T_{lum/IR/sol(low)} - T_{lum/IR/sol(high)} \quad (2.3)$$

$$\Delta R_{lum/IR/sol} = R_{lum/IR/sol(low)} - R_{lum/IR/sol(high)} \quad (2.4)$$

$$T_{lum/IR/sol(avg)} = \frac{T_{lum/IR/sol(low)} + T_{lum/IR/sol(high)}}{2} \quad (2.5)$$

$$R_{lum/IR/sol(avg)} = \frac{R_{lum/IR/sol(low)} + R_{lum/IR/sol(high)}}{2} \quad (2.6)$$

where $T(\lambda)$ and $R(\lambda)$ represent the measured spectral transmittance and reflectance, respectively. Referring to **Figure 2.1**, Φ_{lum} is the standard luminous efficiency function of photonic vision^[17] (red curve) for λ in the range of 380-780 nm, and $\Phi_{IR/sol}$ is the IR/solar irradiance spectrum distribution (blue curve) for air mass 1.5.^[18] Φ_{sol} represents an overall yearly average for mid-latitudes including diffuse light from the ground and sky on a south facing surface tilted 37° from horizontal. In addition, the $T_{lum/IR/sol(avg)}$ (**Equation 2.5**) and $R_{lum/IR/sol(avg)}$ (**Equation 2.6**) are the average integrated $T(\lambda)$ and $R(\lambda)$ in the corresponding λ range obtained at both low and high temperatures. The qualification of thermochromic smart windows typically examines two key factors, namely T_{lum} and ΔT_{sol} .

Figure 2.1 Spectra used in Equation 2.1-2.6: the red curve – the photopic luminous efficiency of the human eyes;^[17] the blue curve – the AM 1.5 solar irradiance spectrum.^[18]

2.3 Thermochromism in VO₂

2.3.1 Phase transition of VO₂

The first time of reporting the thermochromism in vanadium dioxide (VO₂) was in 1959 by F. Morin *et al.*^[19] He proposed the concept of metal-to-insulator transition in vanadium oxides with the aid of demonstrating the hysteresis loop of VO₂ conductivity as a function of temperature (**Figure 2.2(a)**). In 1971, J. Goodenough reported that a pure bulk VO₂ crystal reveals a semiconductor-to-metal transition at a critical temperature (τ_c) of 341K (i.e., 68 °C),^[20] which is corresponding to the structural phase change upon crossing τ_c . VO₂ presents a semiconductor behavior at the low-temperature monoclinic phase (denotes as VO₂(M) phase and shows in **Figure 2.2(b)**), while the VO₂ crystal alters to a rutile structure (namely VO₂(R) phase and shown in **Figure 2.2(c)**) and behaves like a metallic material if $T > \tau_c$.^[21] The underlying physics of VO₂ phase transition has been discussed for many years,^[22,23] but unclear yet. The conventional explanations of the mechanisms can be generally categorized into two types, namely Peierls-like^[21,24] and Mott-Hubbard-like.^[25–27] Geometrically, the difference between two phases of VO₂ is the lattice position of V atoms at the different temperature. V

atoms dimerize and twist in a zig-zag way along the c-axis at the low-temperature semiconducting state,^[3] leading to lattice distortion upon heating to the high-temperature rutile phase. This structural transition is highly reversible in the VO_2 thin films or other nanostructures and hence induces the switchable optical, electrical and magnetic properties with the dependent of temperature in different applications.

Figure 2. 2 (a) Conductivity variations of different vanadium and titanium oxides as the function of temperature. Reprinted with permission from Reference ^[19]. Copyright 1959, American Physical Society. (b) The monoclinic crystal structure of VO_2 in the low-temperature semiconducting state when $T < \tau_c$. (c) VO_2 rutile phase at the high-temperature metallic state if $T > \tau_c$. Reprinted with permission from Reference ^[21]. Copyright 2002, John Wiley & Sons, Inc.

2.3.2 Optical properties and optical constants of VO₂

The VO₂(M) phase is relatively IR transparent, which permits the solar energy in-flow to warm up the room or space in a cold occasion. However, if the ambient temperature is higher than τ_c , the majority of IR transmittance is blocked, but the visible transmittance is maintained nearly unchanged. Due to the presence of the intrinsic IR-switchable thermochromic properties, VO₂ has been intensively studied as the functional material used in the applications of thermochromic smart windows since the early 1980s.^[28–30]

Figure 2.3(a) and **2.3(b)** demonstrate the typical reflectance and transmittance spectra, respectively, of a 50 nm thick VO₂ coating on a glass substrate.^[31] **Figure 2.3(a)** indicates that in the λ range of *ca.* 500–1300 nm, VO₂ thin film reveals higher reflectance in the low-temperature semiconducting state as compared with the high-temperature reflectance measured in the metallic state. The excessive reflectance in the semiconducting phase is highly unwanted, because it causes low T_{lum} (**Figure 2.3(b)**) at the maximum luminous efficiency of human eyes^[17] (**Figure 2.3(c)**), eventually leading to small ΔT_{sol} .

The intrinsic issue of the phenomenon above is that VO₂ possess much higher refractive index (RI or ‘ n ’) at a lower temperature^[32] in the λ range of *ca.* 500–2000 nm (**Figure 2.3(d)**). Since the extinction coefficient (k) (**Figure 2.3(e)**) is fairly low at the cold state, it means that the spectral absorption ($A(\lambda)$) of VO₂ is insignificant at the low temperature.^[32] Based on the energy conservation law (**Equation 2.7**) at each wavelength:

$$T(\lambda) + R(\lambda) + A(\lambda) = 1 \quad (2.7)$$

Low $T_{lum(avg)}$ ($=\frac{T_{lum(low)}+T_{lum(high)}}{2}$) and insufficient ΔT_{sol} ($=T_{sol(low)}-T_{sol(high)}$) are predominately resulted from the intrinsically high-RI of VO₂ at the

low-temperature state. By utilizing the formulas described in **Equation (2.1)** and **(2.3)**, the $T_{\text{lum(avg)}}$ of the 50 nm VO₂ thin film (in **Figure 2.3**) is approximately 37.4%, while the ΔT_{sol} is only *ca.* 6.5%. Most conventional VO₂ continuous thin films can achieve T_{lum} of *ca.* 50%, but ΔT_{sol} is limited around 5%,^[31,33,34] which is inadequate for commercializing VO₂ thin films in the practical applications.

Figure 2.3 Typical spectral reflectance (a) and transmittance (b) of a 50 nm thick VO₂ film on a glass substrate in the low-temperature semiconducting (solid blue) and high-temperature metallic (dotted red) states, respectively. (c) Solar irradiance spectrum and relative luminous efficiency of the human eye as a function of wavelength. Reprinted with permission from Reference ^[31]. Copyright 2011, Elsevier B.V. Refractive index (d) and extinction coefficient (e) of pure VO₂ at the cold (semiconducting; dashed blue) and hot (metallic; solid red) states, respectively. Reprinted with permission from Reference ^[32]. Copyright 2013, Optical Society of America.

2.4 Synthesis Methods

2.4.1 Synthesis of VO₂ continuous thin films

Continuous VO₂ thin films can be prepared by a variety of deposition methods. Physical vapor deposition (PVD), chemical vapor deposition (CVD) and sol-gel synthesis are the common approaches for satisfying different film quality requirements. Among the PVD methods, reactive sputtering coupling with an inert gas atmosphere is the most common PVD techniques, and most of VO₂ thin films are fabricated using radio frequency (RF) magnetron sputtering,^[33,35] direct current (DC) magnetron sputtering^[36–38] or ion beam sputtering.^[29,39] Physical sputtering methods can provide uniform films on a relatively large scale. However, the deposition rate is slow, and the adhesion between films and substrates is unacceptable for practical smart window applications. On the other hand, CVD involves chemical reactions during the deposition process, and it accelerates the deposition rate and provides good film adhesion. The production of VO₂ thin films is based on the reactions of organometallic precursors^[28,40] and also requires the subsequent reduction of the primarily formed vanadium oxides in other oxidation states.^[41,42] The deposited films are pure and compact as well as showing excellent conformal coverage with high uniformity. However, it is challenging to precisely control the stoichiometry during CVD process if using the multi-component precursors. Also, both PVD and CVD techniques require expensive deposition equipment, which increases the cost of manufacturing and restricts the applications for the large-scale production.

Sol-gel synthesis provides a cost-effective alternative solution for achieving the full coverage of VO₂ thin films on the large glass substrates. The synthesis process usually involves the use of vanadium alkoxide precursors, associated with a thermal pyrolysis procedure that anneals the sample up to 600 °C in vacuum or a reducing gas atmosphere. As the VO₂ synthesis methods develop over a few decades, the eco-unfriendly vanadium alkoxide precursors are gradually phased out

and replaced by a new generation of vanadium (IV/V) solutions, e.g., VOCl_2 or $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$.^[43–45] To reduce the $\text{VO}_2(\text{M})$ sintering temperature below the softening temperature of glass substrate (570 °C), I. Takahashi *et al.*, Z. Lu *et al.* and N. Yuan *et al.* recommended several feasible low-temperature manufacturing processes,^[43,46,47] but they have failed to simplify the sintering procedures to less than two steps. N. Wang *et al.* has reported a straightforward route of synthesizing the highly crystallized $\text{VO}_2(\text{M})$ thin films., successfully obtaining films with high ΔT_{sol} via the use of one-step thermolysis of $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ($n \approx 2$) precursors in a vacuum tube furnace.^[48]

2.4.2 Synthesis of VO_2 nanoparticles

As compared with continuous VO_2 thin films, VO_2 nanoparticles ($\text{VO}_2\text{-NP}$) reveal their distinctive thermochromic properties. As an example, the decrease of particle size increases both the transmittance contrast and the distinction of electric resistance at the two structural phases of VO_2 .^[49] Meanwhile, $\text{VO}_2\text{-NP}$ could be utilized to assemble the alternative nanostructures, such as nanocomposites,^[50,51] on the various low-temperature-endurance substrates by vortex mixing. There are many works of literature demonstrating the methods for manufacturing $\text{VO}_2\text{-NP}$, for instance, a) thermolysis of solution-based V^{4+} precursors,^[52–55] b) hydrothermal treatment^[56–60] and c) multi-step sol-gel technique.^[61]

In general, the thermolysis (also known as pyrolysis) process involves the thermodecomposition of $(\text{NH}_4)_5[(\text{VO})_6(\text{CO}_3)_4(\text{OH})_9] \cdot 10\text{H}_2\text{O}$ at elevated temperature (350–550 °C) in the nitrogen or argon atmosphere. The annealing temperature, gas flow rate and the concentration of precursors influence the crystallinity^[53] and the stoichiometry of VO_2 crystals.^[55] During the thermal annealing process, the V^{4+} -containing precursor is decomposed into the VO_2O_4 intermediate and CO , CO_2 , NH_3 gasses. The pure monoclinic phase of VO_2 can be fully crystallized only if the annealing temperature is higher than 400 °C.^[53] Also, C. Zheng *et al.* found that the absorption in the IR region shows a blue-shift for the

oxygen-rich VO₂ crystals (i.e., VO_{2.00-2.07}), while the oxygen-deficient VO_{1.96-1.98} crystals indicate a slight red-shift.^[55] Therefore, for obtaining high-temperature VO₂ nanocrystals, thermolysis processes usually require the complex control of annealing conditions, constantly consume a large amount of thermal energy and release green-house gasses thru the process. These drawbacks make the thermolysis process less and less feasible in the recent years as compared to the other one-pot manufacturing approach, namely, hydrothermal treatment.

The synthesis of VO₂-NP *via* hydrothermal approach commonly reduces vanadium pentoxide (V₂O₅)^[56,59] or ammonium metavanadate (NH₄VO₃)^[60] in the presence of oxalic acid (H₂C₂O₄). This process allows to add the tungsten (W) doping agent to reduce the τ_c of W-doped VO₂-NP close to room temperature (25 °C). The as-synthesized products are composed of the rod-like and asterisk-shaped VO₂ nanocrystals^[56,59] as shown in **Figure 2.4**. The particle size, morphology, and composition are highly dependent on the reaction conditions in the precursor formation, such as the concentration of vanadium source, processing temperature, and the pH of the precursor solution. W. Li *et al.* reported that decreasing the vanadium concentration leads to the production of near-spherical nanocrystals with the size of 20-50 nm (**Figure 2.5(a)**), while the particles may grow in the longitudinal direction with increasing the content of vanadium in the precursor (**Figure 2.5(b) and 2.5(c)**).^[58] The decrease of the particle size improves thermochromic properties (**Figure 2.5(d)**) but also widen the hysteresis of VO₂ phase transition (**Figure 2.5(e)**). However, the hydrothermal methods also suffer from a few shortcomings, such as the impurity of VO₂(B), small yield and the prolonged processing time (normally 1-3 days), which are the obstacles for the large-scale manufacturing in real life practices.

Figure 2.4 Typical VO_2 crystals produced by the hydrothermal method: (a) low-resolution transmission electron microscope (TEM) image and (b) field-emission scanning electron microscope (SEM) image. Reprinted with permission from Reference [59]. Copyright 2008, American Chemical Society.

Figure 2.5 SEM images of the VO_2 particles obtained at different concentrations of vanadium: (a) Sample A 0.5 mol L^{-1} , (b) Sample B 0.1 mol L^{-1} , (c) Sample C 0.05 mol L^{-1} . (d) Transmittance spectra of Sample A, B and C at low (25°C) and high (90°C) temperature states. (e) Differential scanning calorimetry (DSC) curves show the hysteresis of VO_2 phase transition temperatures of Sample A, B and C. Reprinted with permission from Reference [58]. Copyright 2014, The Royal Society of Chemistry.

The sol-gel method is rarely used for preparing VO₂-NP unless the particles formed as the dopants inside the silica matrix. S. Mukherjee and A. K. Pal successfully synthesize VO₂ nano-fillers (5-10 nm diameter) in the glass matrix by sintering the vanadium-oxide-doped silica gel (the mixture of 2 mol% vanadyl sulfate in the solvent of tetraethylorthosilicate (TEOS)) at 700-900 °C.^[61] The particle size grows bigger with increasing the calcination temperature (as comparing between **Figure 2.6(a)** and **2.6(c)**), and the oxidation of VO₂ may occur if the temperature is elevated higher than 800 °C (as illustrated in **Figure 2.6(e)** and **2.6(f)**).

Figure 2. 6 TEM images of VO₂-NP in the silica matrix, which is calcined at (a) 700 °C and (b) 900 °C, respectively. X-ray diffraction (XRD) patterns of VO₂-NP in the silica matrix, which is calcined at (e) 900 °C and (f) 800 °C, respectively. The insets (b) and (d) are the high-resolution TEM (HRTEM) images of individual crystallized VO₂-NP at the corresponding sintering temperatures. Reprinted with permission from Reference ^[61]. Copyright 2008, IOP Publishing Ltd.

2.5 Contemporary Solutions for Enhancing Both T_{lum} and ΔT_{sol}

VO_2 is a promising candidate for the application of thermochromic smart windows. However, the major two shortcomings, low T_{lum} and insufficient ΔT_{sol} , obstruct the commercialization of VO_2 -based thermochromic coatings. Hence, this section focuses on the reviews of the contemporary solutions for achieving the simultaneously enhanced T_{lum} and ΔT_{sol} . The topics are comprising of 1) nanothermochromism and nanocomposites, 2) anti-reflection coatings (ARC), 3) nanoporous films and 4) nano-patterning structures.

2.5.1 Nanothermochromism and nanocomposites

Li S. *et al.* initiated a new concept, called “nanothermochromism”, and utilized the calculations based on the effective medium theory (EMT) to demonstrate the pronounced advantages of the VO_2 -NP dispersed in a dielectric matrix (Section 2.5.1.1).^[62] The outstanding thermochromic properties of VO_2 nanocomposites attract a plenty of attentions in the recent five years, and Section 2.5.1.2 reviews those remarkable experimental results obtained by embedding the pure, doped or core-shell structured VO_2 -NP in the different matrix.

2.5.1.1 Effective medium theory and simulations

A. Effective medium theory: The simulation models exploited by S. Li *et al.* are the dilute nanocomposites which are composed of VO_2 -NP as the fillers and the dielectric materials (RI similar to glass or polymer) as the matrix.^[62,63] **Figure 2.7** schematically displays the structural models for three types of nanoparticles, namely a) spherical nanoparticles (**Figure 2.7(a)**),^[62] b) prolate spheroids (**Figure 2.7(b)**)^[62] and c) core-shell structured nanoparticles (**Figure 2.7(c)**).^[63] The medium with the ellipsoidal particles is examined with the consideration of different aspect ratios (m), which are the quotients between the variance major axis (a) and minor axis (c) as shown in **Figure 2.7(b)**.^[62]

Figure 2.7 Simulation models of VO₂ nanocomposites, composing of VO₂-NP with a dielectric function of ϵ_p embedded in a matrix with a dielectric function of ϵ_m . The nanoparticles are taken to be (a) spherical, (b) prolate and (c) in the core-shell structure, respectively. The aspect ratio (m) is defined for the prolate spheroids as the ratio between the major (a) and minor (c) axes. ϵ_c and ϵ_s stand for the dielectric functions of the core (diameter x) and the shell (thickness t), respectively. $\hbar\omega$ represents the electromagnetic radiation with photon energy. (a) and (b): Reprinted with permission from Reference [62]. Copyright 2010, American Institute of Physics. (c): Reprinted with permission from Reference [63]. Copyright 2011, American Institute of Physics.

The Maxwell-Garnett EMT widely applies to estimate the optical properties of composite layers, composing of isolated particles embedded in a continuous matrix. It works best when the volume fraction or “filling factor” of the particles (f) is small^[62] and the radii of nanoparticles are much smaller than the wavelength.^[64] According to the theory, the nanocomposite, comprising of nanoparticles and the matrix, has an effective dielectric function (ϵ^{MG}):

$$\epsilon^{MG} = \epsilon_m \frac{1 + \frac{2}{3}f\alpha}{1 - \frac{1}{3}f\alpha} \quad (2.8)$$

where ϵ_m is the dielectric permeability of the matrix, which is set to 2.25 (represents typical glass and polymers) for all the simulations below.

For solid spheroidal particles (**Figure 2.7(a)**), f is determined as 0.01 and the polarizability α is given by:

$$\alpha = \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_m + L(\varepsilon_p - \varepsilon_m)} \quad (2.9)$$

where ε_p is the dielectric function of the particles, and L is the corresponding factor of depolarization.

Especially for a random distribution of ellipsoidal particles (**Figure 2.7(b)**), α can be calculated as:

$$\alpha = \frac{1}{3} \sum_{i=1}^3 \frac{\varepsilon_p - \varepsilon_m}{\varepsilon_m + L_i(\varepsilon_p - \varepsilon_m)} \quad (2.10)$$

where L_i is the triplet of depolarization factor and must fulfill $\sum L_i = 1$. Both the major axis (a) and minor axis (c) have a direct effect on the value of L_i .

In the case of core-shell structure (**Figure 2.7(c)**), the polarizability is described as:

$$\alpha = 3 \frac{(\varepsilon_s - \varepsilon_m)(\varepsilon_c + 2\varepsilon_s) + \Omega(2\varepsilon_s + \varepsilon_m)(\varepsilon_c - \varepsilon_s)}{(\varepsilon_s + 2\varepsilon_m)(\varepsilon_c + 2\varepsilon_s) + \Omega(2\varepsilon_s - 2\varepsilon_m)(\varepsilon_c - \varepsilon_s)} \quad (2.11)$$

where ε_s and ε_c are the dielectric constants of nanosphere core (diameter x) and the shell (thickness t), respectively. Ω is the volumetric ratio between the inner core and the outer shell and it can be calculated as:

$$\Omega = \left(\frac{x}{2t+x}\right)^3 \quad (2.12)$$

Therefore, f is altered for the core-shell case as the following relationship with Ω :

$$f = \frac{0.01}{1-\Omega} \quad (2.13)$$

B. Simulations – the nanocomposites with embedded spheroidal nanoparticles: The thickness of composite is set to $5\ \mu\text{m}$ with $f=0.01$, which means that the effective thickness containing VO_2 -NP is $50\ \text{nm}$. **Figure 2.8(a)** and **2.8(b)** present the simulation data of spheroids oriented with their symmetry axes perpendicular to the substrate, while the results of randomly oriented nanoparticles are displayed in the **Figure 2.8(c)** and **2.8(d)**.^[62] The aspect ratio ranging from $0.1 < m < 10$ are investigated by the calculations using EMT. **Figure 2.8(a)** and **2.8(b)** implies that if the particles are oriented consistently, the $T(\lambda)$ increases with increasing the aspect ratio regardless of the phase structures of VO_2 . However, for randomly oriented particles (**Figure 2.8(c)** and **2.8(d)**), the highest $T(\lambda)$ can be achieved only when $m=1$ at both low- and high-temperature states. It is worth noting that the pronounced minima for the metallic VO_2 -NP (**Figure 2.8(b)** and **2.8(d)**) shifts from $\lambda \approx 1500\ \text{nm}$ to $\lambda \approx 1200\ \text{nm}$ with increasing m . The minimum of transmittance is dominated by surface plasma (SP) absorption and the corresponding wavelength to the SPs can be altered by varying the shape of the incorporated particles.^[62]

Figure 2.8 Simulated spectral transmittance of the spheroids with their symmetric axes perpendicular to the substrate at the low-temperature semiconducting state (a) and high-temperature metallic state (b), respectively; Simulated spectral transmittance of the randomly oriented spheroids at the semiconducting phase (c) and metallic phase (d), respectively. Reprinted with permission from Reference [62]. Copyright 2010, American Institute of Physics.

The typical thermochromic properties (T_{lum} and T_{sol}) of different types of VO₂ nanocomposites are summarized in **Figure 2.9(a)-2.9(d)** with the comparison of VO₂ continuous thin films (**Figure 2.9(e) and 2.9(f)**).^[62] Apparently, both T_{lum} and T_{sol} of nanocomposites are superior to those of the continuous films with 50 nm thickness. The oriented spheroids achieve the highest T_{lum} close to 80% upon $m=10$, which satisfy the major requirement for the applications of architectural windows. If the particles are randomly oriented, the spheres with $m=1$ present the best combination of T_{lum} (73% at the semiconducting state and 63% at the metallic state) and T_{sol} (73% at the semiconducting state and 56% at the metallic state). Meanwhile, the simulation outcomes imply that the spherical particles (*i.e.* $m=1$) has the potential to yield the largely enhanced ΔT_{sol} of 17% (vs. 7% for the continuous 50 nm VO₂ films) and provide high T_{lum} at the same time. This remarkable achievement makes VO₂ nanocomposites much closer to real life applications of smart glazing.

Figure 2.9 (a) and (b) are the integrated T_{lum} and T_{sol} of nanocomposites with oriented spheroids (the symmetric axes perpendicular to the substrate) as a function of different aspect ratios; (c) and (d) are the integrated T_{lum} and T_{sol} of nanocomposites with randomly oriented spheroids as a function of different aspect ratios; (e) and (f) are the integrated T_{lum} and T_{sol} of continuous thin films as a function of different thickness. Reprinted with permission from Reference [62]. Copyright 2010, American Institute of Physics.

C. Simulations – the nanocomposites with core-shell structured nanoparticles: For the calculations, the refractive index of the matrix is set to $n_m = \epsilon_m^{1/2} = 1.5$, appropriate for typical glass or polymer. The shells, comprising VO_2 , has its refractive index n_s equal to that expressed in **Figure 2.3(d)**.^[65] Similar to solid spheroids, $f=0.01$ and the medium thickness is $5\ \mu\text{m}$. Calculations are executed with varying the RI of core, n_c and changing ratio of x/t . For example, the computed spectral transmittance of $n_c = 1$ at both low-temperature semiconducting and high-temperature metallic states are exhibited in **Figure 2.10**.^[63] $T(\lambda)$ can be seen to decrease with increasing x/t ratio. The minima of $T(\lambda)$ reveals a red shift from around 1200 nm to 1500 nm when x/t increases from 0 to 20, indicating a damped SP resonance effect due to the conduction electrons in the metallic phase of VO_2 .^[63]

Figure 2.10 Spectral transmittance for core-shell structured VO_2 -NP ($n_c=1$) in a dielectric matrix (a) at the low-temperature semiconducting state and (b) at the high-temperature metallic phase. The inset in (a) shows the VO_2 core-shell structure for simulations. Adapted from Reference [63]. Copyright 2011, American Institute of Physics.

Figure 2.11 demonstrates the adverse effect of higher x/t ratio to T_{lum} and T_{sol} which becomes more pronounced with increasing n_c . The largest solar modulation is 20.9% (**Figure 2.11(e)**), which occurs for hollow nanospheres ($n_c=1$) with $x/t=10$, superior to the performance of solid nanospheres (*ca.* 17%). However, T_{lum} shows a concomitant decrease from 73% (solid) to 59% (hollow) at the semiconducting state and from 63% (solid) to 49% (hollow) at the metallic state.

Moreover, the inverted core-shell structures (VO₂ as the core and the dielectric material as the shell) were also investigated by S. Li *et al.*, illustrating the simulation results of the outmost shell with a refractive index ranging from 0 to 2.5 surrounding VO₂ core.^[63] However, besides improving the chemical stability of the VO₂ cores, the inverted design does not result in any remarkable enhancement for the solid nanoparticles.

Figure 2.11 Effect of x/t and n_c on the transmittance of the composites with core-shell nanospheres in the dielectric medium ($n_m = 1.5$). (a) and (b) reveal T_{lum} in the semiconducting and metallic state, respectively. (c) and (d) show T_{sol} in the semiconducting and metallic state, respectively. (e) displays the corresponding ΔT_{sol} obtained by subtracting (c) by (d). VO_2 serves as the material of shell and the refractive index of cores (n_c) are altered to 1, 1.5, 2 and 2.5. Reprinted with permission from Reference [63]. Copyright 2011, American Institute of Physics.

2.5.1.2 The applications of nanothermochromism

A. Pure VO_2 -nanoparticles embedded in the dielectric host: In the recent decade, plentiful methods for preparing fine crystallized VO_2 -nanoparticles have

been explored, and different size ranges of nanoparticles are dispersed in the organic host materials to implement the concept of “nanothermochromism” practically.^[66,67] The compositions and optical performances of the nanocomposites with pure VO₂-nanoparticles are summarized in **Table 2.1**.

Table 2. 1 Thermochromic properties of pure VO₂-nanoparticles dispersed in different dielectric matrix

Host material	Nanoparticle size (nm)	Composite thickness	$T_{lum(low)}$ (%)	$T_{lum(high)}$ (%)	ΔT_{sol} (%)
Polyurethane (PU) ^[66]	29-72 (solid-state reaction)	-	54.2	53.7	9
Polydime-thylsiloxane (PDMS) ^[67]	10-200 (thermolysis)	75 μ m	Averaged T_{lum} =50.7		12

N. Shen *et al.* used the solid-state reaction forms the aggregations of spherical VO₂-NP with the phase transition temperature τ_c ranged from 43.5 °C to 59.3 °C, which can be tuned by controlling the annealing temperature and annealing time.^[66] The reduction of τ_c may be due to the presence of amorphous VO₂ surrounding the crystallized phases. Meanwhile, the nanoparticles synthesized using this method exhibit better chemical stability (i.e., anti-oxidation and acid-resistance) than those prepared by the hydrothermal process. However, their best-performing composite only shows ΔT_{sol} of 9%, which is smaller than other contemporary results.

Alternatively, T. Moot *et al.* employed an elastomeric matrix, PDMS, to accommodate 10-200 nm VO₂-NP in the stretchable composite films.^[67] The effective amount of VO₂ grows proportionally with increasing film thickness, therefore, ΔT_{sol} is amplified from 0.97% to 11.9% by changing film thickness from 15 μ m to 75 μ m. Also, due to the elasticity, the film thickness can be easily thinned by stretching the films, which induces the formation of voids at the high-stress area and thus, facilitate a significant enhancement of T_{lum} from 45.6% to 55.4% (due to

the introduction of a lower RI material) as well as a slight promotion of ΔT_{sol} from 7.6% to 8.1% (due to the blue-shift of plasma resonance spectral position).

B. Doped VO₂-nanoparticles embedded in the dielectric host: The primary reason for doping other elements into VO₂-NP is to reduce τ_c from *ca.* 70 °C to around room temperature. Upon substituting V atoms with F, Mg, W or Zr atoms,^[51,57,68,69] both VO₂(M) and VO₂(R) lattice structures are distorted due to the structural defects brought by the dopants. As increasing the doping level, the structural difference between high-temperature and low-temperature states is diminished, which, in turn, leads to the reduction of the latent energy of VO₂ phase transition, therefore resulting in the decrease of τ_c .^[57] The corresponding thermochromic properties of doped-VO₂ nanocomposite films are categorized in **Table 2.2** according to the types of doping materials and doping levels.

As indicated by the doping effects of F, Mg, Zr and W+Zr, the increment of dopant concentration usually deteriorates ΔT_{sol} due to the appearance of lattice defects and morphological changes in the nanoparticles.^[57] Except for Mg and W+Zr dopants, T_{lum} can be fairly maintained by F-doping^[68] or slightly increased by introducing Zr^[69] into VO₂ lattice. Among all the dopants shown in **Table 2.2**, F^[68] and W+Zr^[69] reveal the strong competency for lowering τ_c to a comfortable temperature at 35 °C and 29 °C, respectively, but large reduction of τ_c requires high doping level at the cost of weakening thermochromic performances.

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Table 2. 2 Optical properties and phase transition temperatures of doped VO₂-nanoparticles dispersed in the polymer host

Host material	Dopant	$T_{lum(low)}$ (%)	$T_{lum(high)}$ (%)	ΔT_{sol} (%)	τ_c (°C)	Doping level (at%)
PU	F ^[68]	47.5	46.3	12	65	0.37
		48.7	45.9	11	35	2.93
	Mg ^[57]	54.2	51.8	11	61	3.8
		50.4	50.1	6	54	7.0
	Zr ^[69]	Averaged T_{lum} =56		15	66	4.2
		Averaged T_{lum} =60		14	64	9.8
	W+Zr ^[69]	58.4	54.3	12	56	0.6W+8.5Zr
		48.6	46.5	5	29	2.4W+8.5Zr
	W ^[51]	Averaged T_{lum} =56		13	46	1.0
	Ti ^[70]	Averaged T_{lum} =53		17	67	1.1
	W ^[50] (in Sb:SnO ₂ /PU)	53.0	49.8	12	-	-
	elemental impurities* ^[51]	45.6	40.0	22	abnormal phase transition	

* Elemental impurities are introduced by stainless steel reactor.

The superior nanothermochromic properties can also be obtained by embedding doped VO₂-NP into the PU matrix. Although Ti-doping fails to reduce τ_c , 1.1 at% Ti achieves the simultaneous improvement of T_{lum} (from 46% un-doped to 53% doped) and ΔT_{sol} (from 13% un-doped to 17% doped).^[70] However, further increasing the doping level of Ti does not benefit more on the thermochromic properties. Furthermore, Z. Chen *et al.* realized that the elemental impurities, i.e., Cr, Fe, Ni, Mg, Si, and W, might be implanted during the hydrothermal synthesis process due to the utilization of stainless steel reactors.^[51] The contaminated VO₂-NP exhibit abnormal phase transitions, which indicate multiple endothermic and exothermic peaks upon heating (**Figure 2.12(a)**) and cooling (**Figure 2.12(b)**). Based on the combination consequence of doping, defects, size effect, *etc.*, the nanocomposite films, comprising VO₂-NP with various elemental impurities, reveal the remarkable ΔT_{sol} of 22% combined with acceptable T_{lum} of 45.6% at low temperature and 40.0% at high temperature.^[51]

Figure 2.12 DSC of VO₂-NP prepared by hydrothermal method at different temperatures: (a) heating progress, (b) cooling progress. Reprinted with permission from Reference ^[51]. Copyright 2014, The Royal Society of Chemistry.

Doping can affect not only thermochromic properties of VO₂-NP but also the color of VO₂-based nanocomposite foils (**Figure 2.13**). This phenomenon is because the doping widens the band gap of VO₂, inducing a blue-shift of absorption edge which is the cause of lightening the original brownish-yellow color to yellowish fading.^[57,68,69]

Figure 2.13 Optical images of doped VO₂-NP embedded in PU matrix with different doping levels. (a) and (b) are reproduced with permission from Reference ^[68] and ^[57], respectively. Copyright 2013, the Owner Societies. (c) is reproduced with permission from Reference ^[69]. Copyright 2014, The Royal Society of Chemistry.

C. Core-shell structured VO₂-nanoparticles embedded in the dielectric host:

The motivation for employing core-shell structure is to protect VO₂-NP from oxidation and maintain the outstanding “nanothermochromism” properties. The coating shell using SiO₂ serves as a barrier layer for oxygen diffusion, preventing thermodynamically unstable VO₂ from being oxidized to V₂O₅ or other oxidation states.^[71] Also, SiO₂ is stable in the acid condition (pH=1) and thereby the shell ensures the encapsulated VO₂ core with a better chemical stability than those uncoated nanoparticles.^[71] **Table 2.3** indicates the typical thermochromic properties of VO₂@SiO₂ in PU nanocomposites.

Table 2.3 Nanothermochromism of core-shell structured VO₂-based nanocomposites

Host material	Core-shell structure	$T_{lum(low)}$ (%)	$T_{lum(high)}$ (%)	ΔT_{sol} (%)	τ_c (°C)	Remarks
PU	VO ₂ @SiO ₂ ^[71]	29.2	26.3	14	56	Un-doped
	V _x W _{1-x} O ₂ @SiO ₂ ^[72]	52.2	48.3	17	40	2 at% W-doped
		50.6	47.5	15	25	3 at% W-doped

Recently, J. Zhu *et al.* demonstrated a systematic work to study the criteria for simultaneously succeeding in high T_{lum} , large ΔT_{sol} , comfortable τ_c and excellent oxidation resistance. Based on four-flux theory, they pointed that in practice, small particle size (*ca.* 20 nm), good crystallinity and well-dispersed composite solution are essential to achieving the outstanding nanothermochromism.^[72] Additionally, W-doped core-shell structure is involved in meeting the practical requirements for building windows in the real world. The promising results (as displayed in **Table 2.3**) of V_xW_{1-x}O₂@SiO₂ nanocomposites can achieve T_{lum} of 50.6% at 20 °C and 47.5% at 90 °C as well as ΔT_{sol} of 15% when 3 at% W is doped into VO₂-NP, which are encapsulated by SiO₂ shell to ensure the excellence of weather-ability.

2.5.2 Nanoporous films

Back in 2007, P. Jin has reported the effect of pores on upgrading the overall

solar modulation performance of the VO₂-coated glass.^[73] The voids, containing air with $n=1$, were introduced in-situ during synthesizing the VO₂ thin films via reactive RF sputtering.^[73] The mobility of the sputtered particles reaching the substrate controls the structure of the sputtered film (porosity) *via* adjusting the substrate temperature, the sputtering pressure or the substrate bias.^[74] The air pores, as a secondary component incorporated with the VO₂ films, allow to improve the light modulating performance through moderating the overall refractive index of the films (n_{film}), which can be roughly calculated based on the linear approximation method with the simplified form as shown below.

$$n_{film} = \sum f_i n_i \quad (2.14)$$

where f_i and n_i are the volume fraction and RI of each component, respectively.

It is worth to notice that **Figure 2.14(a)** and **2.14(b)** can be more intuitively compared by matching the mass thickness. That is to say that the thickness of the VO₂ thin film containing 50% porosity is exactly half of the value of the pure VO₂ containing no voids. Specifically, in the VO₂ film having a thickness of 50 nm free of voids (**Figure 2.14(b)**), the T_{lum} of the low-temperature semiconducting phase is 32%, while the same parameter is amplified to 52% when the film adopts 50% volume of pores (**Figure 2.14(a)**). Likewise, the ΔT_{lum} and ΔT_{sol} in the 50% VO₂ porous structure (the shaded areas in the **Figure 2.14(a)**) is found to be much higher than the modulation abilities of the pure thermochromic film containing no voids (the shaded areas in the **Figure 2.14(b)**).^[73]

Figure 2.14 Integrated transmittances and luminous/solar modulation abilities as a function of (a) the thickness of VO₂ (50 vol%)+Air (50 vol%) deposited on glass, or (b) the thickness of pure VO₂ deposited on glass. Reproduced with permission from Reference [73]. Copyright 2007, Japanese Patent 2007171759A.

L. Kang *et al.* has also confirmed the similar porosity effect based on both optical simulations and experiments.^[75] They use the optical admittance recursion to simulate the results of both T_{lum} and ΔT_{sol} under the different conditions of porosity and film thickness. As revealed by **Figure 2.15(a)**, theoretically, the enhanced ΔT_{sol} (solid black lines) can be achieved without significantly deteriorating T_{lum} (dash-dotted red lines) due to the effective reduction of Fresnel reflection by introducing voids. In practice, the nanopores are formed with the utilization of polyvinylpyrrolidone (PVP) in the VOCl₂ aqueous solutions and the VO₂-based nanoporous structures are finally materialized (as demonstrated in **Figure 2.15(b)**) by post-annealing with a N₂ atmosphere at 500 °C for 1 h. The 102 nm thick film with the averaged nanopore size of *ca.* 28 nm uncovers the optimal outcomes as $T_{lum(low)}=43.3\%$, $T_{lum(high)}=39.9\%$ and $\Delta T_{sol}=14.1\%$.

Figure 2.15 (a) Simulated T_{lum} at low-temperature semiconducting state (dash-dotted red lines) and ΔT_{sol} (solid black lines) as a function of porosity and thickness of the VO_2 -based nanoporous films, respectively. (b) SEM image of 147 nm thick VO_2 nanoporous films deposited on the fused silica substrates. The inset shows the cross-section of the deposits. Reproduced with permission from Reference ^[75]. Copyright 2011, American Chemical Society.

The precursors showing the self-assembly ability, such as cetyltrimethylammonium vanadate (CTAV), has proved the possibility of the fabrication of VO_2 -based nanoporous structures.^[76] The organic carbon chains are burnt out at 500 °C in air and the crystallized VO_2 films are formed based on the reduction of V_2O_5 by the H_2/Ar gas. Dip-coating speed controls the film nanostructures, which are distinct from those prepared by the polymer-assisted deposition method. These films presents a facile micro (size of 20-50 μm as displayed in **Figure 2.16(a)**)/nano (size of 100-500 nm referring to **Figure 2.16(b)**) hierarchical porous structure, which forms a “light-leak” template and facilitates to attain largely enhanced T_{lum} (*ca.* 25% improvement as compared with VO_2 solid films in the similar thickness).

Figure 2.16 (a) Low magnification SEM image of CTAV-based VO₂ films with micropores. (b) High magnification SEM zoom-in image of part of (a) shows the encapsulated nanopores. Reprinted with permission from Reference [76]. Copyright 2013, American Chemical Society.

Figure 2.17 Schematic illustrations of the process for preparing the control films and VO₂-based nanoporous films via evaporation and lyophilization, respectively. Reprinted with permission from Reference [77]. Copyright 2014, American Chemical Society.

So far, the best combination of thermochromic properties is pronounced by X. Cao *et al.* The nanoporous VO₂ films are prepared by lyophilization, also known as the freeze-drying method. As illustrated in **Figure 2.17**, the sol-gel based VO₂²⁺ precursor is frozen at low temperature and low pressure to remove the solvent via sublimation, while the normal solvent evaporation process causes the formation of continuous films.^[77] **Figure 2.18** evidences that the lower temperature leads to the higher porosity, which is the key factor to induce the remarkable thermochromic performance of $T_{\text{lum(avg)}}=50\%$ and $\Delta T_{\text{sol}}=14.7\%$.

Figure 2.18 SEM images of (a) control film (evaporation), (b) and (c) freeze-dried sample with pre-freezing at $-20\text{ }^{\circ}\text{C}$ and $-30\text{ }^{\circ}\text{C}$, respectively. Reproduced with permission from Reference [77]. Copyright 2014, American Chemical Society.

2.5.3 Nano-patterning structures

The biomimetic nano-patterned VO_2 films are bioinspired by the nature of moth-eye (**Figure 2.19(a)**), which offers the wide-angle anti-reflection (AR) effect attributed to the highly compact and periodically tapered nanostructure (**Figure 2.19(b)**).^[78] The mechanism of “moth-eye” AR is schematically illustrated in **Figure 2.19(c)**, which indicate that the sub-wavelength nanocone structuring smoothens the discrepancy between n_{air} and n_{film} gradually by means of creating a RI gradient^[78] from air to the substrates, resulting in diminishing of Fresnel reflection.

Figure 2.19 (a) High resolution optical picture of the moth eyes; (b) SEM image reveals the periodically tapered nanostructures of the moth-eye; Reprinted with permission from

Reference ^[78]. Copyright 2011, The Royal Society of Chemistry. (c) illustrate the AR effect brought by the sub-wavelength nanostructures.

In 2013, A. Taylor *et al.* reported a series of simulation findings of incorporating the “moth-eye” AR effect with VO₂ thermochromic properties.^[32] A conformal layer of VO₂ is coated on the array of silica nano-cones, which is locally distributed in a hexagonal arrangement (**Figure 2.20(a)-2.20(c)**). The base-width (W) is designed with the principle $W = P\sqrt{\frac{4}{3}} - 2C$, so as to maximize the area density of air/VO₂ interfaces, where P and C denote as the pitch size (periodicity) and the thickness of VO₂ coatings, respectively (**Figure 2.20(a)**). To examine the AR efficiency, the height of the nano-cone structure is designed within the range of 250 nm to 1200 nm and the pitch size is limited to *ca.* 130 nm to circumvent the height difference to be resolved by the incident light (up to 42 ° incident angle). The parameter optimization is done by finite difference time domain (FDTD) simulation method, which infers that increasing the aspect ratio of the nanostructure tends to attain the outstanding ΔT_{sol} . Therefore, the highest aspect ratio of height=1150 nm and base-width=132 nm is employed to achieve the largest ΔT_{sol} of 23.1% together with $T_{\text{lum(avg)}}$ of 36.5%, while the outstanding $T_{\text{lum(avg)}}$ of *ca.* 68.5% is obtained with ΔT_{sol} of 15.5% when the height=500 nm and the base-width=135 nm.

Figure 2. 20 Cross-section (a), top (b) and three-dimensional (c) views of the biomimetic paraboloid cones in a local hexagonal arrangement. W , P , C and H are denoted as the base-

width, the pitch size, the coating thickness and the height difference, respectively. Reprinted with permission from [32]. Copyright 2013, Optical Society of America.

X. Qian *et al.* has embodied the VO₂-coated “moth-eye” nano-patterning structures in practice (**Figure 2.21(a)**),^[79] where the fused silica nanocone array template is prepared by sacrificing the densely packed polystyrene (PS) spheres using the reactive ion etching (RIE) method. The size of PS spheres controls the periodicity (**Figure 2.21(b)**), which should be smaller than a given wavelength to avoid the resolution issue of incident light. Besides the effective AR effect from the gradient RI, they emphasize that the smallest periodicity of 210 nm leads to the largest enhancement of $T_{\text{lum(avg)}}$ from 40.5% (planar VO₂ film) to 44.5% (**Figure 2.21(c)**) and the most obvious increment of ΔT_{sol} from 5.7% (planar VO₂ film) to 7.1% (**Figure 2.21(d)**). However, the ΔT_{sol} is still insufficient (*ca.* 7%) for the practical application of VO₂-based thermochromic smart windows.

Figure 2.21 (a) Cross-sectional atomic force microscopy (AFM) profile for the samples with different periodicity. (b) Cross-sectional SEM image of the sample with 210 nm

periodicity. (c) and (d) summarize the typical thermochromic properties of VO₂@SiO₂ nanocone structures with different periodicity as compared with the planar VO₂ films. Reproduced with permission from Reference ^[79]. Copyright 2014, American Chemical Society.

Besides the VO₂-coated “moth-eye” nanostructure, M. Zhou *et al.* first introduce the periodically ordered pores in the thermochromic VO₂ films by utilizing the colloidal lithography approach.^[80] The array of PS spheres serves as the template to create the patterned pores when PS spheres are burnt out during pyrolysis. Prior to thermal annealing, the template is immersed into V⁴⁺ precursor (VOSO₄ and NH₄HCO₃ solutions in sequence) with controlled concentrations, so as to synthesize a monolayer of VO₂(M) films with different patterned morphologies (**Figure 2.22(a)-2.22(c)**). The immersing/annealing process is repeated for a few times to obtain the multi-layer structure with the controllable space volume of VO₂. The results imply a proportional relationship between the number of layer and ΔT_{sol} when the number of patterned layers increases from 1 ($\Delta T_{\text{sol}}=3.2\%$) to 3 ($\Delta T_{\text{sol}}=7.9\%$). However, similar to the experimental results of the nanocones patterning, the periodic porous structure is unable to meet the requirement of real-life smart window applications, which ΔT_{sol} should not be smaller than 10%.

Figure 2.22 SEM images of morphology variation of periodic porous VO₂(M) films prepared with different precursor concentration: (a) 5 mmol L⁻¹, (b) 10 mmol L⁻¹ and (c) 15 mmol L⁻¹. (d) Corresponding optical performance of samples (a)-(c). Reprinted with permission from Reference [80]. Copyright 2013, The Royal Society of Chemistry.

2.5.4 Anti-reflection coatings

Optical reflection, also known as Fresnel reflection, is a fundamental phenomenon that happens when light propagates across an interface between two media with different RI. Based on **Equation 2.7**, the excessive reflection causes a loss of transmittance. For the reduction of Fresnel reflection, two approaches are employed: [81] a) the inhomogeneous layers: the smooth transition of RI from air to substrate (*e.g.*, the biomimetic moth-eye nanostructure); b) the interference-type multiple layer stack: introducing the additional dielectric films with the moderate RI (*i.e.*, ARC). The method a) has been discussed in details in Section 2.5.3. In this section, the development of the ARC-coated VO₂ films in the recent thirty years is discussed in the aspects of the fundamental theories and the AR effects on the thermochromic properties.

2.5.4.1 Determination of optical constants

The calculations of optical constants possess fundamental and technological significance, because the outcomes deliver the key parameters for the design and modeling of optical components. From the transmittance spectra of a transparent coating on a non-absorbing (or weakly absorbing) substrate, n (RI) and k (extinction coefficient) can be accurately determined using the envelop method derived by J. C. Manifacier *et al.*^[82] and Swanepoel.^[83]

The value of n at the different wavelength can be determined by using the envelop method curve with the adjacent transmittance maxima (T_M) and minima (T_m), as shown in the following equations:

$$n = \sqrt{N + \sqrt{N^2 - n_s^2}} \quad (2.15)$$

where N is defined as

$$N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2} \quad (2.16)$$

where n_s is the RI of the substrate. (in this thesis, $n_s=1.46$ for fused silica)

The value of k can be calculated from the empirical formula:

$$k = \frac{\alpha \lambda}{4\pi} \quad (2.17)$$

where λ is the wavelength and α is the absorption coefficient and defined as:

$$\alpha = -\frac{1}{t} \ln A \quad (2.18)$$

where t is the film thickness which can be measured and

$$A = \frac{P + \sqrt{P^2 + 2QT_\alpha(1 - R_2R_3)}}{Q} \quad (2.19)$$

where

$$P = (R_1 - 1)(R_2 - 1)(R_3 - 1) \quad (2.20)$$

$$Q = 2T_\alpha(R_1R_2 - R_1R_3 - 2R_1R_2R_3) \quad (2.21)$$

where R_1 , R_2 , and R_3 is the reflectance of at the interfaces of air-film, film-substrate, and substrate-air, respectively.

$$R_1 = \left[\frac{1-n}{1+n} \right]^2 \quad (2.22)$$

$$R_2 = \left[\frac{n-n_s}{n+n_s} \right]^2 \quad (2.23)$$

$$R_3 = \left[\frac{n_s-1}{n_s+1} \right]^2 \quad (2.24)$$

$$T_\alpha = \sqrt{T_M T_m} \quad (2.25)$$

2.5.4.2 Effect of refractive index

The AR effect brought by the intermediate coating is predominately dependent on the coating's RI, as long as the coating is much thicker than a wavelength of light (also known as “thick-film effect”).^[84] In the experiments conducted in this thesis, the ARC thickness is about a micrometer. Therefore, the effect of RI on decreasing the Fresnel reflection is investigated in the optical design, targeting to achieve high transmittance for VO₂-based smart windows.

Based on the simplified form of Fresnel equation, the reflectance (R) can be deduced as a function of the RI-substrate (n_s) and RI-coating (n_c)^[85] according to the following equation:

$$R = \frac{(n_s - n_c)^2}{(n_s + n_c)^2} \quad (2.26)$$

Therefore, high reflection may be theoretically reduced to the minimum by adopting a specific ARC layer on top of the VO₂ substrates, if n_{ARC} could be tuned to the vicinity of $\sqrt{n_{VO_2}}$ (as shown in **Figure 2.23**).

Figure 2.23 Spectral RI of continuous VO₂ thin films (from Reference [65]) at both low (solid black line) and high (solid red line) temperature with the corresponding square root values (dashed lines) are shown in the λ range of 250-2500 nm.

2.5.4.3 The application of ARC on VO₂-based films

ARC has been of interest for research for boosting the thermochromic performance of the underlying VO₂-based substrates. Many types of the dielectric materials can be applied as either the single-layer or multi-stacking ARC for VO₂ with using different deposition techniques. ARC also exhibit the ability to protect the thermodynamically-unstable VO₂ from oxidation, which is normally caused by the exposure to the humid air or high temperature.^[86]

A. Single-layer ARC (ARC/VO₂): Back in 1987, the studies that reported by S. M. Babulanam *et al.* proposed the idea of applying a single-layer ARC on top of VO₂ continuous thin films.^[30] **Figure 2.24** demonstrates that he used a 100 nm thick SiO₂ overcoat (prepared using reactive RF magnetron sputtering) to enhance the $T_{lum(avg)}$ of an 85 nm VO₂ film from 39% to 45%. However, at the same time, the SiO₂ ARC undesirably blocks the near-IR transmittance at the low-temperature semiconducting phase of VO₂ (as indicated in **Figure 2.24(a)**). This causes the nearly complete loss of ΔT_{sol} .^[30]

Figure 2. 24 Comparison of the spectral transmittance of coating a 100 nm SiO₂ ARC on an 85 nm VO₂ thin film (solid line), uncoated VO₂ on glass substrate (dashed line) and bare glass (dotted line): (a) at the low-temperature (Temp=20 °C < τ_c) semiconducting state; (b) at the high-temperature (Temp=85 °C < τ_c) metallic state. Reproduced with permission from Reference [30]. Copyright 1987, Elsevier Science Publishers B.V.

In the recent couple decades, various ARC materials have been laminated as a single top layer on the continuous VO₂ thin films to acquire high $T_{lum(avg)}$ and ΔT_{sol} as summarized in **Table 2.4**. TiO₂ is used as a multifunctional ARC in the double-layered film structure (i.e., ARC/VO₂) by P. Jin *et al.* TiO₂ not only shows both increments in T_{lum} and ΔT_{sol} but also reveal the capability of photocatalysis and UV-stopping.^[10] Based on a survey of the ARC candidates' RI, ZrO₂ ($n \approx 2.2$) matches the optimal outcomes of the optical calculations carried out by G. Xu *et al.* ZrO₂ ARC contributes only the improvement of T_{lum} , in turn, it depresses the transmittance contrast at 2000 nm as referring to **Table 2.4** and **Figure 2.25(b)**.^[87] CeO₂ is also considered by H. Koo *et al.* due to its high refractive index.^[88] Likewise, prior to experimental processing, optical calculations are performed using transfer-matrix method. The largest ΔT_{sol} of 15.3% can be achieved by pulse laser depositing a layer of 150 nm CeO₂ ARC on the 89 nm VO₂ thin film substrate, but it retards the enhancement of T_{lum} . Nevertheless, the aforementioned studies operate the expensive deposition methods that are not suitable for mass production. In 2011, Z. Chen *et al.* fabricated SiO₂/VO₂ and TiO₂/VO₂ bilayers using low cost

sol-gel method. With spectral simulations and film optimizations, the rutile TiO_2/VO_2 reveals slightly larger ΔT_{sol} enhancement but smaller AR effect on improving T_{lum} as compared with SiO_2/VO_2 .^[44]

Table 2. 4 Recent studies of single-layer ARC on the continuous VO_2 thin films

Single-layer ARC	Deposition techniques		$T_{\text{lum(avg)}} (\%)$		$\Delta T_{\text{sol}} (\%)$		T% contrast* @ 2000 nm (%)	
	VO_2 film	ARC	w/o ARC	w/ ARC	w/o ARC	w/ ARC	w/o ARC	w/ ARC
TiO_2/VO_2 (2002) ^[10]	RF-sputtering	RF-sputtering	32	47 ↑	4.4	7.0 ↑	53	39 ↓
ZrO_2/VO_2 (2004) ^[87]	RF-sputtering	RF-sputtering	32	51 ↑	-	-	45	39 ↓
SiO_2/VO_2 (2011) ^[44]	Sol-gel and post-annealing	Sol-gel	40	51 ↑	5.9	7.2 ↑	54	48 ↓
TiO_2/VO_2 (2011) ^[44]	Sol-gel and post-annealing	Sol-gel	42	47 ↑	13.2	15.1 ↑	56	46 ↓
CeO_2/VO_2 (2013) ^[88]	Pulse Laser Deposition	Pulse Laser Deposition	30	31 ↑	11.6	15.3 ↑	48	46 ↓

* Note: T% contrast indicates the absolute difference between low temperature (*ca.* 20°C) and high temperature (80-90°C) spectral transmittance at $\lambda=2000$ nm.

Figure 2. 25 (a) Spectral transmittance and (b) hysteresis loop (showing the transmittance @ $\lambda=2000$ nm when the temperature changes reversely from 20 to 80 °C) of VO_2 films deposited on SiO_2 substrate with (solid line) and without (dashed line) a single layer of ZrO_2 ARC. Reproduced with permission from ^[87]. Copyright 2004, Elsevier B.V.

B. Alternative multi-stacking ARC (ARC/VO₂/ARC or ARC/VO₂/ARC/VO₂/ARC): P. Jin *et al.* managed to manufacture the TiO₂/VO₂/TiO₂ three-layer films by making a good use of RF-sputtering.^[89] As tabulated in **Table 2.5**, T_{lum} rises from 31% to 56% at the detriment of ΔT_{sol} , which drops from 3.9% to 2.9%. In the same way, the alternative triple layers α -SiO_x/VO₂/ α -SiO_x causes the undesirably large decrease of ΔT_{sol} from 6.5% to 4.5%, when it marginally elevates T_{lum} from 31% to 35%.^[90] In 2009, N. R. Mlyuka *et al.* presented their work on producing both a three-layer structure of TiO₂/VO₂/TiO₂ (different deposition method involved as compared with P. Jin's work in 2003) and a novel five-stack TiO₂/VO₂/TiO₂/VO₂/TiO₂ films.^[11] The five-layer film structure evidences its distinguishable advantage on doubling ΔT_{sol} , but it requires the repetitive manufacturing procedures and complex control of processing parameters. Thereby, there is no further development of multi-stacking VO₂-based film structures in the recent years of research.

Table 2. 5 Recent studies of multi-layer ARC on the continuous VO₂ thin films

Multi-layered Films with ARCs	Fabrication techniques		$T_{lum(avg)}$ (%)		ΔT_{sol} (%)		T% contrast* @ 2000nm (%)	
	VO ₂ film	ARC	w/o ARC	w/ ARC	w/o ARC	w/ ARC	w/o ARC	w/ ARC
TiO ₂ /VO ₂ /TiO ₂ (2003) ^[89]	RF- sputtering	RF- sputtering	31	56 ↑	3.9	2.9 ↓	51	36 ↓
α -SiO _x /VO ₂ / α - SiO _x where $x = 0.3$ (2008) ^[90]	RF- sputtering	RF- sputtering	31	35 ↑	6.5	4.5 ↓	43	20 ↓
TiO ₂ /VO ₂ /TiO ₂ (2009) ^[11]	Reactive DC Magnetron Sputtering	Reactive DC Magnetron Sputtering	44	60 ↑	4.5	6.0 ↑	47	26 ↓
TiO ₂ /VO ₂ /TiO ₂ / VO ₂ /TiO ₂ (2009) ^[11]	Reactive DC Magnetron Sputtering	Reactive DC Magnetron Sputtering	41	44 ↑	6.7	12.1 ↑	39	38 ↓

* Note: T% contrast indicates the absolute difference between low temperature (*ca.* 20°C) and high temperature (80-90°C) spectral transmittance at $\lambda=2000$ nm.

2.6 Question Raised from pure VO₂-nanoparticles based nanocomposites

S. Li *et al.* propose “nanothermochromism” to tackle the intrinsic issues of VO₂ continuous thin films, namely insufficient T_{lum} and ΔT_{sol} . The simulated results suggest that dispersing spheroidal VO₂-NP in a dielectric host can offer almost doubled T_{lum} and the largely enhanced ΔT_{sol} simultaneously. Therefore, N. Shen *et al.* and T. Moot *et al.* synthesized highly crystallized VO₂-NP and embedded them as nanofillers into the PU or PDMS polymer matrix.^[66,67] However, none of these pure VO₂-NP based nanocomposites could provide the remarkably high $T_{lum}>60\%$ together with large $\Delta T_{sol}>10\%$ to satisfy the modern architectural glazing requirements.^[91]

Moreover, in the aspect of VO₂-NP synthesis methods, most of the contemporary fabrications involve thermolysis^[52–55] and hydrothermal techniques,^[56–60] which requires a constant supply of heating energy and incurs a high risk of danger during the processing due to high temperature (in the furnace) and high pressure (in the autoclave). Thermolysis needs the complex control of annealing conditions and may release green-house gasses to the environment. Also, it is difficult to control the shape of VO₂ nanocrystals if using the hydrothermal method, which usually produces the rod-like or asterisk-shaped VO₂ products. The yield-to-cost ratios of both common approaches are restricted due to the costly equipment requirement, the complex precursor preparation and the size of the “baking” crucible or the autoclave. Therefore, it is necessary to figure a straightforward manufacturing process to produce the fine crystalline VO₂-NP without the rigorous requisites of processing conditions.

2.7 Questions Raised from The Biomimetic “Moth-eye” Structures

Although the biomimetic moth-eye structures show the potential to significantly enhance $T_{lum(avg)}$, the design requires the high aspect ratio of the periodic nanocone structures to enlarge the area density of air/VO₂ interface and

ensure the spatial volume of VO₂ for acquiring high ΔT_{sol} . For example, as simulated by A. Taylor *et al.*, the most pronounced T_{lum} (ca. 70%) can be achieved with $\Delta T_{\text{sol}}=15.5\%$ only if the height of nanocones is 500 nm and the base-width is limited around 130 nm (due to the restriction of pitch size).^[32] However, there is no physical implementation that could obtain the tapered nanostructures with such an extreme high aspect ratio, which challenges the modern technologies of nano-fabrication. Also, the template with nanocone arrays becomes more and more fragile since the tip is sharpened with increasing the aspect ratio. Hence, so far, there is only one physical embodiment of this biomimetic “moth-eye” idea, while the $T_{\text{lum(avg)}}$ and ΔT_{sol} are only 45% and 7.1%, respectively, which is still a distance from the optimal simulation results.^[79]

2.8 Questions Raised from Depositions of VO₂-patterning Nanostructures

To the best of the author’s knowledge, there are only two previous studies reporting on the deposition methods of VO₂-patterning nanostructures prior to the author’s work: 1) VO₂-coated “moth-eye” nanostructure by X. Qian *et al.* and 2) periodic porous VO₂ films by M. Zhou *et al.* Both of them employ PS spheres as the templates and have to operate the post-annealing process to crystallize VO₂(M) from aqueous V⁴⁺ precursors as well as burn out the PS spheres to form vacancies. Nevertheless, the shape and dimension of the patterning are passively determined by the size of PS spheres, and the concentration of precursor affects the crystallinity and the distribution of the VO₂ nanostructures. The post-annealing process makes the deposition on the low-temperature-endurance substrate inapplicable. Also, in order to increase the film thickness with controllable layers, the immersing-annealing procedures has to be repeated for 3 times or more to obtain the maximum but still not significant ΔT_{sol} around 8%. Therefore, a new deposition concept is wanted to realize the direct deposition of VO₂-NP (no heating involved) with the active controls of line-width, thickness and FF, etc.

2.9 Question Raised from Single-layer ARC on VO₂ Substrates

All aforementioned ARC materials successfully present their advantages on improving T_{lum} or ΔT_{sol} of continuous VO₂ thin films, but only at the cost of diminishing transmittance contrast at $\lambda=2000$ nm. According to our previous work,^[92] heating Si-Al gel based ARC at 100 °C acquires the noticeable enhancements of T_{lum} from 44% to 48% and ΔT_{sol} from 6.0% to 7.7%. In addition, the transmittance contrast at $\lambda=2000$ nm is well-maintained, with the discernible marginal increment from 14% to 18%. Thus, Si-Al gel could be an optimum choice of single layer ARC. Besides Si-Al gel, in the previous study, the sol-gel based TEOS ARC also give rise to ca. 14% enhancement of T_{lum} and act as an anti-oxidation layer to protect the underlying VO₂ films from the harsh ambient conditions.

Moreover, there is no ARC design aiming to solve the intrinsic issue of VO₂, which VO₂ has the unwanted high RI in the low-temperature semiconducting phase, causing high Fresnel reflection at the cold state and ultimately depressing ΔT_{sol} due to $\Delta T_{\text{sol}} = T_{\text{sol}(\text{low})} - T_{\text{sol}(\text{high})}$. Therefore, based on the theory illustrated in Section 2.5.4.2, designing an ARC with the RI close to $\sqrt{n_{\text{VO}_2(\text{low})}}$ may significantly lessen the reflection at low temperature and improve ΔT_{sol} .

Furthermore, all the previous studies experience the ARC materials selection *via* examining the RI of different dielectric candidates. There is no research considering the tunability of the RI in one ARC material. The RI-tunable overcoat might be able to apply to different types of VO₂ substrate or different optical devices with distinct RI requirements.

2.10 Ph.D. in The Context of Literature

Firstly, a scalable approach for preparing pure VO₂-NP based thermochromic nanocomposites is considered with the mechanically grounded

VO₂-NP homogeneously dispersed in a transparent silica-alumina (Si-Al) gel. The VO₂ solid content and composite thickness is investigated to optimize the combination of T_{lum} and ΔT_{sol} .

Secondly, the RI-tunable sol-gel based ARC are carefully designed to offer more AR effect at the VO₂ low-temperature condition (*i.e.* increasing more $T_{\text{lum(low)}}$ than $T_{\text{lum(high)}}$), thereby maximizing ΔT_{sol} for various VO₂ substrates, e.g., continuous films, nanocomposites and periodic micro-patterning films. The RI tunability circumvents the complex materials selection and optical design and paves the way for practical applications of VO₂-based smart windows.

Furthermore, the Ph.D. studies also initiate a new VO₂-based “nanogrid” concept by the assistance of FDTD simulations. The nanogrid structures physically allow more short-wavelength visible light to pass through the holes, while retaining the advantages of long-wavelength NIR modulating abilities of VO₂. The dimension and shape of the nanostructure, as well as the periodicity and film thickness are taken into optimization for winning both high T_{lum} and remarkable ΔT_{sol} simultaneously.

Lastly, the VO₂ grid-patterning concept can be experimentally realized in the micro-scale by utilizing the newly innovated electrodeposition method, which is based on altering the ionic strength on the electrode surface, causing the irreversible VO₂-NP deposition without occurring the reduction-oxidation (red-ox) reactions. The new electrochemical implementation is straightforward, clean and low-cost, and it offers the active controls of line-width, the thickness of deposits and FF via regulating the applied electrical potential and deposition time.

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Chapter 3

Experimental Methodology

The precursors and preparation methods for vanadium dioxide (VO_2) nanomaterials were presented, also the basic principles of the chosen methods. Followed are the techniques that used for the characterization of the prepared VO_2 nanomaterials, including AFM, SEM, TEM, UV-Vis-NIR spectroscopy, XPS, XRD, DLS, adhesion test, etc. Detailed principles of these techniques are illustrated. These techniques cover the morphology, size, distribution, thickness, adhesion, elemental composition, thermochromic properties of VO_2 nanomaterials. Simulations based on the Finite Difference Time Domain (FDTD) method were developed to achieve high T_{lum} while maintaining large ΔT_{sol} of VO_2 -based “nanogrids”.

3.1 Rationale for selections of materials, synthesis and characterization

3.1.1 Materials

3.1.1.1 Precursors for VO₂(M) synthesis

In general, the chemical precursors for synthesizing the monoclinic phase vanadium dioxide (VO₂(M)) materials include metal oxide^[1]/ alkoxide^[2]/ inorganic salts^[3] as well as the V^{IV} precursors, *e.g.*, V(AcAc)₄^[4] and VO(AcAc)₂.^{[5][6]} In preparation stage, the precursors are normally heated to the temperature around 600 °C to obtain the crystallized VO₂(M) after dip/spin-coating. However, it is difficult to prepare the V^{IV} precursors, while for the annealing process for V^V precursors it usually requires an additional reducing step.^[7] Based on V^V precursor, a one-step annealing process was developed to prepare thin VO₂(M) films. Firstly, the vanadium powder was dispersed in a 30% H₂O₂ suspension and the mixture was stirred rigorously in an ice bath. Then, the obtained yellowish solution was warmed up to 50 °C with unceasing stirring until the color of the solution was observed as yellow→dark red→yellow. The obtained precursor was aged at the ambient temperature to form a gel in the dark red color, which was finally annealed in vacuum to attain the VO₂(M) films.

3.1.1.2 Sol-gel solutions for ARC

Two different AR solutions including Si-Al based solution and TEOS based solution were prepared via sol-gel method. 1) *Si-Al based solution*: Aluminum tri(secbutoxide) (ASB) was dissolved in 90 mL H₂O at 80 °C with vigorous stirring for 4 min. HNO₃ was added to the solution to adjust the pH to 3-4, followed by continuous stirring for 2 h. Subsequently, 10 g PVP was mixed with the solution and cooled down to room temperature with continuous stirring for 30 min. Furthermore, the mixture was merged slowly with trimethoxysilane (MTMS) (65 mL) and methanol (130 mL), and finally agitated ultrasonically for one more hour.

2) *TEOS based solution*: A TEOS precursor was diluted according to the molar ratio as TEOS:ethanol (95%):H₂O = 1:8.14:2. Hydrochloric acid (HCl, 37%) was dropped into the mixture until pH < 2. The solution was stirred for about 2 h followed by aging for at least one day. The formulated solutions were magnetically stirred for at least 6 h to get homogeneous suspensions.

3.1.2 Synthesis

3.1.2.1 Sol-gel method

To date, techniques, such as ion implantation,^{[8][9]} chemical vapor deposition (CVD),^[10–12] sputtering deposition,^{[13][14]} and pulsed laser deposition (PLD)^[15–17] have been used to fabricate VO₂ films, due to the advantages of precisely controlling the oxygen partial pressure.^[18] However, these techniques usually require complex and expensive equipment for gas-phase deposition processes. Intensive efforts have been devoted to developing new techniques, which are more feasible and cost effective. As one of the most intensively used methods, sol-gel processing could resolve the problems mentioned above. In the field of VO₂ film deposition, the sol-gel method has many advantages, such as low cost, easy operation, large-area deposition and the options of metal doping, such as Mo,^[19] Au,^[20] W and Ti,^[21] F^[22] and Mg.^[23] Generally, the goal of sol-gel processing method is to control the surfaces and interfaces of materials in the early stages of production. Usually, the sol is the dispersion of colloidal particles in a liquid solution, while the gel is rigid, interconnected networks with the vacancies in the size of a few μm and composed of polymeric chains with the length larger than 1 μm (in average).^[24] In the other hand, the incorporation of VO₂ nanoparticles into sol-gel matrix makes sure its dispersion and gelation to form a VO₂ network, which is beneficial to enhance both its T_{lum} and ΔT_{sol} . The processing steps that are taken to make VO₂/sol-gel monoliths are usually as follows:^[24] (i) *Mixing*. By mechanical mixing of colloidal particles, a suspension of colloidal powders is formed at a certain concentration that avoids precipitation. (ii) *Casting*. Due to its low viscosity,

the matrix can be cast onto a substrate. The substrate needs to be chosen carefully because it has influences on the performance of adhered VO₂ nanocomposites. (iii) *Gelation*. With time, the sol-gel matrix and the colloidal VO₂ nanoparticles link together to the formation of a 3D network. (iv) *Aging*. During aging, polycondensation continues with a localized solution and also the reprecipitation of gel network, which decreases the porosity and increases the thickness. (v) *Drying*. During the drying process, the adsorbed liquid evaporates from the matrix. (vi) *Densification*. Densification of the films usually needs high temperature heating. The custom-selective steps are usually required according to the specific systems.

3.1.2.2 Bead milling

Bead (or ball) milling is a process to reduce the micro-sized particles to the nano-sized particles. Simply, it is a container filled with beads into which powders are put and subsequently it is mechanically rotated to crush particles into nano-size. A typical instrument of wet bead milling is shown in **Figure 3.1(a)**. **Figure 3.1(b)** illustrates the movements of beads and powders in milling process. Since the rotation directions of bowl and turn disc are in contrary, the centrifugal force is synchronized in turn. The friction derives from the beads and the powder, and the mixture is milled during the rolling in the inner wall of the bowl and the striking against the inverse wall. Generally, the bead (or ball) milling process could be sequenced as the following stages: 1) *Initial stage*. At this stage, by the compressive forces, powder particles are flattened due to the collision with the balls. Though the shape of individual particles changes at this stage, however, no net change in mass occurs. 2) *Intermediate stage*. At this stage, cold welding and fracturing are the dominant milling procedures. 3) *Final stage*. During this stage, considerable reduction and refinement in powder particle size is evident. 4) *Completion stage*. The powder particles possess an extremely deformed structure. Due to its simplicity and scalability, the mechanical bead milling method is chosen to attain the nano-sized VO₂ particles in the following chapter.

Figure 3.1 (a) The equipment for wet bead milling: Dyno-Mill Research Lab WAB. Copyright @ Eskens. (b) Schematic presentation of motion of the ball and powder mixture.

3.1.2.3 Electrodeposition

Electrodeposition is an electrochemical process, also known as electroplating, which is utilized to deposit a material onto an electrode by the passage of electric current through the electrochemical system, as shown in **Figure 3.2(a)**. Electrochemical deposition is usually adopted to the growth of metals and conducting metal oxides, but not confined to these materials. Followed are several advantages^{[25][26]} of electrochemical deposition: 1) By adjusting the electrochemical parameters, the morphology and thickness of the nanostructures can be controlled precisely; 2) Relatively compact and uniform deposits could be synthesized based on well-defined template; 3) One can get relatively high deposition rate; 4) The equipment used in electrochemical system is usually inexpensive, because there is commonly no requirements for either high vacuum system or high reaction temperature. Usually, electrochemical deposition adopts the reduction-oxidation (red-ox) process of molecular or ionic species occurred on the electrode surface to form nanostructured films, which relies significantly on the electrochemical deposition conditions. However, in the current thesis, we adopted an alternative approach for direct electrochemical deposition of nanoobjects from their aqueous dispersions involving no red-ox reactions. By altering the ionic strength through electrical potential (0.05-0.5 V) in the vicinity of the electrode, locally aggregation and irreversible deposition of VO_2 nanoparticles occurred only on the conductive part of the electrode surface. This approach could also be used to

deposit other nanomaterials, such as zero-dimensional (0D) gold nanoparticles (AuNP), one-dimensional (1D) carbon nanotubes (CNT) or two-dimensional (2D) graphene oxide (GO). This new concept provides a one-step solution for the formation of nanostructures with the intact nanoobjects and preserves their inherent physical or chemical properties, which are essential for device performance, *e.g.*, flexible displays, smart windows, solar cells and chemical/bio-sensors.

One should be aware that the approach we use is different from electrophoretic deposition (EPD), even though these seem to be similar and confusing. In EPD, there is no red-ox reaction involved, and the principle driving force is the combination of the particles' electrophoretic mobility and the charges under an applied potential in the suspension.^[27] EPD usually involves a very high electric field, *e.g.* Zirconia (15 V),^[28] Ni nanoparticles (180 V),^[29] Titanate nanotubes (40 V),^[30] CNTs (34 V),^[31] due to the fact that excessively low electric field resulted in poor quality, low density, non-uniform coatings, which did not adhere to the substrate.^[32] For a comprehensive overview in the field of EPD of CNTs, please refer to the reference^[32] for more details.

Figure 3.2 (a) Schematic presentation of the electrodeposition system. (b) Two-electrode, three-electrode and four-electrode cell setup. (c) Measured electrochemical potential of the entire cell. Point A: working electrode, point E: counter electrode.

In electrodeposition system (**Figure 3.2(a)**), working electrode (WE) is usually the electrode which the studied reaction occurs. Commonly used WE

includes Au, Pt, Ag, glassy carbon electrode (GCE), *etc.* Referencing electrode (RE) is an electrode with a well-known and consistent potential. Usually, it is used as a reference for measuring the potential in the electrochemical cell. Commonly used RE includes Ag/AgCl, Ag/AgBr, saturated calomel, Hg/HgSO₄, Hg/Hg₂O, Cu/CuSO₄, *etc.* The purpose of counter electrode (CE) is, in the electrochemical cell, to close the current circuit. Typically, it is an inert material such as graphite, gold or platinum. A pair of the working and counter electrodes is mandatory in all electrochemical experiments (with non-zero current). As per the usage of electrodes in the electrochemical systems, the systems could be classified into the two-electrode, three-electrode and four-electrode system (**Figure 3.2(b)**). 1) *Two-electrode system*. WE and Sense (S) are linked into the primary WE, while RE and CE are linked into a counter (or quasi-reference) electrode. The two-electrode system measures the potential of the whole electrochemical cell: WE, electrolyte, and CE. If the potential of the entire electrochemical cell seems as the one presented in **Figure 3.2(c)**, a two-electrode system possesses the sense lead (point A) and the reference lead (point E). 2) *Three-electrode system*. The RE is isolated from CE, in turn, serves as the third electrode. This electrode is positioned at a point very close to WE. The sense points are A and—roughly—B (**Figure 3.2(c)**). A distinct experimental advantage over two-electrode setup is that three-electrode system measures only a half the cell. The potential changes are measured independently at the WE from the changes occurring at CE. (iii) *Four-electrode system*. The S is separated from WE as well as the RE (**Figure 3.2(b)**). This mode evaluates the potential difference between point B and point D (as shown in **Figure 3.2(c)**). In this setup, the potentials at WE and CE are not analyzed. The measured signal reveals the influence of the applied current on the electrochemical suspension. In the current thesis, we used the three-electrode system to deposit VO₂ nanoparticles to the electrode surface, using Cu plate (grid) as the WE, Ag/AgBr as the RE, and Pt as the CE.

3.1.2.4 Dip-coating method

Dip-coating method is the commercially applied, historic coating process among a variety of wet chemical film deposition strategies. In 1939, Jenaer Glaswerk Schott & Gen. received the first patent on the “sol-gel derived silica films” and demonstrated the success and simplicity of this film-forming method.^[33] This straightforward coating approach deposits the matrix uniformly on a substrate, such as small cylinders and chunks, while the liquid overcoat was then solidified slowly on the substrate to form a homogenous film.^[34] Basically, the dip-coating process could be divided into three important technical stages as follows (**Figure 3.3**): 1) *Immersion and dwelling*. At a constant speed, the substrate is immersed in the precursor solution and it is remained in the solution for a sufficient interaction time to ensure the wetting throughout. 2) *Deposition*. When the substrate is pulled upward at a constant speed, a layer of the solution is deposited on the substrate and the thickness of the film is subjected to the withdraw speed. Usually, with increasing the speed, a thick film could be expected to form and the excessive precursor will drain from the substrate due to the gravity. 3) *Evaporation*. The evaporation (or film solidification) process can be accelerated by heating treatment. A further heating treatment after the dip-coating process may need to get rid of organic residuals or promote the crystallization of the oxides.

Figure 3. 3 Schematic representing the dip-coating process.

Comparing with conventional film deposition techniques, namely CVD, sputtering or evaporation, the sol-gel method is more economic with less requirements of the equipment. The function of finely tailoring micro-/nano-structure of the deposited film is one of the most outstanding features of the solution-based dip-coating process over other coating methods.^[35] Taking the advantage of dip-coating into account, we use this method to form the sol-gel based anti-reflection coatings (ARC) on the various types of VO₂ substrates for offering RI-tunable (by post-coating heat treatment) AR effect for different VO₂-based thermochromic applications. More details of the preparation processes would be discussed in Chapter 6.

3.1.3 Characterization

3.1.3.1 Atomic force microscopy

The invention of scanning tunneling microscope (STM) has been achieved by the Nobel Laureate, Gerd Binnig and Heinrich Rohrer. This achievement enables the imaging resolution of the individual surface in the unprecedented nano-scale.^[36] The successful applications of STM stimulates the development of scanning probe microscopes (SPM), for instance atomic force microscope (AFM), which mechanically scans over a sample surface with a sharp tip and is now one of the most successful devices.^[37] However, unlike STM, AFM could be adopted to study conductors, semiconductors, and also insulators, which is quite suitable for the imaging of the topography of VO₂ substrates in our study. Besides, AFM provides a general method for measuring non-destructive surface profilometry at a resolution of 10 nm and even down to atomic level.^[38] AFM adopts a flexible cantilever, which is actually a kind of spring, to gather the force between sample surface and the tip. This concept of imaging a sample surface *via* imposing a force is universally applicable and can be adopted to magnetic and electrostatic forces, as well as to the interatomic interaction between sample surface and the tip.^[39] In AFM, the attractive or repulsive force between sample surface and the tip is transformed into

a bending of the cantilever. Depending on whether the interaction between the tip and sample surface is attractive or repulsive, the cantilever will be curved towards or away from the detecting surface correspondingly.

3.1.3.2 Electron microscopy

The smallest interval that human eyes can distinguish two points is approximately 0.1-0.2 mm, which is the visual limitation of mankind. A microscopy was invented to help people to zoom in to the “tiny world” with the dimension of less than 0.1 mm. The resolution of a modern microscope is determined by the quality and quantity of the lenses, as well as the wavelength of the illuminating radiance. For instance, the wavelength of white (visible) light is in the range of 400-700 nm with the average at 550 nm, which limits the resolution of white light about 200-250 nm, and obstacles its application in nanoscience. In order to break the limitation of the optical microscopies, the electron microscopy (EM) was developed by utilizing the electron beam as the source of radiance, instead of light. Since the electron beam possesses a much shorter wavelength than light, the resolution of EM can reach to 0.5 Å.^[40] By the way, the invention of EM has been one of the most important achievements due to its impact on materials science, biology, virology and medicine, *etc.* In current thesis, the average size of VO₂ nanostructures is about 100 nm. Hence, we choose EM for the characterizations of size, morphology and elements mapping.

Two commonly used EMs are scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

SEM adopts a focused beam, consisting of electrons with the intensive energy, to interact with the outermost layer of the solid samples and collect the information from a specific surface area. SEM presents the 2D images with spatial resolution and reveals the specimen data, including the morphology, chemical composition, and crystalline structure.^[41] Using the scanning mode, the square

areas with the width in the range of 5 μm -1 cm could be imaged with the conventional SEM techniques (magnification: 20-fold - 30,000-fold, spatial resolution: 50-100 nm). Moreover, SEM has the function to execute the chemical analyses at the selected points, which facilitate the (semi-)quantitative determination of the elemental compositions (incorporation with the attachment of energy-dispersive X-ray spectroscopy (EDX)) as well as crystal structures and orientations (in the mode of electron backscatter diffraction (EBSD)).

Also from electron-specimen interactions, TEM is a powerful technique for understanding various information of sample at very high spatial resolution, including size distribution, morphology, crystal structure, defects, strain, chemical information down to atomic level, etc. Different from SEM to collect information at the surface of the specimen, the transmitted electrons in TEM that passed through the thin sample are collected to form images, which is why to call it “transmission” electron microscopy. Therefore, to allow electrons to transmit through the sample, TEM sample must be very thin (sample thickness is typically less than 200 nm, depending on the composition of the sample and the expected information to get from TEM characterization). Magnifications of up to 1, 000, 000X and resolution below 1 nm could be achieved in TEM. Besides the atomic-resolution lattice images, TEM could provide chemical information of the specimen at a vertical resolution equal or smaller than 1 nm, which enables the chemical detection of the individual nanocrystals.^[42] Furthermore, the structural analysis (even the elements distribution) of a single nanoparticle could be fully achieved by using a precisely focused electron probe.

Both SEM and TEM techniques provide the state-of-the-art information (*i.e.* morphology, crystallinity, elemental distribution and composition) that we need to analyze the VO₂/Si-Al nanocomposites, and the VO₂ grid-patterning deposits from electrodeposition process in the present study.

3.1.3.3 UV-Vis-NIR spectroscopy

In general, a spectrophotometer illuminates a sample with particular wavelengths of light, and measures the reflected or absorbed/transmitted signals. The relationship between absorbance and wavelength generates a spectrum that characterizes the sample. The detection range of UV-Visible-NIR (UV-Vis-NIR) spectroscopy is 200-2500 nm wavelength or 50000-4000 cm^{-1} wavenumbers, which is commonly classified into three regions:^[43]

Ultra-violet (UV): 200-400 nm (wavelength) or 50000-25000 cm^{-1}
(wavenumbers)

Visible (Vis): 400-800 nm (wavelength) or 25000-12500 cm^{-1} (wavenumbers)

Near-infrared (NIR): 800-2500 nm (wavelength) or 12500-4000 cm^{-1}
(wavenumbers)

UV-Vis-NIR spectroscopy is usually adopted to investigate the reflectance, transmittance, or absorbance of photovoltaic materials. In the recent decade, VO_2 becomes a well-studied thermochromic materials, and it undergoes the reversible structural transitions between the monoclinic phase and the tetragonal phase when crossing the critical temperature (τ_c) at 68 °C.^[44] At this phase transition, the optical properties of VO_2 in the NIR range change reversibly from a reflective state above the T_c to a transparent state below the T_c , while the visible transmittance remains almost constant. Therefore, in the current thesis, we adopt UV-Vis-NIR spectroscopy to study optical properties of VO_2 with the temperature change. The evaluations of VO_2 thermochromic performance are according to the thorough illustrations in Section 2.2.

3.1.3.4 X-ray diffraction

X-ray diffraction (XRD) has been employed for many years as a non-destructive technique to investigate the structures (in an atomic scale) of either

crystalline or amorphous specimens. Different specimens reveal the unique XRD patterns, which is as a function of the 2θ angle and can derive a variety of the crystallographic information, including lattice size/strain, chemical composition, the orientation of crystal, *etc.* Since this technique is non-destructive, it allows many kinds of the testing materials, *e.g.*: minerals, metals (alloys), inorganic and organic compounds, and polymers, *etc.*

Figure 3.4 (a) Monoclinic (M_1) phase of semiconducting VO_2 ($T < \tau_c$), in which two different types of oxygen could be determined. (b) Rutile/tetragonal structure of VO_2 ($T > \tau_c$), in which the large red balls are V^{4+} elements and the small blue dots are O^{2-} elements. Reproduced with permission from Reference [45]. Copyright 2002, John Wiley & Sons, Inc.

In the present thesis, VO_2 nanomaterials reveal the temperature-responsive semiconductor-to-metal phase transition at $\tau_c = 68^\circ\text{C}$. When increasing the ambient temperature and passing the τ_c , the low-temperature monoclinic structure of VO_2 (**Figure 3.4(a)**) changes to the rutile phase with the tetragonal lattice structure (**Figure 3.4(b)**). Hence, we choose XRD to characterize the structural phase changes of VO_2 nanomaterials upon temperature change.

3.1.3.5 X-ray photoelectron spectroscopy

The examination of the superficial chemical composition in the atomic scale is frequently implemented by X-ray photoelectron spectroscopy (XPS), which detects a depth of only 50-100 Å from the surface of a specimen. The analysis process employs the monochromatic X-rays, which interacts with the surface elements of the specimen, and detects the energy distribution of electrons ejected from the specimen, which contains information regarding the chemical oxidation state, electronic structure, and atomic composition.^[46] Hence, surface composition and electronic environment could be nondestructively determined with XPS.

In the present thesis, we used electrodeposition method to form thin VO₂ films on the Cu electrode. The Cu electrode was applied a potential, which could cause the oxidation of Cu to the formation of Cu^{m+} (m = 1 or 2), inducing an increase of ionic strength near the electrode surface, thereby forming the irreversible deposits of VO₂ nanoparticles on the conductive part of the electrode. Therefore, to characterize the oxidation states of Cu^{m+} ions that discharged from Cu substrates, we adopted XPS technique, and the Cu 2p peaks reveal the state of Cu ions that confined inside the vanadium dioxide nanoparticles (VO₂-NP) assembled films during the electrodeposition. The specific illustration would be found in the following results part of the thesis.

3.1.3.6 Surface profilometry

The thickness of VO₂ layers on the substrate has a profound effect on its performance in smart windows application. In this study, we used surface profilometer to measure the thickness of VO₂-based substrates. Generally, the profilometer consists of two components: 1) the detector with a fine tip to touch the sample surface in analysis and 2) a flat stage to fix the sample with vacuum. Either the detector or the stage can move when the other component is stable. For common lab usage, there are two choices of profilometers with the different operating

mechanisms: 1) *stylus type*: it requires a scratch on the coating layer to form a “step” for the physical probe to measure the height difference (**Figure 3.5**); 2) *optical type*: a light probe is involved to replace the physical tip and detect the surface topography with 3D presentation. Specifically, the stylus-type surface profilometers possess high sensitivity and high Z resolution, which necessitates the physical contact of the tip and the surface, as well as the feedback of force. The mechanical force between the sample and the probe is monitored constantly, and the height difference (against the initial reference point) is recorded instantly by using a mechanical feedback loop. The feedback system is adopted to maintain a certain amount of torque on the arm, which is also named as ‘setpoint’. The position of the arm holder is varied in the Z direction to reconstruct the topography of the sample in the processing unit. However, the rigid detecting probe of a stylus-type profilometer is very volatile to samples with soft surface and the tip could be easily contaminated. Since the probe adopts a 3D movement with the intimate contact of the sample surface, the rate of the measurement is relatively slow as compared to the non-contact optical profilometers. Also, the resolution of measurements is restricted by the dimension and shape of the physical tips.

Figure 3. 5 Schematic representation of a stylus profilometer with the contact of stylus tip and the sample.

3.1.3.7 Dynamic Light Scattering

Dynamic light scattering (DLS) is also recognized as quasi-elastic light scattering or photon correlation spectroscopy. In current thesis, DLS is utilized to analyze the size distribution of VO₂ nanoparticles. This technique irradiates a beam of the monochromatic light, *e.g.*, a source of laser, to a suspension with spherical-like particles in Brownian motion, which causes the fluctuations in light scattering with time that are proportional to particle's size. Therefore, it is possible to calculate the spherical particle size distribution according to these fluctuations. There are several advantages of DLS method: Firstly, the experiment duration is quite short, and it is almost automatized; secondly, this method has modest costs.

3.1.3.8 Adhesion test

The adhesion ability of VO₂ thin films on the substrate plays a critical role for its application in smart windows. In this thesis, we tested the adhesion of VO₂ deposits, obtained from the ionic strength induced electrodeposition, based on the cross-hatch tape adhesion test according to the American Standard Testing Method (ASTM) D3359-09.^[47] The adhesion grade can be calculated according to the ASTM D3359 standard for adhesive test (**Figure 3.6**),

$$\eta = \frac{N-N^*}{N} \times 100\% \quad (3.1)$$

where η represents the percent area removed, N^* denotes as the pixels of remains in the lattices and N stands for the pixels of all the intact lattices.

Figure 3.6 Representation of the ASTM D3359 standard pictures.^[47]

3.1.4 Simulation – Finite Difference Time Domain

Finite Difference Time Domain (FDTD) method is a numerical tool for implementing the simulations of the computational electrodynamics *via* searching an approximate solution to the associated system of differential equations. This modelling approach can perform a wide range of frequencies in a single program and deal with the non-linear properties of the materials in a natural manner. Specifically, for the current research, a key point in VO₂-based thermochromic smart windows is to achieve high T_{lum} while maintaining the large ΔT_{sol} . In this thesis, numerical optimizations using parameter search algorithms have implemented through a series of FDTD simulations^[48] by varying film thickness, cell periodicity, grid dimensions and variations of grid arrangement to realize the best performing results of T_{lum} and ΔT_{sol} .

To exercise the simulation, a commercial software (FDTD solution, Lumerical Inc. Vancouver, Canada) was chosen. We used a uniform mesh size of 3 nm (x, y, and z directions). The optical constants of materials were taken in the spectrum range from 300 nm to 2500 nm.^[49] The dielectric dispersion profiles of the materials were fitted by the multi-coefficient model that relies on an extensive set of basic functions. To calculate the frequency dependent transmittance, perfectly matched layer (PML) boundary conditions were set for the Z direction, and Bloch boundary conditions were applied to X and Y directions of the simulation region. The VO₂ nanogrid films were supported by a glass substrate, the entire system was suspended in air/vacuum, and the incident beam was modeled as a plane wave traveling along the Z-axis. Field monitors were placed at fixed Z position below the surface of the VO₂ nanogrid film to detect the intensity of the transmitted beam.

3.2 Principles of characterization tools

3.2.1 Atomic force microscopy

In general, there are five essential components in force microscopes:^[39] 1) a flexible cantilever with a sharp tip, 2) the deflection sensing components connected to the cantilever, 3) a central control system to manage the deflection of the cantilever according to the feedback of the tip-specimen interaction force, 4) a piezoelectric scanning system, which shifts the sample in a raster way with the reference to the tip. 5) a data-processing unit with a monitor, which transforms the recorded signal into a 3D image indicating the topography of the sample surface. As schematically demonstrated in **Figure 3.7(a)**, the detective probe of AFM is a sharp tip, which is made of silicon or silicon nitride. The dimension of the tip is typically height < 5 μm and diameter < 10 nm at the apex. The sharp probe is positioned at the unoccupied end of the cantilever, which is 100-500 μm in length. The bending or deflecting of the cantilever was caused by the interaction forces between the sharp probe and the specimen surface according to Hooke's law as follows:^[50]

$$F = -\delta_c \times k_c \quad (3.2)$$

where F is the force, δ_c is the cantilever deflection, k_c is the cantilever spring constant, as shown in **Figure 3.7(b)**. The cantilever spring constant can be calculated from the following equation:

$$k_c = \frac{E \cdot w}{4} \left(\frac{t}{l} \right)^3 \quad (3.3)$$

where E is the Young's modulus, w , t and l are the width, thickness and length of the cantilever. The cantilever spring is an essential component in AFM. The spring needs to be as soft as possible since a maximum deflection for a given force is usually required. While, at the same time, a stiff spring with high resonant frequency is necessary to minimize the sensitivity to vibrational noise near 100 Hz. The resonant frequency, f_0 , of the cantilever spring system is as follows:

$$f_0 = \frac{1}{2\pi} \left(\frac{k_c}{m_0} \right)^{\frac{1}{2}} \quad (3.4)$$

where m_0 is the effective mass that loads the spring.

There are two types of movements that are usually used during the AFM analysis: either the tip scans over a specific area of the specimen, or the tip is fixed and the specimen is moved beneath the tip. The attractive/repulsive interactions between the specimen and the sharp tip induce the deflections of the cantilever, which are measured and analyzed by the detector. Following the deflection of the cantilever, the angle of the reflected laser varies accordingly, and the spot is projected on the different locations of the photodetector. The four quadrant photodiodes are applied to compare and compute the deflection signal, and finally a computer plot a 3D image to visualize the topography of the specimen.

Figure 3.7 (a) Schematic representation of the AFM system. (b) Schematic representation of the cantilever tip in contact with the sample. (c) A general approximation of the tip-sample force against the distance. Image is sourced from the internet. Copyright © JPK Instruments (Source <http://www.jpk.com/index.2.en.html>)

In AFM, one of the most exciting results is the discovery that atomic resolution could be achieved when the tip is in contact with the specimen during scanning. Conceptually, this imaging contact mode is like using a stylus profilometer to measure the topography of surface atoms. The AFM achieves high resolution by applying a very small loading force on the tip, typically in the range of $10^{-11} \sim 10^{-7}$ N, which makes the contact area between the tip and the specimen extremely small.^[39] Typically, several forces contribute to the deflection of an AFM cantilever. The distance regime (*e.g.*, the tip-specimen spacing) determines the type of force that could be sensed. Regarding the forces between the cantilever tip and the specimen surface, different detection modes can be used (**Figure 3.7(c)**), including: 1) *Contact mode*. Contact and Force modulation modes both stay entirely in the repulsive part of the curve. In contact mode, a single value of the force is chosen, and in force modulation mode the force is varied. 2) *Intermittent contact mode (or tapping mode)*. Intermittent contact mode moves between the attractive and repulsive parts of the curve. The maximum force perpendicular to the specimen might be higher or lower than that in contact mode, but this is only applied for a short part of the cantilever cycle. Therefore, the sample damage and lateral drag could both be reduced comparing to contact mode for some specimens. 3) *Non-contact mode*. The non-contact mode is the only one that stays in the attractive region of the curve. However, this makes it difficult to control. Therefore, it is not used that often.

3.2.2 Electron microscopy

Found by Ernst Abbe in around 1870,^[40] the resolution of the microscope is limited to about half of the wavelength of the illumination source used to image the sample. One way to solve this limitation is to adopt an illumination source with a much shorter wavelength than photons, which turns to be electrons. The wavelength of an electron could be calculated as follows, which was based on the discovery of Louis de Broglie that every particle or matter propagates like a wave, known as wave-particle duality.^[51]

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2meV}} \quad (3.5)$$

where λ is the wavelength, h is the Planck's constant (6.626×10^{-34} J seconds), m is the mass of the particle and v is the velocity of the particle. Since the mass of an electron is 9.1×10^{-31} kg and $e = 1.6 \times 10^{-19}$, substituting these values into the above equation, then one can get λ in the following form,

$$\lambda = \frac{12.25 \times 10^{-10}}{\sqrt{V}} \quad (3.6)$$

where the value of λ could be calculated at a given accelerating voltage (V). As could be derived from the above equation, with the increasing of acceleration voltage, the wavelength of electrons decreases, followed by the resolution of the microscope.

3.2.2.1 Scanning electron microscopy

The schematic presentation in **Figure 3.8(A)** indicates the essential parts of a typical SEM. These components contribute to seven co-operational systems so as to produce high-resolution SEM images showing the explicit results with the controllable brightness, contrast, magnification, depth of field, *ect.*^[52] A brief introduction of each system is illustrated in sequence as the following items: 1) *Vacuum system*. When operating an electron beam, a vacuum system is a must because the electrons would diffuse or scatter rapidly if the electrons collide with other molecules. 2) *E-beam generation system*. This system is located at the top of SEM equipment (**Figure 3.8(A)**) and equips with an electron gun, which heats up the tungsten or LaB₆ filament to emit an energy-intensive electron beam (primary) to “illuminate” the surface of the specimen. 3) *E-beam manipulation system*. A plenty of electromagnetic lenses and coils are installed in the column of SEM and they are essential to manage the spot size, position, and shape of the electron beam by altering the electromagnetic field surrounding the electron beam. 4) *Beam-specimen interaction system*, which monitors and determines the sorts of electric signals to be examined. 5) *Detection system*. In order to characterize the

specimen from different angle, different types of detectors are required and installed in the specimen chamber to collect the emissions of the energy/particle generated during or after the electron/specimen interactions. 6) *Signal processing system*. This unit treats the electronic signals that are collected by the detection system and performs the supplementary digital processing of the SEM images. 7) *Display and recording system*. This is the final step to transform the digital signal to the photos of the selected area on a specimen with necessary imaging parameters. Also, this system can record the in-situ results during the imaging process with the assistance of the photographic or magnetic media.

Figure 3.8 (A) Schematic representation of the main components of a typical SEM, including electron column system, scanning system, detector system, vacuum system and electronics control system. Image is sourced from the internet. Copyright @UCR (Source <http://cfamm.ucr.edu/>). (B) Atom-high energy electron interactions. The inner electron shells of atoms are labeled according to standard notation (the innermost states are K, L, etc.) a) Low-angle scattering electrons scattered in this way pass to the next layer of atoms with very little loss of energy. b) High-angle scattering electrons. c) Emission of secondary electrons and characteristic X-rays. d) Emission of secondary electrons and Auger electrons.

As demonstrated in **Figure 3.9(a)**, when the energy-intensive electron beam is focused on the selected area of the specimen in vacuum, the incident (primary)

electrons penetrate the surface to a depth of *ca.* 1 μm and interact with the interior structure of the specimen in the both elastic and inelastic manners, which result in the electrons-specimen interactions within a limited region, that is also known as “the interaction volume”. The volume size can be increased by increasing the energy of primary electron beam, while enhancing the average atomic number (‘heavy’ elements) of the sample reduces the interaction volume. Eventually, the resolution of a SEM is determined by the scope of the interaction volume. Moreover, different interactions (**Figure 3.8(B)**) between the electrons and the solid induce the emissions of a variety of electrons or radiations, such as secondary electrons (SE) and back-scattered electrons (BSE) to produce SEM images, as well as Auger electrons and the characteristic X-ray radiation for performing the composition/elemental analysis, and also some photons of light.^[41] The imaging is primarily implemented by collecting the emitted electrons/radiations from the specimen. Since different emissions reveal the distinguishable variances of the emission energy, the excitation energy of the primary beam and angular distributions, *etc.*, they require the applications of different types of detectors to collect the signal for the image-processing. By correlating the specimen scan position with the detected signal, an image of the specimen is then formed. In general, each detected signal affords a specific type of imaging in SEM. Usually, the SEM adopts primary SE and BSE. As for SE, the sampling depth is in the range of 10-100 nm, and the interaction diameter is identical to the size of emitting BSE. SE are generated from the depth much smaller than the one of BSE. The SE images (SEI) reveal the morphology and topography of the specimen by collecting the signals from the electrons escaped from the solid with 250 eV excessive energy, while the energy-intensive electrons occurred almost 180 ° from the orientation of the incident beam are utilized to produce the BSE photographs. The generation of BSE is dependent on the average atomic number at the different positions on the specimen, hence indicating the compositional distribution with the different brightness and contrast.

Figure 3.9 (a) Schematic representation of the interaction volume. Image is sourced from the internet. Copyright @ GLA (source <http://www.gla.ac.uk/>). (b) Schematic representation of information transfer to form an image in SEM.

In the sight of digital domain, a SEM image is presented as a 2D intensity map, which displays the details of the specimen in pixel according to the signal intensity at each spot collected by the detector (**Figure 3.9(b)**). In order to capture an adequate data for each point, the incident beam needs to remain at the point for a dwell time prior to scanning on the next one. There is no “true” photograph (*i.e.*, only digital images available) in SEM, which is a distinct difference as compared with the optical microscopy or TEM.

The SEM magnification relies on the excitation of scan coils rather than the excitation of objective lens, which decides the beam focus. The actual area scanned by the focused beam is much tinier than the image shown on the monitor. Since the length of the monitor is unchanged, the low or high magnification of SEM images can be realized by shrinking or enlarging the dimension of the scanned area, respectively. Therefore, the linear magnification of the digital image (M) can be

represented by the ratio between the length of the examined area on the specimen (L_{spec}) and the constant dimension of the displayed image on the monitor (L_{mon}) (**Figure 3.9(b)**) as shown in the equation below.

$$M = \frac{L_{mon}}{L_{spec}} \quad (3.7)$$

3.2.2.2 Transmission electron microscopy

Although TEM is similar to SEM in many ways, there are many differences when analyzing TEM samples. Usually, the thickness of SEM samples is sufficient for a focused beam to be contained within the volume, *e.g.*, no primary beam transmits because it could not pass through the specimen. This could induce the primary beam to scatter in the specimen, and many factors need to be considered when dealing the raw X-ray data for quantitative analysis, *e.g.*, incident beam energy, sample density and take-off angle, which might have a profound influence on the quantitative results in SEM. While, in TEM, this is not the case since the specimen is beam transparent. Usually, the thickness of specimen is in the order of 100 nm or even less. On the other hand, the primary beam energy in TEM is much higher and has higher penetrating power than that in SEM. As illustrated in **Figure 3.9(a)**, the interaction volume in TEM in the path of the focused beam is much smaller than that in SEM. Consequently, spatial resolution is much better than SEM due to the fact that there is much less primary beam is scattered in the specimen. While, if the sample is much thicker than 100 nm, the results might need to be rectified for density and absorption.

Imaging: The electron gun at the top of the column generates a beam of electrons, which are confined by the condenser aperture and focused by the condenser lens. The high angle electrons are eliminated from the electron beam, which then shines on the surface of the specimen and partially transmits through the thin part of the specimen. Subsequently, the objective lens focuses again the transmitted electrons to produce the real-time image on the phosphor screen or the

camera with the charge coupled device (CCD). The corresponding TEM image is magnified along the way passing through the intermediate and projector lenses at the lower part of the TEM column. Finally, the image can be observed when it is projected on the phosphor screen.

Meanwhile, TEM is able to obtain the selected area electron diffraction (SAED) pattern, which is widely applied to execute the two fundamental analysis processes as illustrated in **Figure 3.10**. The SAED pattern contains a central bright spot that involves both the direct-beam and a few scattered electrons (**Figure 3.10**), and the distribution of the electrons attributes to the compositions of the sample.^[53] When the subsequent image is created by the direct-beam electrons (**Figure 3.10(a)**), it is called a bright-field (BF) image. On the other hand, **Figure 3.10(b)** demonstrates how the diffracted/scattered electrons or a portion of the diffraction circle forms the dark-field (DF) images.

Figure 3.10 Ray diagrams showing the way that the objective lens and objective aperture are used in combination to produce (a) a BF image formed from the direct electron beam,

(b) a displaced-aperture DF image formed with a specific off-axis scattered beam. Reproduced with permission from Reference [53]. Copyright 2009, Springer.

Diffraction: An electron can be easily deflected by other electrons or the nucleus of an atom when they approach each other closely, because an electron carries one negative charge and has a substantially light weight. The electrostatic effects, also known as the Coulomb interactions, lead to the scattering of electrons, which is the basic of TEM imaging. Similar to SEM, the scattering of electrons could be classified in two ways: elastic scattering and inelastic scattering (referring to **Figure 3.9(a)**). Diffraction is a unique type of elastic scattering. The angular distribution of scattering could be observed as diffraction patterns (DP) which is formed by the scattered spots. In TEM, a simple and fundamental operation step is to employ a confinement aperture or an electron detector with the size that just allows the electrons that have went through a certain number of angular derivations. Therefore, we can select which electrons to be used and what information would be presented in the image. It is essential to know the relationship between the electron-scattering mechanism and the data obtained by TEM, which could start from the scattering of an isolated atom,^[53]

$$\sigma_{atom} = \int_{\theta}^{\pi} d\sigma = 2\pi \int_{\theta}^{\pi} \frac{d\sigma}{d\Omega} \sin \theta d\theta \quad (3.8)$$

where σ_{atom} is the cross section of a single, isolated atom, $d\sigma/d\Omega$ is differential cross section, θ is a particular scattering angle. This equation gives an easy way to determine the cross section for a given atom (σ_{atom}) for all values of θ by working out the integral of $(d\sigma/d\Omega)\sin \theta$ from 0 to π . Considering the specimen contains N atoms/unit volume, then the scattering from the specimen could be defined as,

$$\sigma_{total} = N\sigma_{atom} \quad (3.9)$$

where $N = N_0\rho/A$, N_0 is the Avogadro's number (in units of atoms mol⁻¹), A is the atomic weight of the scattering atoms in the specimen (kg mol⁻¹), which has density ρ (kg m⁻³), then the equation can be rewritten as,

$$\sigma_{total} = N\sigma_{atom} = \frac{N_0\sigma_{atom}\rho}{A} \quad (3.10)$$

Thus, σ_{atom} is, in a unit distance, the number of scattering events that the electron treks through the specimen. If the thickness of a specimen is defined as t , the probability of scattering can be calculated as:

$$\sigma_{total}t = \frac{N_0\sigma_{atom}(\rho t)}{A} \quad (3.11)$$

The above equation is a universal expression of all the affecting factors that varies probability of the scattering in a physical sample.

3.2.3 X-ray diffraction

XRD is a powerful technique to acquire the crystallography information of the crystallized samples based on the wave-particle duality of the incident X-rays. The incident source of XRD is a beam of the monochromatic X-rays, which strike on the surface of the specimen with a certain angle. Similar to SEM, the incident beam penetrates the surface and interacts with the crystal structure of the testing materials in the way of scattering the X-rays. The resultant X-rays from the crystallized specimens are interfered in either constructive or destructive way, which is well-known as ‘diffraction’. The Bragg-Brentano diffraction (as shown in **Figure 3.11**) is commonly utilized in XRD analysis. The pattern of X-ray diffractions is constantly recorded by altering the angle of the incident beam by θ and the angle of the scattered beam by 2θ . The scattering intensity $I(2\theta)$ plotted in the y-axis is as a function of the scattering angle (2θ). Different modes can be selected during the $\theta/2\theta$ scan, i.e., either rotating both the sample stage by θ and the detector by 2θ with remaining the X-ray emitter stable, or fixing the sample stage with moving the generator of X-ray and the detector by θ simultaneously/clockwise/anticlockwise. To govern all the rotations, a goniometer located at the central of XRD instrument is essential.^[54]

Figure 3.11 Geometry of Bragg-Brentano diffraction. Reproduced with permission from Reference [54]. Copyright 2006, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

When a crystal with an interplanar spacing d (crystal lattice constant) is irradiated by X-ray beam with a comparable wavelength λ , the constructive interference between elastically scattered X-ray beams can be obtained at specific angles 2θ when the Bragg's Law is satisfied

$$n\lambda = 2d\sin\theta \quad (3.12)$$

where n is any integer. In most diffractometers, the X-ray wavelength λ is fixed, and the diffraction angle θ is measured by goniometer. Therefore, the crystal lattice constants d can be determined by above equation.

The Bragg's Law could be derived geometrically from the following **Figure 3.12**. The distance between each crystallographic lattice plane is d and the angle between the plane waves of X-rays and the lattice planes is θ . There is a difference of the travel distance between the top X-ray radiance and the one beneath. The distance difference can be varied by the different configuration of atoms^[54] and it induces the phase shift of two reflected X-rays those are collected by the detector. The phase shift consists of two portions, AB and BC . The reflected X-rays with the constructive interference can be attained only when

$$n\lambda = AB + BC \quad (3.13)$$

$$AB = BC \quad (3.14)$$

$$n\lambda = 2AB \quad (3.15)$$

$$\sin\theta = AB/d \quad (3.16)$$

$$AB = d\sin\theta \quad (3.17)$$

therefore

$$n\lambda = 2d\sin\theta \quad (3.12)$$

Figure 3.12 Visualization of the Bragg equation.

When X-rays transit through thin films, an attenuation of intensity occurs due to absorption effect,^[54] which can be described by Lambert-Beer law. The initial intensity I_0 that enters the specimen will be exponentially damped to an amount of $I = I_0 \exp(-2\mu l)$ after a path of $2l$, where the linear attenuation coefficient $\mu = \rho\mu_m$, in which μ_m is the mass absorption coefficient, ρ is the mass density. The dominant effect of the absorption on a diffraction is the variation of the scattered intensity, which is shown in **Figure 3.13** of the $\theta/2\theta$ scan. The intensity reduction of the total X-ray beam is the sum of all possible paths within the limits of 0 to $l_{\max}$,

$$\int_0^{l_{\max}} \exp(-2\mu l) dl \quad (3.18)$$

where $l = z/\sin\theta$, then $dl = dz/\sin\theta$. Here, $z = 0$ and $z = t$ account for the surface of the film and the film-substrate interface. The solution of the integral yields

$$\frac{1}{2\mu} \left\{ 1 - \exp\left(-\frac{2\mu t}{\sin\theta}\right) \right\} \quad (3.19)$$

In the limit of an infinitely thick sample $t \rightarrow \infty$ which is equivalent to $t \gg 1/\mu$, the result $1/(2\mu)$ is observed. In the following, the absorption factor is denoted by the ratio of the absorption for a sample of finite thickness with respect to an infinitely thick sample

$$A = \int_0^t / \int_0^\infty \quad (3.20)$$

The application of this procedure results in the absorption factor for the $\theta/2\theta$ configuration

$$A_{\theta/2\theta} = \left(1 - \exp\left(-\frac{2\mu t}{\sin\theta}\right) \right) \quad (3.21)$$

Figure 3. 13 Absorption effect in a thin-film sample during a $\theta/2\theta$ scan.

3.2.4 X-ray photoelectron spectroscopy

XPS performs the elemental analysis at only the superficial layer of a solid specimen. A chamber with the ultra-high vacuum (UHV) environment is important to allow the monoenergetic soft X-rays to bombard the surface and emit electrons with high energy. The schematic representation of an XPS instrument was shown in **Figure 3.14(a)**, including the X-ray source, UHV system, sample stage, electron collection lens, electron energy analyzer, electron detector, *etc.*

Figure 3.14 (a) Schematic representation of an XPS instrument. (b) Schematic representation of the photoemission process.

During measurement, the incident photons ($h\nu$) transfer the energy to the bombarded electrons. Once this energy is larger than the binding energy of between electrons, the bombarded electrons is capable to conquer the work function (ϕ) of the solid and escape from the specimen (**Figure 3.14(b)**). The loss of the electrons causes the ionization of the inner shell of the atom (A). Based on the law of energy conservation:

$$E(A) + h\nu = E(A^*) + E_{kin} + \phi \quad (3.22)$$

$$E_{kin} = h\nu - [E(A^*) - E(A)] - \phi = h\nu - E_B - \phi \quad (3.23)$$

where E_B is the binding energy relative to the Fermi level E_F and E_{kin} is the kinetic energy of the photoelectron (relative to the vacuum level E_v). The photoelectron spectra are derived from the kinetic energy distribution of the photoelectron, which is examined by the electron analyzer. The binding energy could be calculated for all core electrons with $E_B < h\nu - \phi$ with a known photon energy ($h\nu$).

3.2.5 UV-Vis-NIR Spectroscopy

According to Lambert-Beer Law, the relationship between the absorbance (A) and the transmittance ($\%T$) could be derived as follows:^[55]

$$A = \lg(I_0/I) \quad (3.24)$$

$$\%T = 100 \cdot I/I_0 \quad (3.25)$$

then

$$A = \lg(100/\%T) \quad (3.26)$$

where I_0 is the intensity of the light entering the sample, I is the intensity of the light emerging from the sample.

As shown in **Figure 3.15**, the testing object is positioned against the outermost wall of the integrating sphere. For measuring the transmittance, the sample is clapped at the front port and close to the incident beam (**Figure 3.15(a)**). In turn, for obtaining the results of reflectance, the sample has to be fixed at the

back port so as to reflect the beam by the interior reflective surface of the sphere prior to reaching the detectors at the central point of the sphere (**Figure 3.15(b)**).

Figure 3.15 Measurements with an integrating sphere: (a) transmittance and (b) reflectance. Image is sourced from the internet. Copyright @ PerkinElmer.

3.2.6 Dynamic Light Scattering

Nanoparticles in a suspension are dispersed by the molecules of the solvents, causing the random motion of the nanoparticles, which is well-known as Brownian motion. When an incident light shines to the dispersion, it is scattered by the drifting nanoparticles and the random motion of particles is passed to the scattered light. The lights scattered by more than two particles will encounter and induce the interference in the either destructive or constructive manner, thereby resulting in the time-dependent fluctuations of the resultant light. The fast photon detector (**Figure 3.16**) analyzes the fluctuations, which are affected by the diffusion rate of the nanoparticles in a certain solvent and also related to the hydrodynamic radii of

the suspended nanoparticles. The following second order correlation function is involved to quantify the corresponding fluctuations.

$$g^2(\tau) = \frac{\langle I(t)I(t+\tau) \rangle}{\langle I(t) \rangle^2} \quad (3.27)$$

where $I(t)$ represents the intensity of the scattered light at time t , and the brackets ' $\langle \rangle$ ' designate the value averaged over the entire t .

The correlation function of a monodisperse suspension could be evaluated using the following equation:^[56]

$$g^2(\tau) = B + \beta \exp(-2\Gamma\tau) \quad (3.28)$$

where B is the baseline of the correlation function at the infinite delay, β denotes the amplitude of the correlation function at zero delay, and Γ indicates the rate of decay, which could be converted to the diffusion constant D for a particle *via* the relationship as shown below:

$$D = \frac{\Gamma}{q^2} \quad (3.29)$$

where q is defined as the magnitude of the scattering vector and it can be calculated by:

$$q = \frac{4\pi n_0}{\lambda_0} \sin(\theta/2) \quad (3.30)$$

where n_0 represents the refractive index (RI) of the solvent, the wavelength of the incident laser is shown as λ_0 , and θ stands for the angle between the detector and the sample cell. Then, based on the Stokes-Einstein equation, the hydrodynamic diameter D_h can be used to calculate the diffusion constant D by which:

$$D_h = \frac{kT}{6\pi\eta D} \quad (3.31)$$

where k is Boltzmann's constant, T is the temperature in K, and η is the solvent viscosity.

Figure 3. 16 Schematic representation of the DLS system. Image is from the internet.
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Chapter 4

VO₂/Si-Al Thermochromic Nanocomposites: Largely Enhanced Luminous Transmittance and Solar Modulation

Vanadium dioxide nanoparticles (VO₂-NP) with the average size of ca. 20 nm are obtained by the straightforward mechanical bead-milling method, which are well-dispersed in a transparent Si-Al gel matrix to form nanocomposites. The VO₂/Si-Al thermochromic nanocomposites are prepared with the different solid contents of VO₂ and the various thickness of the composites. With 10% VO₂ loading and 3 μ m foil thickness, high luminous transmittance ($T_{lum(20^{\circ}C)}=63.7\%$ and $T_{lum(90^{\circ}C)}=54.4\%$), and large solar modulation ability ($\Delta T_{sol}=12\%$) can be achieved. This current approach provides an industrial scalable preparation method with the optimized thermochromic performance for practical smart window applications.

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4.1 Introduction

Vanadium dioxide (VO₂) is of a great interest as the promising candidate for the thermochromic smart windows, because it exhibits an excellent temperature-responsive behavior at a critical transition temperature (τ_c) of 341 K (68 °C) near room temperature.^[1] However, the insufficient solar modulation ability (ΔT_{sol}) and the low luminous transmittance (T_{lum}) in the VO₂-based continuous thin films hinder the applications of smart windows in practice.^[2–7]

To tackle this issue, S. Li *et al.* firstly proposed a distinct concept of “nanothermochromism” (by using simulations), which can be attained by integrating VO₂ nanoparticles (VO₂-NP) in a transparent matrix.^[8] Their simulation results suggested that VO₂-NP dispersed in a dielectric host are more advantageous than VO₂ continuous thin solid films, since the former offers much higher T_{lum} together with the enhanced ΔT_{sol} than the latter. According to the previous studies of the pure VO₂-NP based nanocomposites, the nanoparticles were synthesized by solid-state annealing^[9] or thermolysis^[10] methods and they were utilized as the functional nanofillers in the various matrix (*e.g.*: polyurethane (PU) and polydimethylsiloxane (PDMS)) in order to obtain the nanocomposite foils on various substrates (*e.g.*: float glass and polyethylene terephthalate (PET)). The corresponding “nanothermochromic” T_{lum} and ΔT_{sol} are summarized in **Table 4.1**; nevertheless, these recent studies of pure VO₂-NP based nanocomposites are unable to provide both high luminous transmittance ($T_{lum} > 60\%$) and large solar modulation ability ($\Delta T_{sol} > 10\%$) simultaneously.

Table 4.1 Summary of recent studies on the pure VO₂-NP based thermochromic nanocomposites

Matrix	VO ₂ -NP size (nm)	Synthesis method	Foil thickness	$T_{lum(low)}$ (%)	$T_{lum(high)}$ (%)	ΔT_{sol} (%)
PU ^[9]	29-72	solid-state reaction	unknown	54.2	53.7	9
PDMS ^[10]	10-200	thermolysis	75 μ m	Averaged T_{lum}=50.7		12

Hereby, we introduce a straightforward and scalable approach to prepare thermochromic nanocomposites with mechanically attrited VO₂-NP dispersed in a transparent Si-Al gel.^[11] With the optimization of VO₂ solid content and the thickness of the composites, the VO₂-based foils with high luminous transparency and large solar modulation ability can be achieved. This result offers *ca.* 16% enhancement of $T_{\text{lum (average)}}$ (59.1% vs. 50.7%) with the comparable ΔT_{sol} of 12%.

4.2 Experimental Methods

4.2.1 Preparation of VO₂-NP

The crystalline VO₂-NP were prepared by the simple bead-milling method. The micro-sized commercial VO₂ powder 23 wt% (originally 99%, Alfa Aesar) was dispersed in an organic solvent, dipropylene glycol methyl ether (DPM), in the presence of a dispersing agent, Disperbyk 180 (4.5 wt%). Subsequently, the obtained dispersion was milled for 4 h in Dyno-Mill Research Lab WAB with the use of zirconia beads (0.2-0.4 mm) at the speed of 4200 rpm, followed by settling in the ambient condition for 2 days. The nano-sized particles with nano-size were suspended in the colloidal solution, which were used for the following experiments.

4.2.2 Preparation of VO₂/Si-Al nanocomposites on float glass

The nano-sized VO₂ particles were dispersed in a Si-Al gel with a series of solid content, explicitly 2.5, 5, 10, 12.5 and 15 wt%. The preparation method of Si-Al gel had been illustrated in the Section 3.1.1.2.^[12] The VO₂-NP and Si-Al gel were mixed using the Vortex Mixer (Thermo Fisher Scientific Inc.) for 1 h to obtain a homogeneous composite gel. Finally, this VO₂/Si-Al gel nanocomposite was casted onto a float glass substrate as shown in **Figure 4.1**.

Figure 4.1 Schematic illustration of the preparation procedures of VO₂-NP and VO₂/Si-Al gel nanocomposite foils on float glass substrates. Reproduced with permission from Reference ^[11]. Copyright 2013, Elsevier Inc.

4.2.3 Characterization

A) XRD: The crystallinity of VO₂-NP before and after bead-milling are examined by XRD using a Bruker D8 Advance diffractometer (U.S.A.) (Cu K α , $\lambda = 0.15406$ nm) with 40 kV and 30 mA. **B) TEM:** The morphologies of both the pure polymer matrix and VO₂@Si-Al nanocomposites were characterized by Carl Zeiss LIBRA[®] 120 in-column energy filter TEM (ZEISS International, Germany) equipped with an integrated OMEGA filter, which also can detect the elemental distributions in the nanocomposites and provide the energy spectroscopic images (ESI) with the mapping results of vanadium (V), silicon (Si) and aluminum (Al). **C) DLS:** The particle size and distribution of the bead milled VO₂-NP in the upper portion of the DPM dispersions were measured by a Nano S particle size analyzer (Malvern Instruments Co., Ltd., U.K.). **D) UV-Vis-NIR Spectroscopy:** The optical transmittance in the range of 250-2500 nm was measured with a Cary 5000 UV-Vis-NIR spectrophotometer (Agilent Ltd., U.S.A.) equipped with a Linkam PE120 system (U.K.) simple Peltier heating & cooling stage.

4.2.4 Calculations of thermochromic properties

The integral luminous transmittance (T_{lum} , 380-780 nm) and solar transmittance (T_{sol} , 280-2500 nm) were calculated based on the recorded spectra using the following expression:

$$T_{lum/sol} = \frac{\int \varphi_{lum/sol}(\lambda)T(\lambda)d\lambda}{\int \varphi_{lum/sol}(\lambda)d\lambda} \quad (4.1)$$

$$\Delta T_{sol} = T_{sol(20\text{ }^{\circ}\text{C})} - T_{sol(90\text{ }^{\circ}\text{C})} \quad (4.2)$$

where $T(\lambda)$ is the recorded foil transmittance, φ_{lum} is the standard luminous efficiency function for the photopic vision of human eyes,^[13] and φ_{sol} is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon).^[14]

4.3 Principle Outcomes

4.3.1 Preparation of crystalline VO₂ nanoparticles

As revealed in **Figure 4.2**, after 4 h milling and 2-day sedimentation, only the VO₂-NP with an average size of *ca.* 329 nm are suspended in the dispersion, which are utilized in this study. The inset presents the XRD patterns of both the commercially available VO₂ micropowder (before bead milling) and the nano-sized VO₂ particles after 4 h bead-milling. The two XRD patterns are normalized to the respective maximum intensities. The XRD data of after-milled VO₂-NP suggest that the after-milling products successfully maintain the monoclinic phase of VO₂ crystals (JCPDS #82-661), while the commercial micro-sized VO₂ powder includes some minor peaks that mostly attribute to the impurity of V₆O₁₃ (JCPDS #89-100). Meanwhile, the widening effect of the full width at half maximum (FWHM) for the main peaks of the after-milled sample can be clearly observed, which is resulted from the size-effects of nanomaterials. To illustrate this phenomenon, theoretical calculations based on the Scherrer equation are applied to the (110) reflection for both before- and after-milled samples. The results indicate that the crystal size of VO₂(M) particles has changed from greater than 100 nm (before milling) to *ca.* 10.7 nm (after milling), which reveals that the bead-milling preparation method leads to an efficient reduction of the VO₂ particle size without distorting its crystal structure and hence facilitating the maintenance of the “nanothermochromic” properties.

Figure 4.2 Particle size and distribution of VO₂ nanoparticles after 4h bead-milling; The Inset XRD patterns are attributed to the commercial VO₂ microparticles (solid red line) and after-milled VO₂ nanoparticles (dotted black line). Reproduced with permission from Reference [11]. Copyright 2013, Elsevier Inc.

4.3.2 VO₂/Si-Al gel nanocomposite with different solid content

Figure 4.3(a) demonstrates the TEM image of pure Si-Al matrix, which has homogeneous appearance and uniform morphology. **Figure 4.3(b)** and **4.3(c)** present the morphology and distribution of VO₂-NP in the Si-Al gel matrix at different magnifications. The after-milling particles are non-spherical in shape and well dispersed in the matrix with no agglomeration, and the particle size is approximately 20 nm. The observed particles size is less than the particle analyzer result (**Figure 4.2**), which could be due to the fact that the agglomerated particles after attrition are de-agglomerated during the Vortex mixing and the PVP in the Si-Al gel facilitates the VO₂-NP to disperse uniformly in the matrix. **Figure 4.3(d)** shows the TEM ESI mapping image with reference to **Figure 4.3(c)**. It is worth noticing that the majority of Si and Al (especially Si) are gathered on the surface of VO₂-NP in contrast to gel phase. Si-Al gel forms a “shell-like” structure which encapsulates the VO₂-NP. The driving mechanism is to lower the total free energy as that the VO₂-NP provide the heterogeneous deposition sites, which are favored by Si and Al particles in the gel.

Figure 4.3 TEM micrographs of (a) pure Si-Al matrix, (b) VO₂/Si-Al gel nanocomposite foil with 10% solid content at a low magnification (x80000), (c) at a higher magnification (x100000), (d) TEM ESI mapping image of 4.3(c) (green: vanadium (V); blue: silicon (Si); red: aluminum (Al)). Reproduced with permission from Reference [11]. Copyright 2013, Elsevier Inc.

Table 4.2 shows the thermochromic performances obtained by utilizing the VO₂/Si-Al nanocomposites with the different VO₂ solid content and the fixed foil thickness of *ca.* 3.3 μm . At a low VO₂ solid content ratio of 2.5 wt%, the composite foil indicates a high T_{lum} but negligible ΔT_{sol} . As VO₂ loading increases to 10 wt%, the T_{lum} is reduced with increasing ΔT_{sol} and the optimized combination of thermochromic properties (T_{lum} of *ca.* 60% and ΔT_{sol} of *ca.* 8%) can be achieved. This could be understood since with increasing VO₂ loading, more thermochromic nanofillers contribute to the enhancement of ΔT_{sol} , while more visible light was scattered and absorbed at the same moment, leading to a reduced T_{lum} . On the other hand, both optical transmittance and solar modulation ability are decreased, when the solid content is greater than 10%. This is due to the fact that when the loading of VO₂-NP exceeds 10%, the dispersion is no longer transparent and uniform. As shown in **Figure 4.4**, the composites prepared in a low (5 wt%) solid content

produces a clear and flawless morphology, while the high (15 wt%) solid content sample presents many large agglomerations of VO₂ particles.

Table 4. 2 The thermochromic properties of VO₂/Si-Al gel nanocomposite foils with different solid content ratios of VO₂ nanoparticles

Solid content of VO ₂ (wt%)	T_{lum} (%)		T_{sol} (%)		ΔT_{sol} (%)
	20 °C	90 °C	20 °C	90 °C	
2.5	80.3	81.9	76.7	76.7	-0.01
5.0	69.8	69.2	67.1	61.6	5.5
10.0	59.5	57.1	59.2	51.3	7.9
12.5	55.6	53.4	56.9	50.1	6.8
15.0	56.0	56.3	57.1	55.5	1.6

Figure 4. 4 Digital photographs of samples with the different solid content of VO₂-NP at 5% and 15%. Reproduced with permission from Reference ^[11]. Copyright 2013, Elsevier Inc.

4.3.3 VO₂/Si-Al gel nanocomposites with different foil thickness

With a fixed VO₂ solid content of 10 wt%, the UV-Vis-NIR spectra of VO₂/Si-Al nanocomposites with different foil thickness (1, 1.4, 2, 3 μ m) are revealed in **Figure 4.5(a)** and the corresponding T_{lum} and ΔT_{sol} are tabulated in **Table 4.3**. It is worth to note that with increasing thickness, the transmission difference at 2500 nm ($T\%$ contrast @ $\lambda=2.5 \mu$ m) is amplified from 1.67%, 6.24%, 6.35% to 13.83% and the overall ΔT_{sol} is boosted from 0.45% to 12.0% (as shown

in **Figure 4.5(b)**), accompanied by the enhanced solar heat shielding ability $(1-T_{\text{sol}}(90^\circ\text{C}))$,^[15] which efficiently assists to minimize the solar heat, as well as the energy demand for space cooling during the hot summer.^[8,16] The digital images of the composites with 1 μm and 3 μm thickness are shown in **Figure 4.5(c)** and both foils are flawless and transparent. The foil with 3 μm thickness reveals a dark brownish color as contrasted to light greenish color in 1 μm foil (due to less solid content). It is worth noting that the sample with foil thickness of 3 μm (and VO₂ solid content 10 wt%) indicates a large ΔT_{sol} of 12.0% with the high $T_{\text{lum}}(20^\circ\text{C})$ of 63.7% and $T_{\text{lum}}(90^\circ\text{C})$ of 54.4%. This combination of nanothermochromic performances is comparable with the recent reported pure VO₂-NP based nanocomposites^[9,10] (as summarized in **Table 4.1**).

Figure 4.5 (a) Transmittance spectra of foils with different thickness, (b) $1-T_{\text{sol}}(90^\circ\text{C})$ and ΔT_{sol} changes with the thickness of VO₂/Si-Al nanocomposites (Note: higher $1-T_{\text{sol}}(90^\circ\text{C})$ indicates better solar heat shielding ability in summer time), (c) Digital photographs of the samples with different foil thickness of 1.03 μm and 3.02 μm , respectively. Reproduced with permission from Reference ^[11]. Copyright 2013, Elsevier Inc.

Table 4.3 The thermochromic properties of VO₂/Si-Al nanocomposite foils with different foil thicknesses

Thickness (μm)	T_{lum} (%)		T_{sol} (%)		ΔT_{sol} (%)
	20°C	90°C	20°C	90°C	
1.0	78.7	79.4	74.9	74.4	0.5
1.4	71.1	71.2	68.1	65.2	2.9
2.0	72.0	69.4	68.8	63.4	5.4
<u>3.0</u>	<u>63.7</u>	<u>54.4</u>	<u>61.9</u>	<u>49.9</u>	<u>12.0</u>

4.4 Conclusions

VO₂-NP with a dimension of approximately 20 nm are successfully obtained by utilizing the industrial scalable bead-milling method. The VO₂/Si-Al nanocomposite foils are formed by incorporating the mechanically attrited VO₂-NP in the transparent Si-Al gel matrix. This straightforward approach produces the pure VO₂-NP based nanocomposites with significantly enhanced $T_{\text{lum(avg)}}$ of *ca.* 60%) and the noticeable ΔT_{sol} of 12%. This combination of both enhanced T_{lum} and ΔT_{sol} is comparable to the contemporary results of pure VO₂-based nanocomposites and promotes the potential thermochromic smart windows to the real life applications.

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Chapter 5

VO₂ Grid-patterning: Simulations and Experiments

This chapter presents a novel “VO₂ nanogrid” concept via using Finite Difference Time Domain (FDTD) simulations for achieving high average luminous transmittance ($T_{lum(avg)}=76.6\%$) while maintaining the solar modulation ability ($\Delta T_{sol}=14\%$). The nanogrids utilize the orderly-patterned nanoholes to favorably transmit visible light with retaining large infrared (IR) modulation. Numerical optimizations using parameter search algorithms have implemented by varying the size and shape of grids, fill factor (FF), film thickness and cell periodicity. Next, an appealing electrochemical deposition approach is used to physically implement the concept of VO₂ grid-patterning. This new approach is based on altering the ionic strength near the electrode surface by applying moderate electrical potentials. VO₂ nanoparticles (VO₂-NP) are electrodeposited on the conductive grids of the flexible electrodes directly (not ‘formed upon deposition’) from their aqueous suspensions without involving the reduction-oxidation (red-ox) of the nanoparticles. The key parameters (i.e. line width, thickness and FF) of the VO₂-NP grid-patterning can be controlled by fine-tuning the deposition conditions. The relationship between FF and thermochromic properties are proved physically with reference to the simulation results. Furthermore, this new electrochemical method can be universally applied to form the grid-patterning of the intact 0D-2D nanomaterials, which are necessary for the nanomaterial-containing devices.

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5.1 Introduction

The energy usage of buildings within the United States of America (U.S.A) is between 20% and 40% of U.S.A. primary energy demand and roughly half of this portion is truly spent on heating or cooling buildings.^[1] So as to cut down the energy consumption of air conditioning, the incorporation of the vanadium dioxide (VO₂) based thermochromic smart windows has been thought of as a “green” resolution to enhance the energy efficiency of buildings.^[2–4] The practical windows need luminous transmittance (T_{lum}) larger than 60%^[5,6] while maintaining moderately high solar modulation (ΔT_{sol}) at the same time. The perplexity of improving the T_{lum} and ΔT_{sol} simultaneously has been attempted *via* simulations with the considerations of a range of VO₂ nanostructures as shown in **Table 5.1** and the efficacy of some simulations have been proved experimentally.^[7–11]

Table 5.1 A comparison of simulated thermochromic performances presented by contemporary VO₂ smart window systems

		ΔT_{sol}	$T_{\text{lum(low)}}$	$T_{\text{lum(high)}}$	Remark
Nanoporosity	Simulation	6%	81%	-	15 nm thickness with 35% porosity ^[10]
Nanocomposite	Simulation	10%	82%	77.5%	Dilute spheroidal nanoparticles with filling factor of 0.01 in a dielectric matrix (dielectric constant $\epsilon_m=2.25$) ^[12]
Biomimetic moth-eye nanostructures	Simulation	15.5%	70%	67%	500 nm tall 135 nm base-width nanostructures coated with 7.5 nm of VO ₂ ^[13]
Ref.: continuous films	Simulation	13.5%	33.5%	26%	100 nm thin solid films ^[14]

Introducing pores (air vacancies) into VO₂ films^[10] moderates the overall optical constants, thereby overcoming the physical limits of VO₂ continuous thin films.^[12] By incorporating VO₂ nanoparticles (VO₂-NP) in a dielectric matrix,^[8,9,12,15] large optical absorption of VO₂ in the continuous films can be mitigated, thereby increasing T_{lum} . Biomimetic nanostructures^[11,13] with high aspect ratio nanocones provide the anti-reflection (AR) functionality, which leads

to the largely improved T_{lum} . Also, the considerable amount of VO₂ deposited on the nanocones template offers the noticeable ΔT_{sol} . However, the process of preparing the fine crystalline VO₂-NP or obtaining the high aspect ratio nanocones usually involves complex procedures, low reproducibility and poor durability.^[9,15,16]

To maximize T_{lum} without the cost of ΔT_{sol} , this study pioneers the novel designs of thermochromic smart windows *via* using the “nanogrid” patterned VO₂-based films.^[17] The grid-patterning structures create the physical pathway for the short-wavelength visible light by introducing nanoholes, while the abundant ridge area is capable of holding a high spatial volume of VO₂, thereby retaining the advantageous long-wavelength near-infrared (NIR) modulating abilities of VO₂ and facilitating to achieve a strong ΔT_{sol} . The dimension and shape of nanogrid design, as well as fill factor (FF), cell periodicity and film thickness are investigated by using the finite difference time domain (FDTD) simulations. The calculated data demonstrate that nanopatterned films offer the significant improvement of T_{lum} without deteriorating ΔT_{sol} , which open a new approach to enhance thermochromic properties for real-life smart windows.

Moreover, the previous experimental studies of the grid-patterned VO₂ (*i.e.* the periodic porous VO₂ nanostructure^[18]) adopted the PS templates and the post-annealing process to passively control the dimensions of the patterns, while the high processing temperature restricted the usage of the low-temperature-endurance substrates (*e.g.*, polymer foils). To tackle these issues, the electrochemical deposition of the crystalline VO₂-NP on the conductive grids is of great interest due to: 1) the electrochemical method offers the active control of the deposits’ dimensions *via* fine-tuning the deposition conditions; 2) the crystallized VO₂-NP eliminate the evolvement of post-annealing and broaden the selection of substrates; 3) the conductive grids provide the skeleton for the straightforward “bottom-up” approach. Nevertheless, electrodeposition is usually driven by the red-ox process of molecular or ionic species, which results in the synthesis of a less-soluble continuous or nanostructured coating on the electrode surface. In the majority of

nanomaterials' electrodepositions, the nanostructures are formed upon deposition. Relatively few previous investigations reported that nanomaterials could be deposited (not 'formed upon deposition') in a single-electrochemical step from their dispersion and under mild potentials. For example, the red-ox of protic solvent was required to alter the pH adjacent to the electrode surface, which diminished the interparticle repulsion and resulted in nanomaterial deposition.^[19–24] However, the electrochemical reduction of target nanoobjects was often observed,^[23,24] which might deteriorate the intrinsic properties of nanomaterials and thus become undesirable for applications. In this respect, electrophoresis should be mentioned, which has been used for the deposition of nanomaterials, yet, under high electrical fields using tens or hundreds of Volts.

Here, a novel approach for implementing the grid-patterned VO₂-NP is developed *via* innovating the ionic strength induced electrodeposition (**Figure 5.1**).^[25] Specifically, a copper electrode is electrochemically oxidized under well-controlled conditions to generate a flux of copper ions. The latter creates a gradient of ionic strength at the vicinity of the Cu electrodes and therefore decreases the electrical double layer (EDL) interparticle repulsion between the negatively charged VO₂-NP, leading to the local deposition of VO₂-NP without involving the red-ox reactions on the nanomaterials. Preliminarily, the morphology, crystallinity and the adhesion-to-substrate of the deposited VO₂-NP are examined on Cu plates to demonstrate the quality of VO₂-NP deposits. The line width, thickness and FF of deposits on Cu-grid/PET substrates are actively controlled by applying very moderate potential (0.05 V) for different deposition time. The relationship between FF of free area and thermochromic performance of VO₂-NP grid-patterning is analyzed with the comparison against the simulated nanogrid results.

Furthermore, this new approach is also extensively applied to directly deposit the zero-dimensional (0D) gold nanoparticles (AuNP), one-dimensional (1D) carbon nanotubes (CNT) and two-dimensional (2D) graphene oxides (GO) on the gridded Cu electrodes with a good maintenance of the original morphology and

materials' properties, which might be necessary for the fabrication of the nanomaterials-containing devices, such as flexible displays, solar cell and chemical/bio-sensors.

Figure 5.1 Schematics of the ionic-strength induced electrodeposition. The Cu electrode generates a flux of Cu ions, which deplete the interparticle repulsion and drive the deposition of VO₂-NP without involving the red-ox reactions. Reproduced with permission from Reference [25]. Copyright 2016, The Royal Society of Chemistry.

5.2 Methods

5.2.1 Simulation Methods

5.2.1.1 Structural models of VO₂-based nanogrid films

Figure 5.2 Three different three-dimensional (3D) models of VO₂-based nanogrid films, (a) square holes in square lattices, (b) circular holes in square lattices and (c) circular

holes in hexagonal lattices are densely packed with defined thickness (d), periodicity (p) and hole length (l)/radius (r) as labeled. Reproduced with permission from Reference ^[17]. Copyright 2015, Optical Society of America.

In order for the nanogrid films not to diffract visible light or be resolved by incident light, the cell periodicity (see **Figure 5.2**), which is defined as the distance between two adjacent holes, should be smaller than the wavelength of the visible light in the medium.^[26,27] The coating thickness should not be too large to degrade window transmittance due to light absorption.^[13] Three structural models used in current optical simulation work are schematically illustrated in **Figure 5.2**, namely square cells with square holes (**Figure 5.2(a)**),^[26,28] square cells with circular holes (**Figure 5.2(b)**)^[29–31] and hexagonal cells with circular holes (the most densely packed) (**Figure 5.2(c)**).^[13,32,33]

5.2.1.2 FDTD simulation

(A collaboration with Prof. Ibrahim Abdulhalim and Dr. Igal Balin)

We performed 3D FDTD simulations using commercial software (FDTD solution, Lumerical Inc. Vancouver, Canada). A uniform mesh size of 3 nm (X, Y, and Z directions) was selected. The optical constants of materials were taken in the spectrum range from 300 to 2500 nm.^[34] The dielectric dispersion profiles of the materials were fitted by the multi-coefficient model that relies on an extensive set of basic functions. To calculate the frequency dependent transmittance, PML boundary conditions were set for the Z direction, and Bloch boundary conditions were applied to X and Y directions of the simulation region. The VO₂ nanogrid films were supported by a glass substrate, the entire system was suspended in air/vacuum, and the incident beam was modeled as a plane wave traveling along the Z-axis. Field monitors were placed at fixed Z position below the surface of the VO₂ nanogrid films to detect the intensity of the transmitted beam.

5.2.2 Experimental Methods

5.2.2.1 Materials

Copper grids (70 μm line width $\times$ 0.4 μm line thickness $\times$ 1 mm spacing, given as a gift from Hanita Coatings, Israel) were pre-formed on polyethylene terephthalate (PET) and cleaned with ethanol (99%, Merck) and deionized (DI) water for 10 min sonication prior to use. The copper plates (25 mm length $\times$ 10 mm width $\times$ 0.5 mm thickness) served as the electrodes and substrates for VO₂-NP massive deposits. The plates were first polished with a 6 μm diamond suspension (Buehler, USA) and cleaned by sequentially sonicating in ethanol, acetone (Gadot, Israel) and DI water for 20 min, followed by Ar plasma cleaning (Diener Electronic, Germany) each side for 10 min. VO₂-NP (99.9%) were purchased from JingCheng Chemicals, China, and dispersed homogeneously in different concentrations (0.5/0.75/1.0 wt%) in DI water by ultra-sonication at 55 °C for 30 min. The AuNP (6-7 nm diameter, 63.2 $\mu\text{g/mL}$) dispersion in water with citric acid as a stabilizer was purchased from British Biocell, UK. The multi-walled CNT (MWCNT) (10-20 nm thickness, 0.5-2 μm length) were obtained from Cheap Tubes Incorporation (USA). The 0.5 wt% MWCNT were dispersed in a mixture of 1 wt% cetyltrimethylammonium bromide (CTAB), 25 vol% N-methyl-2-pyrrolidone (NMP) and DI water prior to electrodeposition. The 0.1 mg/mL GO dispersion in DI water was purchased from GRAnPH, Spain. NH₄Cl, KCl, K₂SO₄, CuCl₂, H₂SO₄ and HCl (37%), were acquired from Sigma-Aldrich and used as purchased. DI water (18.3 M Ω /cm, EasyPure UV, Barnstead, UK) was used for all the experiments.

5.2.2.2 Electrodeposition

All electrodeposition experiments were performed with a CHI 750B potentiostat (CH Instruments, USA) at room temperature using a standard three-electrode setup with an Ag/AgBr wire as a quasi-reference electrode (QRE) and a

Pt wire as a counter electrode. The working electrodes were the substrates, namely Cu grids on PET and Cu plates. A constant potential (which was varied between experiments) was applied to the working electrode for 10 to 180 s. After deposition, the films or grids were blow-dried with N₂ or Ar flow and the samples were placed in the vacuum desiccator overnight before characterization. The deposits thickness was investigated using a home-made Teflon O-ring electrochemical cell with a defined deposition area of 19.63 mm². Additionally, the deposits were immersed in 0.01 mol/L HCl for 1 to 5 min with magnetic stirring for removing copper ions. Only for checking the morphology of the massive deposition on bulk Cu plates, a 2.5×10⁻⁴ mol/L H₂SO₄ was added to the suspension.

5.2.2.3 Adhesion test

The adhesion between the VO₂-NP deposits and substrate was evaluated by the use of a cross-cut tape test, following American Standard Testing Method (ASTM) D 3359-09^[35] using a 3M Scotch® # 600 transparent tape.^[36–38] The VO₂-NP deposited on Cu plate was cross-cut into a lattice pattern. The tape was pasted firmly over the lattice for 90±30 s before removing rapidly at an angle close to 180 °. The tape tests were repeated three times at the same location by using a new area of the tape for each time. For reporting the adhesion strength, the calculation of the area affected was done by using Photoshop software CS version (Adobe System Inc., USA) according to the following **Equation 5.1**.

$$\text{Percent area removed} = \frac{\text{Pixels before applying the tape} - \text{Pixels after removing the tape}}{\text{Pixels before applying the tape}} \times 100\% \quad (5.1)$$

5.2.2.4 Characterizations

A) DLS: The (zeta) ζ-potential and average particle size of VO₂-NP were measured using Zetasizer Nano-ZS instrument (Malvern instruments, UK) at

various pH values and ionic strengths. The pH was measured just prior to the ζ -potential measurement and the selected electrolytes were added (in various concentrations) to the 1 wt% VO₂-NP dispersion to achieve a series of ionic strengths. The ζ -potentials of 63.2 $\mu\text{g/mL}$ AuNP and 0.05 wt% MWCNT were determined by the same instrument without altering the pH of solutions. **B) SEM:** The size and shape of nanomaterials were characterized by the extremely high resolution SEM (XHR-SEM) Magellan TM 400L (FEI, USA), which was equipped with an EDX detector (X-Max 20, Oxford Instruments, UK) for analyzing the composition before and after removing the copper ions. **C) TEM:** Characterization of AuNP and the elemental mapping of V and Cu were carried out using high resolution TEM (HRTEM) Tecnai F20 G2 (FEI, USA) with EDX detector (X-Max 20; spectral resolution 133 eV) and high angular annular dark-field (HAADF) detector, allowing high resolution scanning transmission electron microscopy (STEM) Z-contrast imaging. **D) XRD:** The XRD patterns within the 2θ range 10° to 60° were recorded on a D8 Advance diffractometer (Bruker AXS, Germany) at room temperature using Cu K α radiation ($\lambda=1.5418 \text{ \AA}$). **E) XPS:** The XPS analysis was performed with Kratos Axis Ultra spectrometer (Kratos Analytical Ltd., UK) using Al-K α monochromatic radiation X-ray source (1486.7 eV) and the binding energies were calibrated using C 1s peak energy as 285.0 eV. Raman scattering was performed on the InVia Raman microscope (Renishaw plc, UK) using a 514 nm laser source. **F) Surface Profilometer:** The thickness of the deposits was measured using a surface profilometer (P 15, KLA-Tencor Co., USA). **G) UV-Vis-NIR Spectroscopy:** The optical transmittance in the wavelength range of 250-2200 nm was recorded using the Lambda 1050 UV-Visible-Near IR spectrophotometer (UV-Vis-NIR, PerkinElmer, USA) with Peltier temperature control accessory.

5.2.3 Calculations of the typical thermochromic properties

In order to quantify the amount of visible light useful for human vision under normal conditions, a photopically averaged transmittance has been defined as T_{lum} . Also, the terms of T_{IR} and T_{sol} are to define the infrared (IR) light and solar averaged

transmittance, respectively, as to quantify the amount of IR or solar thermal energy entering a building. Upon these determinations, the modulations of transmitted luminous, IR and solar energy are characterized as ΔT_{lum} , ΔT_{IR} and ΔT_{sol} and they can be integrated by using the mathematical relationships stated below as **Equation 5.2** and **5.3**:

$$T_{\text{lum/IR/sol}} = \frac{\int \phi_{\text{lum/IR/sol}}(\lambda) T(\lambda) d\lambda}{\int \phi_{\text{lum/IR/sol}}(\lambda) d\lambda} \quad (5.2)$$

$$\Delta T_{\text{lum/IR/sol}} = T_{\text{lum/IR/sol}(\text{low})} - T_{\text{lum/IR/sol}(\text{high})} \quad (5.3)$$

where $T(\lambda)$ represents the measured spectral transmittance. Φ_{lum} is the standard luminous efficiency function of photonic vision,^[39] and $\Phi_{\text{IR/sol}}$ is the IR/solar irradiance spectrum distribution for air mass 1.5^[40] as it represents an overall yearly average for mid-latitudes including diffuse light from the ground and sky on a south facing surface tilted 37° from horizontal. The wavelength range used for T_{lum} is 380-780 nm corresponding to the limits of human vision. The wavelength range used for T_{IR} is 780-2500 nm (for simulation) or 780-2200 nm (for experiments due to the instrument limitations), while the IR light from 2200 to 2500 nm carries the negligible solar irradiance/energy.^[40] The calculation of T_{sol} uses the wavelength of 300-2500 nm (for simulation) or 280-2200 nm (for experiments due to the instrument limitations), which account for *ca.* 99% of terrestrial solar energy.^[40]

5.3 Principle Outcomes of Simulations

5.3.1 Square nanoholes in the square cells

The contour (see **Figure 5.3**) suggests that with fixed periodicity, larger holes lead to increased T_{lum} and depressed ΔT_{sol} , which is consistent with other observations.^[8,41] The table inserted as **Table 5.2** shows three selected samples and it suggested that T_{lum} could be enhanced without much sacrifice on ΔT_{sol} compared with continuous thin films. For an unknown reason, the sample with the period size of 180 nm and hole size of 80 nm as highlighted gives both enhanced $T_{\text{lum(avg)}}$ (29.0

vs. 26.0 %) and ΔT_{sol} (14.7 vs. 11.1 %) compared with continuous films. This proves the efficiencies of nanogrid VO₂ structures, which has the great potential to enhance both T_{lum} and ΔT_{sol} .

Figure 5.3 Thermochromic properties for square holes perforated in VO₂ square cells at different values of periodicity and square hole length. Contour lines (red dashed) of ΔT_{sol} are overlaid upon a contour map of T_{lum} . Reproduced with permission from Reference [17]. Copyright 2015, Optical Society of America.

Table 5.2 Thermochromic properties of selected samples in Figure 5.3.

Thickness (nm)	Periodicity (nm)	Square hole size (nm)	T_{lum} (%)		T_{IR} (%)		T_{sol} (%)		ΔT_{sol} (%)
			Low temp.	High temp.	Low temp.	High temp.	Low temp.	High temp.	
110	-*	-*	26.3	25.6	37.0	13.0	29.1	18.0	11.1
	150	60	31.6	31.5	44.1	19.8	34.4	23.7	10.7
	180	80	31.1	26.8	45.7	16.2	34.9	20.2	14.7
	180	90	32.3	32.6	48.3	24.4	36.5	26.2	10.3

*Reference: 110 nm solid thin film

5.3.2 Structure design for nanogrids

Different nanostructures may induce different optical performance due to light interaction with different shapes of holes and cells. To exploit the shape and size effects, the nanogrid films are fixed the thickness at 110 nm and determined

the periodicity at 180 nm. The computational results for each system are schematically displayed in **Figure 5.4(a)-5.4(d)** respectively.

According to **Figure 5.4(a)**, by inserting square holes into square cells with increasing hole length, the T_{lum} at both low and high temperature (black and red bar) are increased dramatically when the FF ($= \frac{\text{Area}(\text{hole})}{\text{Area}(\text{cell})}$) reaches to *ca.* 70% at the sacrifice of the ΔT_{sol} (blue bar). $T_{\text{lum}(\text{low})}$ elevates dramatically from hole length of 30 nm to hole length of 150 nm, whereas the value is surpassed by $T_{\text{lum}(\text{high})}$ once hole length is greater than 90 nm, leading to an undesirable spectrum overlap in the visible range (*i.e.* negative ΔT_{lum}). Since the short-wavelength visible light carries half of energy in the entire solar spectra,^[42] the negative ΔT_{lum} induces an observable degradation in ΔT_{sol} , which is undesirable for a good thermochromic performance.

The large increments of T_{lum} with increasing hole size also occur in the circular hole design systems either in square cells or in hexagonal cells as illustrated in **Figure 5.4(b)** and **5.4(c)**. By comparing with square holes, the circular one reveals better thermochromic behaviors, because T_{lum} is doubled without jeopardizing ΔT_{sol} appreciably. The highest averaged T_{lum} has been enhanced to 63%, together with securely maintained ΔT_{sol} at 9.2%, when 80 nm radius circular holes arrange in 180 nm period hexagonal cells.

By summarizing the relationship between FF and the transmission, it suggested that the T_{lum} , T_{IR} and T_{sol} at both low and high temperature are dominantly controlled by FF instead of the hole size or shape. This gives a general guideline for enhancing T_{lum} . In contrast, increasing the FF has much more complicated effects on the transmission difference between high and low temperatures as shown in **Figure 5.4(f)**, which is to the advantage of the possibility to enhance both T_{lum} and ΔT_{sol} simultaneously via increasing the FF. It is of interest to observe that the ΔT_{IR} , ΔT_{sol} and ΔT_{sol} relate with the FF in a parallel way.

Figure 5.4 Relationship between nanogrids' parameters and thermochromic properties in terms of (a) square holes (hole length varied from 30 to 150 nm) in square cells; (b) circular holes (hole radius varied from 20 to 80 nm) in square cells; (c) circular holes (hole radius varied from 20 to 80 nm) in hexagonal cells; (d) four different structural systems with similar FF; (e) solar transmittance and (f) light modulation ability as a function of FF of nanogrid films. Reproduced with permission from Reference [17]. Copyright 2015, Optical Society of America.

5.3.3 Circular nanoholes in the hexagonal cells

5.3.3.1 Thickness effect

As T_{lum} could be largely enhanced by increasing FF, circular holes in hexagonal cells are chosen for further study due to the closest packed characteristics of such structure. In order to achieve ΔT_{sol} much higher than that of continuous VO₂ thin film, thickening the nanogrid films could be a feasible solution to raise VO₂ content and compensate the slightly sacrificed ΔT_{sol} when the FF is increased (referring to **Figure 5.4(c)**). With fixed periodicity and hole size, ΔT_{sol} and T_{lum} were studied by increasing film thickness. The highest ΔT_{sol} achievable is 16.7% if the film thickness is as thick as 400 nm (see **Figure 5.5(a)**). T_{lum} keeps decreasing as the thickness increases. It is of great interest that as compared to simulated continuous thin films (see **Figure 5.5(b)**), the turning point of the thickness (defined by the point where thickening loses its effect on increasing ΔT_{sol}) of the nanogrid films can be much thicker (400 nm) than that of the continuous film (160 nm).

Figure 5.5 Computed (a) thickness effect on ΔT_{sol} (black) and $T_{\text{lum(avg)}}$ (blue) for nanogrid films with period=180 nm and hole radius=80 nm, and (b) thickness effect on continuous thin films (dashed black) and perforated nanogrid films (solid red). Reproduced with permission from Reference ^[17]. Copyright 2015, Optical Society of America.

5.3.3.2 Periodicity and FF

Figure 5.6 (a) Computed spectra of transmittance for VO₂ nanogrid films with different periodicity and FF as compared to continuous thin films. (Note: All film thickness=300 nm) (b) solar transmittance and (c) light modulation ability as a function of periodicity. Reproduced with permission from Reference [17]. Copyright 2015, Optical Society of America.

The influences of periodicity and FF on the optical behaviors are presented in **Figure 5.6(a)** with the fixed hole radius of 120 nm and the fixed film thickness of 300 nm. An obvious blue shift of the transmission peaks could be observed with reducing periodicity and increasing FF; meanwhile both transmission at high and low temperature increases dramatically. This is indicated in **Figure 5.6(b)** and transmission at both visible and NIR ranges could be enhanced significantly. Compared with continuous film, T_{lum} increases from 4.3 to 12.6% when the FF increases to 0.666. As the hole is touching the edge of the cell (*e.g.*: period=240 nm and radius=120 nm) with corresponding FF of 0.907, T_{lum} can be abruptly enhanced to nearly three times as compared with the sample where the FF is 0.773. Similar trends can be observed in both NIR transmission and solar transmission which

suggests that with touching holes, the whole solar transmission could be boosted enormously. The periodicity effects on modulation (**Figure 5.6(c)**) are more complicated. $\Delta T_{\text{lum}}/\Delta T_{\text{IR}}$ can be increased from 0.3%/18.8% (continuous film) to 5.0%/24.3% (the touching holes sample with corresponding largest FF). This, to a large extent, favors the largely enhanced ΔT_{sol} (8.6 vs. 14.0%) compared with continuous films.

5.3.4 Optimizations of parameters

The thermochromic properties of best performing samples are listed in **Table 5.3**. As hexagonal cells/circular holes provide the largest possible FF, good combinations of high transparency ($> 70\%$) with moderately high ΔT_{sol} ($>13\%$) could be obtained with touching-hole design (*i.e.* $p=2r$). This finding surpasses the best reported simulation results such as nanoporous thin film and nanothermochromic coatings (**Table 5.1**). Although the ΔT_{sol} is slightly lower (14.0% vs. 15.5%) than the biomimetic moth-eye nanostructuring, the $T_{\text{lum(avg)}}$ is higher (76.5% vs. 68.5%). It should be noted that such biomimetic moth-eye structure with 500 nm height and 135 nm base-width nanocone structuring is of a great technical challenge to achieve in practice.

Table 5.3 Typical thermochromic properties for the samples with optimized nanogrids' parameters

<i>Hexagonal cells + Circular holes</i>	Thickness $d = 300$ nm	
	Periodicity = 160 nm radius = 80 nm	Periodicity = 240 nm radius = 120 nm
	FF: 0.907	FF: 0.907
$T_{\text{lum}(20\text{ }^{\circ}\text{C})}$	<u>78.8</u>	<u>79.2</u>
$T_{\text{lum}(100\text{ }^{\circ}\text{C})}$	<u>75.7</u>	<u>74.2</u>
ΔT_{lum}	3.1	5.0
$T_{\text{IR}(20\text{ }^{\circ}\text{C})}$	89.9	90.8
$T_{\text{IR}(100\text{ }^{\circ}\text{C})}$	64.7	66.4
ΔT_{IR}	25.2	24.3
$T_{\text{sol}(20\text{ }^{\circ}\text{C})}$	80.3	80.5
$T_{\text{sol}(100\text{ }^{\circ}\text{C})}$	67.2	66.6
ΔT_{sol}	<u>13.0</u>	<u>14.0</u>

Lastly, it should be mentioned that diffraction effects from the periodic structures were considered and found to be negligible. For window applications it is essential that the light transmittance will be direct, *i.e.* the window should not be diffractive. In order to evaluate possible diffraction effects in VO₂ perforated film, the transmitted diffraction efficiencies at different orders were calculated using Rigorous Coupled Wave Analysis (RCWA).^[27] In the simulation, the circular holes were replaced with rectangular holes of the same surface area to reduce computation time. The calculations were performed for the optimum structure with the largest period. The diffraction depends on the ratio of the period to the wavelength and hence the highest effect is supposed to occur in the largest period and the shortest wavelengths. Therefore, the sample tested was with the period size of 240 nm, square hole size 212 nm, and thickness 300 nm. The transmission contribution is found mainly due to the zeroth order whereas the higher diffraction order efficiencies are up to 5% in the 500-600 nm range while it is less than 0.5% throughout the wavelength range 550-2500 nm.

5.4 Principle Outcomes of Experimental Implementations

5.4.1 Selection of metallic ions for efficient ionic-strength induced electrodeposition

In the absence of steric stabilization, VO₂-NP are surrounded by surface charges (**Figure 5.1**) and stabilized in the aqueous solutions homogeneously, based on the electrostatic interactions. According to the classic Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the total interaction energy is the sum of van der Waals (VDW) attraction and EDL repulsion.^[43,44] The EDL repulsion force/energy depends on the ionic concentration (c_i) of the electrolyte,^[45] which can be adjusted to ionic strength (I) by taking into account of both c_i and the ion valence (z_i) of all electrolyte species according to **Equation 5.4**:

$$I = \frac{\sum_i c_i z_i^2}{2} \quad (5.4)$$

Figure 5.7(a) presents the effect of different ions on the particle size of VO₂-NP dispersed in water. As evidenced, the electrolytes of monovalent cations, *i.e.* K⁺ and NH₄⁺, cause the increase of particle size (particle aggregation) at high concentration of these cations, but at a much lower concentration of the divalent ions, *i.e.* Cu²⁺. This implies that Cu²⁺ is able to enhance the ionic strength sharply and decrease the stability of VO₂-NP in water dispersions dramatically. This could be qualitatively understood using DLVO theory, which indicates that increasing ionic strength causes a compression of the diffuse parts of the EDL around the particles, diminishing electrostatic repulsion forces, and thereby promoting aggregation (particles approaching particles) or deposition (particles approaching a collector surface).^[46,47] Furthermore, the ζ -potential of the VO₂-NP dispersed in pure water is *ca.* -40 mV (**Figure 5.7(b)**), which is clearly pH dependent; however, the average particle size is independent of the pH. The quantitative interpretation of these phenomena is that colloidal particles start rapid aggregation once the c_i of counter-ions (M^{n+}) is equal or greater than the critical coagulation concentration (CCC),^[48] which is the minimum concentration of M^{n+} needed to induce aggregation of nanoobjects. As revealed by the DLS results (**Figure 5.7(a)**), $CCCs$ of KCl/NH₄Cl/CuCl₂ are 2.5, 2.5 and 0.25 mmol/L, respectively, which shows considerable dependence upon the charge number (z) of M^{n+} . The CCC is proportional to z^{-6} - z^{-2} and depends on the ζ -potential of nanomaterials.^[47] The CCC_{CuCl_2} is ten times smaller than CCC_{KCl/NH_4Cl} and the ratio is $2^{-3.32}$ (0.25:2.5), which is in line with the Schulze-Hardy rule which was revised for low ζ -potential particles^[49] (common for different nanomaterials).^[47,50,51] Theoretically, increasing z of M^{n+} to 3⁺, *e.g.*, Fe³⁺>Cu²⁺>Ag⁺, would cause efficient aggregation at even lower concentrations. However, it is worth noticing that M^{n+} tends to be more hydrolyzed in the higher oxidation states and therefore it requires substantially more acidic conditions^[52] to be stabilized as compared to the lower valence state of M^{n+} . Hence, to generate stable highly charged species requires employing high ionic strength due to the additional acidity, which will make it impossible to control the deposition electrochemically.

Figure 5.7 DLS results show: (a) the ionic concentration (or ionic strength) effects of different cations on the average particle size of VO₂-NP. The inset is the zoom-in image for c_i in the region of 0-0.3 mmol L⁻¹; (b) the effect of pH on the ζ -potential (blue spheres) and the average particle size (black triangles) of VO₂-NP; (c) Cu 2p XPS peaks of the VO₂-NP deposited on Cu substrate at 0.1 V (vs. Ag/AgBr) for 45 s. Reproduced with permission from Reference [25]. Copyright 2016, The Royal Society of Chemistry.

In the new electrodeposition concept, the c_i (or I) is the key factor for inducing the nanomaterial deposition and this can be electrochemically controlled by applying an electrical bias for a certain duration in order to generate sufficient M^{n+} . A flux of M^{n+} diffuses along a mean-square distance (x) during the deposition time (t). Since $x \propto \sqrt{Dt}$ is based on diffusion law,^[53] in which D denotes the diffusion coefficient, the average c_i can be approximately represented by **Equation 5.5**:

$$c_i \propto \frac{Q}{zFA\sqrt{Dt}} \quad (5.5)$$

where Q is the total charge collected by the electrode (for faradic processes), A is the deposition area on the electrode and F stands for the Faraday constant. In an example of applying the deposition concept, a copper electrode is employed to deposit VO₂-NP which are dispersed in water, and Cu²⁺ serves as the main source (see XPS of the deposit in **Figure 5.7(c)**) of the counter-ions, *i.e.* $z=2$, and is responsible for increasing I . Upon applying a potential of 0.05 V (vs. Ag/AgBr) for 20 s, the average c_i of Cu²⁺ close to electrode surface is *ca.* 0.398 mmol/L based on the measurements of Q (as a function of time), A , and considering $D_{Cu^{2+}} = 7.14 \times 10^{-6} \text{ cm}^2/\text{s}$ (at 25 °C).^[54] Thus, the electrochemically generated c_i (or I) is greater than the CCC_{CuCl_2} (0.25 mmol/L). The calculations (tabulated in **Table 5.4**) theoretically demonstrate that applying a moderate potential ($\ll 1$ V) to the copper electrode for a short time can easily generate the abrupt increment of c_i (or I) near electrode surface, which is adequate for inducing the rapid coagulation of VO₂-NP and eventually obtaining massive deposition of nanomaterials on the substrate (working electrode). Hence, choosing copper ions as a source for the alteration of the c_i (or I) offers two advantages: 1) their relative stability in the aqueous environment and 2) the ease of electrochemically boosting the $c_{Cu^{2+}}$ at the electrode surface.

Table 5.4 Electrochemically generated c_i (average) of Cu²⁺ close to electrode surface under different electrodeposition conditions

<i>Deposition time (s)</i>	<i>Potential (V) (vs. Ag/AgBr)</i>	<i>Cumulative charge (μC)</i>	<i>Average c_i of Cu^{2+} (mmol L^{-1})</i>
10	0.00	81	0.25
20	0.00	164	0.36
	0.05	180	0.40
	0.10	208	0.46
	0.15	234	0.52
	0.20	277	0.61
50	0.05	445	0.98
Ref.: CCC_{CuCl_2}	-	-	0.25

5.4.2 ‘Red-ox free’ electrodeposition of VO₂-NP on Cu plates

Figure 5.8(a) shows that indeed the ionic strength-induced electrodeposition is highly effective for depositing VO₂-NP massively in a compact microstructure. The XHR-SEM images of the deposits formed as a result of applying a moderate potential of 0.1 V *vs.* Ag/AgBr for 45 s indicate clearly that the nanoparticulate structure of VO₂-NP is intact (**Figure 5.8(b)**), as compared with the original size and shape of VO₂-NP (**Figure 5.8(c)**). It is worth mentioning that deposition is not driven by migration as in electrophoresis,^[55–57] which is evident by the very low (≤ 0.1 V *vs.* Ag/AgBr) applied potential that generates a flux of copper ions. The nanoparticle size is below 100 nm as demonstrated in **Figure 5.8(b)**, which is essential for achieving excellent nanothermochromic performance.^[58] **Figure 5.8(d)** displays the cross-section of the deposited film. It reveals the interface between the deposits and the Cu surface, which alludes the rapid assembly process of VO₂-NP to the substrate that leads to the formation of a porous film. The XRD results (**Figure 5.8(e)**) imply that the crystallinity and oxidation state of VO₂ (monoclinic phase, JCPDS# 82-661) are well maintained in the applied potential range from -0.1 V to 1.3 V (*vs.* Ag/AgBr) without producing vanadium oxide impurities in other oxidation states (such as V₂O₅ and V₂O₃). However, it was found that if the potential is increased to 1.5 V, the degree of crystallinity may be reduced since some minor peaks disappear (**Figure 5.8(e)**). In addition, the adhesion between VO₂-NP deposits and copper substrates was examined according to ASTM D 3359-09 cross-cut tape test.^[59] The test results (in the Appendix **Table A.1**) reveal that only small flakes along edges and at intersections of cuts were peeled off by the tape. The percent area removed is only *ca.* 8.3% after repeating the tape test for three times, which indicates very good adhesion and reliability for practical applications.

Figure 5.8 XHR-SEM images of low (a) and high (b) magnification top-view and (d) cross-section of VO₂-NP deposited on Cu plates at 0.1 V (vs. Ag/AgBr) for 45 s; (c) XHR-SEM images of VO₂-NP dispersed in DI water; (e) XRD patterns of VO₂-NP deposited under different potentials (−0.1–1.5 V) as comparing with the patterns of the commercial VO₂-NP (monoclinic). Figure (e) is reproduced with permission from Reference [25]. Copyright 2016, The Royal Society of Chemistry.

5.4.3 Deposition on Cu-grid/PET flexible substrates with the control of line width and thickness

Figure 5.9 (a) Optical images for the 0.75 wt% VO₂-NP dispersion deposited on flexible Cu grid/PET substrate under 0.05 V (vs. Ag/AgBr) for 40 s. Notice that the grid is transparent. SEM images of the intersections on the grid deposited using 0.75 wt% dispersion under 0.05 V for (b) 20 s (dashed-line area reveals Cu grids beneath the deposit), (c) 60 s, (d) 80 s. Notice that the VO₂-NP deposit is brighter and the PET substrate is darker. (e) Line width (deposited 0.75 wt% dispersion) and deposits thickness (excluding the height of Cu line and using 1 wt% dispersion) as a function of the square root of deposition

time. Reproduced with permission from Reference ^[25]. Copyright 2016, The Royal Society of Chemistry.

It is also worth noticing that deposition occurs initially only on the conductive part (dashed-line area in **Figure 5.9(b)**) of the flexible substrate (**Figure 5.9(a)**). The width of deposition can be controlled by the deposition time and can extend beyond the Cu grid borders (**Figure 5.9(c)** and **5.9(d)**). The results (**Figure 5.9(e)**) show that the average VO₂-NP line width and the deposits thickness increase linearly with the square root of deposition time (t). The slope of line width growth is approximately equal the square root of $2D_{Cu^{2+}}$, which suggests that the growth of deposited line depends predominately on the diffusion of Cu²⁺. Since the deposited samples were completely dried prior to measure the thickness, the thickness of the deposit increases slowly as compared with the growth rate of line width. This is due to the evaporation of solvents and the shrinking of the nanoparticles layer. Furthermore, AFM was employed to analyze the surface roughness of Cu lines, which might affect the ionic strength distribution in the vicinity of electrode and so modulate the deposition of nanomaterials. As shown in **Figure 5.10**, the surface of Cu lines is relatively smooth. The roughness in a $5 \times 5 \mu\text{m}^2$ area is 33 nm, which is substantially smaller than the diffusion layer and therefore the thickness of nanomaterial deposits. Therefore, surface roughness of the electrode does not have a significant effect on the deposition of nanomaterials in this approach.

Figure 5. 10 AFM analysis scans a $5 \times 5 \mu\text{m}^2$ area on the Cu line to demonstrate the topography of the electrode. Reproduced with permission from Reference [25]. Copyright 2016, The Royal Society of Chemistry.

5.4.4 FF and thermochromic properties of VO₂ grid-patterning smart windows

By prolonging the deposition time from 20 to 100 s while applying a moderate potential of 0.05 V, the VO₂-NP deposit progressively covers most of the substrate and therefore reduces the FF of free area from *ca.* 63% to 12%. It is of great interest and importance that the corresponding solar energy modulation abilities (i.e.: ΔT_{lum} , ΔT_{IR} , ΔT_{sol}) exhibit similar tendencies (**Figure 5.11(a)**) as compared with the previous simulation results (referring to **Figure 5.4(f)**). The experimental results suggest that the modulation abilities are better than that predicted by simulation. This is presumably attributed to the micro-sized opening, which reveals the advantage of amplifying the transmittance contrast in the IR region (ΔT_{IR}) as compared to the simulated nanogrid structure. Clearly, the smaller FF of free area results in the larger enhancement of ΔT_{sol} , which is attributed to the increment of total quantity of VO₂-NP and the growth of deposition thickness.

In contrast to VO₂ continuous film, increasing thickness no longer deviates the grid from a dynamic light modulator to a static absorber^[58] if exceeding

approximately 600 nm thickness limitation. Comparing the best-performing experimental results (0.75 wt% VO₂-NP dispersion deposited for 80 s to achieve 1.24 ± 0.11 μm VO₂ thickness on Cu grid) with the highest computed continuous film results (presented in Section 5.3.3.1) (**Figure 5.11(b)**), shows that $T_{\text{lum(avg)}}$ has dramatically improved by 143% (from 15.8% (thin film) to 38.4% (grid-pattern)) and ΔT_{sol} is enhanced from 12.1% (thin film) to 13.9% (grid-pattern) simultaneously. The NIR switching efficiency at $\lambda=2000$ nm is as large as 53%, which is superior to the contemporary report of VO₂ periodic porous structure.^[18] Electrodepositing of relatively diluted VO₂-NP dispersion (0.5 wt%) for a short time (20 s) obtains the deposits thickness (exclude Cu grid height) of 141 ± 19 nm and substantially improves $T_{\text{lum(avg)}}$ to 57.7% with a good combination of $\Delta T_{\text{sol}}=10.5\%$, which is comparable to the periodic porous design.^[18]

Figure 5.11 Performance of the VO₂-NP electrodeposited on a Cu grid: (a) Modulation abilities as a function of the FF (of free area) for the experimental and simulated results. (b) Transmittance spectra for the highest simulated continuous film (presented in Section 5.3.3.1) and the best experimental results of the VO₂-NP grid patterns. Figure (b) is adapted from Reference ^[25]. Copyright 2016, The Royal Society of Chemistry.

Furthermore, the EDX mappings of V and Cu (**Figure 5.12(a)-5.12(d)**) confirm that the copper ions interact with VO₂-NP only superficially and that several Cu clusters (<10 nm) form either at the inter-particle junction area or on the surface of VO₂-NP. It was found that two-thirds of all trapped copper ions can be

substituted by protons *via* simply immersing the sample in 0.01 mol/L HCl for 1-5 min, which is evidenced by EDX results (**Figure 5.12(e)**).

Figure 5.12 (a) TEM image of VO₂-NP deposits; (b) HAADF image of mapping area; (c) EDX mapping of V (in blue color); (d) EDX mapping of Cu (in orange color); (e) EDX of VO₂-NP deposits before and after immersing in 0.01 mol/L HCl for different durations. Reproduced with permission from Reference [25]. Copyright 2016, The Royal Society of Chemistry.

5.4.5 Extensive applications of ionic-strength induced electrodeposition to different dimensional nanomaterials

The new electrodeposition method can be universally applied (**Figure 5.13**) to deposit a variety of nanomaterials, such as 0D VO₂-NP and AuNP, 1D MWCNT, and 2D GO nanosheets. The ζ -potentials of AuNP (stabilized by citrate), MWCNT (stabilized by CTAB) and GO are *ca.* -22, +40 and -37 mV, respectively. As shown in **Figure 5.13(e)**, by applying moderate potentials (0.05-0.5 V), different types of nanomaterials can be effectively deposited at the conductive Cu grids, which are patterned on the substrate of PET. The size and shape of all nanostructures are well maintained as comparing the SEM and TEM images for particles in dispersion (**Figure 5.13(a1)**-**5.13(d1)**) and on the substrate after the deposition process (**Figure 5.13(a2)**-**5.13(d2)** and **Figure 5.13(a3)**-**5.13(d3)**).

Figure 5.13 (a) SEM images of VO₂-NP: (a1) in a dried droplet from the dispersion and (a2, a3) after electrodeposition under 0.05 V for 40 s; (b) TEM images of AuNP: (b1) in a dried droplet from the dispersion and (b2, b3) after electrodeposition under 0.2 V for 90 s; (c) SEM images of MWCNT: (c1) in a dried droplet from the dispersion and (c2, c3) after electrodeposition under 0.2 V for 90 s; (d) SEM images of GO: (d1) in a dried droplet from the dispersion and (d2, d3) after electrodeposition under 0.5 V for 180 s; (e) Optical images of different nanomaterials deposited on the conductive Cu grids. The inset of (b2) shows the SAED pattern of AuNP deposits. Reproduced with permission from Reference [25]. Copyright 2016, The Royal Society of Chemistry.

The characterizations of VO₂-NP have been elaborated in the previous sections. Besides that, the Selected Area Electron Diffraction (SAED) pattern (the inset of **Figure 5.13(b2)**) obtained from AuNP deposits is consistent with the

crystallography of gold. Also, the high resolution TEM image (**Figure 5.13(b3)**) clearly presents the lattice fringes of AuNP, which is in accordance with the d-spacing of Au (111) phase. The XPS analyses of MWCNT deposited on Cu substrates reveal that the atomic concentration of carbon is slightly reduced by 2% and the oxygen content is marginally increased up to 1.6 at% if the applied potential increases to 2 V, but there is no observable C-O or C=O peak generated by the new electrodeposition process. The MWCNT deposits show similar XPS results at the same peak position as compared with the commercial dispersion (**Figure A.1** in the appendix). Thus, this indicates that no significant red-ox reaction occurs on MWCNT during the new electrodeposition process. The Raman spectra of the GO dispersion (control) and GO electrodeposited on Cu grid/PET consist of two predominant D and G bands along with their weak 2D bands (**Figure A.2** in the appendix). The G band is due to the in plane stretching motion between sp² carbon atoms, while the D band indicates structural defects, edge effects and dangling sp² carbon bonds in disordered graphene-based materials. The D and G peak positions for all samples are centered at 1351 cm⁻¹ and 1598 cm⁻¹, respectively, without distinguishable peak shifting due to electrodeposition. Moreover, the Raman intensity ratio between D and G bands (I_D/I_G), which is often used to explain the redox state of GO (**Figure A.2**) showed only a marginal change of 1%-2% decrement of I_D/I_G . A typical increase of I_D/I_G involves the electrochemical reduction of GO.^[60,61] The slight change of I_D/I_G implies that the moderate potentials (≤ 1 V) are insufficient to oxidize GO with noticeable effects.

5.5 Conclusions

Numerical optimizations using parameter search algorithms have been executed through a series of FDTD simulations with taking account of film thickness, geometrical design of nanoholes and cells as well as periodicity and FF. This simulation study presents a novel concept for achieving high T_{lum} for thermochromic smart window applications *via* VO₂-based nanogrid films while maintaining the significant ΔT_{sol} (substantially larger than 10%) as required for

smart architectural window applications. Increasing the FF could tremendously enhance T_{lum} , and the largest possible T_{lum} (*ca.* 80%) could be acquired *via* touching-hole configuration in the “hexagonal cells with circular holes” design. Thickness effects on enhancing ΔT_{sol} is limited to less than 200 nm in continuous films, whereas it is extended up to 400 nm by adopting periodic perforating structure. This opens up a new concept for thermochromic VO₂-based films to satisfy the real-life requirements for smart window applications.

Exploiting the new ionic strength induced electrodeposition method, shows promises for the implementation of grid-patterned VO₂ smart foils. The "red-ox free" deposition method of VO₂-NP opens up a new avenue to achieve excellent thermochromic properties by using a straightforward electrochemical approach. The deposited film is composed of the original semiconducting-metallic phase transitional VO₂-NP, without affecting their morphology and crystallinity, and therefore well maintaining the thermochromic properties with the active control of line width, thickness and FF. This is the first time for demonstrating the pure VO₂-NP massive deposition on the flexible Cu-grid/PET substrates through utilizing the ionic-strength induced electrochemical method with applying very moderate potentials. The new deposition method is likely to provide a simple and straightforward route towards future designing of novel devices with alleviating the reliance on the nanomaterials' intrinsic properties, and therefore will greatly broaden where and how various nanomaterials can be integrated and deposited, such as in energy-related applications.

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Chapter 6

RI-tunable Anti-reflection Coatings: Maximizing Solar Modulation Ability for VO₂-based Thermochromic Smart Windows

Previous studies of anti-reflection coatings (ARC) solely focused on increasing T_{lum} while neglecting ΔT_{sol} , which is the major energy-saving index. The intrinsically low solar modulation ability (ΔT_{sol}) is because VO₂ has a higher refractive index (RI) from $\lambda=500$ nm to $\lambda=2200$ nm at a lower temperature state of VO₂, i.e.: $n_{VO_2(low)} > n_{VO_2(high)}$, which causes the unwanted high reflection at the low-temperature semiconducting phase of VO₂. This study aims to investigate the sol-gel based ARC with tunable RI (1.47-1.92 at $\lambda=550$ nm) to offer more AR effects at the cold state, thereby maximizing ΔT_{sol} for not only VO₂ nanocomposites but also continuous thin films and periodic patterned films. The best performing ARC could maximize ΔT_{sol} (from 15.7% to 18.9% for VO₂ nanocomposites) and increase $T_{lum(avg)}$ (from 39% to 44% for VO₂ nanocomposites) simultaneously, and these results surpass the ever-reported ARC-coated VO₂ smart windows. The presented RI-tunable ARC not only paves the way for practical applications of VO₂-based nanostructures in the smart windows, but also circumvents the complex materials selection and optical design.

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6.1 Introduction

Thermochromic glazing provides an energy-saving solution by using vanadium dioxide (VO₂), based on highly reversible semiconductor-metal phase transition at a τ_c of 341 K (68 °C). VO₂ could inhibit energy in-flow from infrared (IR) region when it behaves as metallic materials (VO₂(R) rutile phase) at high temperature, while the semiconductor state (VO₂(M) monoclinic phase) at low temperature transmits IR to warm up indoor space when the ambient temperature is lower than τ_c .^[1,2] The luminous transmittance (T_{lum}) (from 380 to 780 nm) remains unchanged at both cold and hot stages.

Although τ_c could be reduced to near room temperature by doping with metal ions of high valence,^[3–7] two significant shortcomings of VO₂ thermochromic materials that obstruct the way towards possible commercialization are low T_{lum} ^[8] and insufficient ΔT_{sol} .^[9] Different approaches have been investigated with the focus mainly on increasing T_{lum} , whereas ΔT_{sol} is hard to control since it is related to solar response difference of two states. For instance, $T_{lum(avg)}$ increases from 34.8% to 38.6% with F-doping^[10] and from 41% to 51% with Mg-doping^[11] but not jeopardizing IR switching ability. Nanoporous film structure could achieve a good thermochromic combination of $T_{lum(avg)} = 42\%$ and $\Delta T_{sol} = 14.1\%$ as a result of the insertion of air phase in the form of pores.^[12] In 1987, the studies reported by S. M. Babulanam *et al.* proposed the idea of anti-reflection coatings (ARC), which facilitates the increment of T_{lum} from 39% to 45% by applying a single layer of SiO₂, but with the almost complete loss of ΔT_{sol} .^[13] Recently, various ARC materials have been laminated with the basis of continuous VO₂ thin films to acquire high $T_{lum(avg)}$ and ΔT_{sol} , as summarized in **Table 2.4** and **2.5** (referring to Chapter 2-literature review). TiO₂ is used as a multifunctional ARC topcoat in the double-layered film structure by P. Jin *et al.*, which showed both increments in T_{lum} and ΔT_{sol} .^[14] ZrO₂^[15] and CeO₂^[16] have also been used as ARCs. However, the depositions of those overcoats are highly energy-consuming and expensive. Low-cost sol-gel methods have been adopted to fabricate SiO₂ and TiO₂ overcoats,^[17]

but it only works on continuous VO₂ films. Moreover, the multilayered ARCs have experimented with TiO₂ and SiO_x^[18–20] with the drawbacks of costly deposition methods, intricate optical design and non-guaranteed enhancements of both T_{lum} and ΔT_{sol} . It is worth noting that as compared with other ARCs, the Si-Al ARC^[21] (elaborated in Section 2.7) shows *ca.* 29% improvements of T% contrast at $\lambda = 2000$ nm as well as the significant increments of both T_{lum} and ΔT_{sol} .

Nevertheless, only fixed refractive index (RI) ARCs on the continuous VO₂ films with the aid of optical simulation were investigated previously, and none of the studies focused on enhancing ΔT_{sol} to tackle the intrinsic physical limitation of VO₂, as it has undesirable higher reflectance at lower temperature in the λ range from 500 to 2200 nm.^[22] Here we propose a facile way to produce tunable RI ARCs by just changing the annealing temperature and the compositions of sol-gel based overcoats to preferentially offer more anti-reflection to the cold state as compared with the hot state (as illustrated in **Figure 6.1**). The results finally lead to the increase of ΔT_{sol} due to the fact of $\Delta T_{\text{sol}} = T_{\text{sol}} (\text{low}) - T_{\text{sol}} (\text{high})$

Moreover, the RI tunability of the ARCs can be extensively applicable to the VO₂-based continuous thin films, nanocomposites and micro-patterned films to strive for further improvement of nanothermochromism.^[23] Furthermore, VO₂ is not the most thermodynamic stable phase in the air.^[21,24–26] Therefore, an anti-oxidation overcoat is a must, especially for the nanocomposites, containing high surface energy vanadium dioxide nanoparticles (VO₂-NP) dispersed in the transparent matrix.

Figure 6.1 Schematic illustration the concept of the RI-tunable ARC applied on the VO₂ substrates, which could preferentially offer more anti-reflection effect at low temperature as compared with that at high temperature

6.2 Experimental Methods

6.2.1 Sample preparation

Two different types of ARC solutions, Si-Al based and TEOS based, were prepared via sol-gel methods. The concentrated Si-Al based solution was synthesized as described in the Section 3.1.1.2. For having prepared TEOS based solution, a tetraethyl orthosilicate (TEOS, Sigma Aldrich) precursor was firstly diluted to 30 wt% TEOS in the solvent of mixed ethanol (95% analytical grade, Sigma Aldrich) and deionized (DI, 18.2 MΩ) water according to the molar ratio of ethanol : DI water = 4 : 1. Hydrochloric acid (HCl, 37%, Sigma Aldrich) was added to the mixture dropwise until pH<2. The solution was stirred for 2 h and followed by aging for 24 h before dip coating on VO₂ continuous thin films. Moreover, for applying ARCs on the VO₂ nanocomposites or patterned microstructures, the concentrated Si-Al solution was further diluted to 50% of its original concentration by using ethanol (99% analytical grade, Sigma Aldrich), while 30 wt% TEOS solution was diluted to 22 wt% TEOS by adding the corresponding amount of ethanol and DI water. All diluted solutions were magnetically stirred for at least 6 h

to form homogeneous suspensions

Continuous VO₂ thin films were deposited on quartz substrates as illustrated in the relevant paper.^[26] A 0.5 wt% VO₂/Si-Al gel mixture was prepared as reported,^[27] which serves as the structural support for the VO₂ micro-patterning films upon drying. Moreover, for nanocomposites samples, VO₂-NP (Jingcheng Chemicals Co., Ltd, China) were uniformly dispersed in DI water after surface modification by PVP (K30), bar coated on the cleaned soda-lime microscopic glass slides (BK7), and then dried at 50 °C for 15 min to form nanocomposite coatings on glass. ARC were dip coated on the top of bare VO₂ continuous thin films, nanocomposites and micro-patterning films at the withdrawing rate of 50-100 mm/min and dried in air at room temperature for at least 24 h before heating to evaporate unnecessary solvents. All the dip-coated ARC layers at the back side of VO₂ substrates were removed using ethanol. Different temperatures (100-300 °C) were employed in the following ARC heating process with the same ramping rates of 1 °C/min to obtain the fine quality of overcoats.

6.2.2 Characterization

A) XRD: The crystalline phases of VO₂ commercial nanopowder were determined by X-ray diffraction (XRD) using the D8 Advance diffractometer (Bruker AXS, USA). **B) SEM:** The dimensions of nanoparticles, as well as the homogeneity of nanocomposites, were characterized by extremely high resolution scanning electron microscopy (XHR-SEM, Magellan, FEI company, USA). **C) DLS:** The Nano-ZS analyzer (Malvern Instruments, UK) was employed to analyze the size distribution and surface potential of VO₂-NP, which were dispersed in pure DI water. **D) UV-Vis-NIR Spectroscopy:** The optical transmittance in the range of 250-2500 nm was measured using a UV-Vis-NIR spectrophotometer (Lambda 950, Perkin Elmer, USA) equipped with a PE120 system (Linkam, U.K.) Peltier heating and cooling stage.

6.2.3 Optical calculation

The integrated luminous transmittance (T_{lum}) and reflectance (R_{lum}), IR transmittance (T_{IR}) and reflectance (R_{IR}), as well as solar transmittance (T_{sol}) and reflectance (R_{sol}) were calculated based on the measured transmittance and reflectance spectra using the following expression as **Equation 6.1** and **6.2**, while the corresponding modulation abilities of transmitted and reflected energy in the different spectrum regions were characterized as ΔT_{lum} , ΔT_{IR} , ΔT_{sol} and ΔR_{lum} , ΔR_{IR} , ΔR_{sol} as indicated in **Equation 6.3** and **6.4**.

$$T_{lum/IR/sol} = \frac{\int \phi_{lum/IR/sol}(\lambda) T(\lambda) d\lambda}{\int \phi_{lum/IR/sol}(\lambda) d\lambda} \quad (6.1)$$

$$R_{lum/IR/sol} = \frac{\int \phi_{lum/IR/sol}(\lambda) R(\lambda) d\lambda}{\int \phi_{lum/IR/sol}(\lambda) d\lambda} \quad (6.2)$$

$$\Delta T_{lum/IR/sol} = T_{lum/IR/sol(low)} - T_{lum/IR/sol(high)} \quad (6.3)$$

$$\Delta R_{lum/IR/sol} = R_{lum/IR/sol(low)} - R_{lum/IR/sol(high)} \quad (6.4)$$

where $T(\lambda)$ and $R(\lambda)$ represent the measured spectral transmittance and reflectance, respectively. ϕ_{lum} is the standard luminous efficiency function of photonic vision^[28] for λ in the range of 380-780 nm, and $\phi_{IR/sol}$ is the IR/solar irradiance spectrum distribution for air mass 1.5^[29] and it represents an overall yearly average for mid-latitudes including diffuse light from the ground and sky on a south facing surface tilted 37° from horizontal. The λ ranges used for $T_{IR/sol}$ or $R_{IR/sol}$ calculations are 780-2500 nm and 250-2500 nm, respectively. $\Delta T_{lum/IR/sol}$ or $\Delta R_{lum/IR/sol}$ is the difference of integrated spectral transmittances or reflectances, which are measured at low temperature (20 °C) and high temperature (90 °C) respectively at the different λ ranges.

The transmittance of single layer ARCs deposited on quartz slides was measured for the calculations of n_{ARC} , which is based on the multi-layer optical theory with Swanepoel method.^[30] The optical constants of quartz substrate were extracted from the literature,^[31] where n_{sub} is a series of values varied with λ and the extinction coefficient, k_{sub} , is approximately equal to zero throughout the

spectrum (250-2500 nm).

6.3 Principle Outcomes

6.3.1 Proof-of-concept of RI-tunability

6.3.1.1 On the VO₂ nanocomposites

As shown in **Figure 6.2(a)**, the spectral RI of continuous VO₂ thin films at both low and high temperature^[22] form an envelope in the λ range of 500-2000 nm. The low-temperature VO₂(M) phase has higher RI than the high-temperature VO₂(R) phase (*i.e.* $n_{VO_2(low)} \gg n_{VO_2(high)}$) in the envelope, leading to more solar reflection at the cold state as compared with the hot state. High reflection depresses $T_{lum(low)}$ as well as $T_{sol(low)}$ which causes the intrinsic issue of low ΔT_{sol} in VO₂ (referring to Equation 5.3). To address such intrinsic issues, the single-layer ARC can be carefully designed to suppress more reflection below τ_c than that above τ_c , which induces a higher ΔT_{lum} and thereby results in larger ΔT_{sol} (*i.e.* enlarging the T% contrast between low and high temperature). The ARC- ΔT_{sol} relationship can be evidenced practically by applying a layer of the diluted Si-Al based ARC on the VO₂/Si-Al nanocomposites. As demonstrated in **Figure 6.2(b)**, obviously, the ARC decreases R_{lum} from *ca.* 13% to *ca.* 6% and meanwhile ΔT_{lum} and ΔT_{sol} are enhanced due to the reduction of ΔR_{sol} (*i.e.* the decrease of $R_{sol(low)} >$ the decrease of $R_{sol(high)}$).

Figure 6.2 (a) Spectral RI of continuous VO₂ thin films (from Ref.^[22]) at both low (solid black line) and high (solid red line) temperature with the corresponding square root values (dashed lines) are shown in the λ range of 250-2500 nm. The green shaded area indicates the RI envelope formed by $n_{VO_2(low)}$ and $n_{VO_2(high)}$. The blue-colored area denotes spectral solar irradiance. (b) Thermochromic properties at different temperature, which are calculated from the $T(\lambda)$ and $R(\lambda)$ of the diluted Si-Al ARC coated VO₂/Si-Al nanocomposites.

6.3.1.2 On the VO₂ continuous thin films

Based on Fresnel equation, high reflection may be theoretically reduced to minimum by adopting a specific ARC layer on top of the VO₂ substrates, if n_{ARC} could be tuned to the vicinity of $\sqrt{n_{VO_2}}$ ^[32] (in **Figure 6.2(a)**: dashed purple line for $\sqrt{n_{VO_2(low)}}$ and dotted pink line for $\sqrt{n_{VO_2(high)}}$). The concept of RI-tunable ARC by the low-temperature heating of the sol-gel based overcoats can be applied not only on the nanocomposites but also on the VO₂ continuous thin films. With the consideration of spectral solar irradiance, the RI of the ARCs obtained at the different annealing temperature are compared at $\lambda=550$ nm in this study since the peak of solar irradiance is located at $\lambda \approx 550$ nm. **Figure 6.3(a)** reports the proportional relationship between n_{ARC} and annealing temperature. Since most of aqueous solvents evaporated slowly with increasing heating temperature at the rate of 1 °C/min, a linear increment of Si-Al based n_{ARC} can be observed from 100 to 250 °C, while the abrupt change of RI happens at 300 °C due to the degradation of polymer components in the Si-Al ARC. The densification process of TEOS sol-gel coatings is gradually completed from 100 to 200 °C and the TEOS-based n_{ARC} is stabilized at ≈ 1.9 from 250 °C onwards. The Si-Al and TEOS-based ARC are able to provide wide RI-tunability from 1.47 to 1.92, which effectively circumvents the ARC materials selection and exhibits the potential to satisfy different RI requirements for a wide range of optical applications

Furthermore, as evidenced in **Figure 6.3(b)**, by altering the RI of the sol-gel based ARC close to $\sqrt{n_{VO_2(low)}}$, more anti-reflection could occur at cold stage compared with hot stage, and consequently a maximized ΔT_{sol} could be obtained for VO₂ continuous thin films. As n_{ARC} (≈ 1.68) is approximately identical to the $\sqrt{n_{VO_2(low)}}$ (≈ 1.69) at $\lambda=550$ nm, ΔT_{sol} of VO₂ continuous films with the concentrated Si-Al based ARC is boosted from 4.3% to 6.3% with the increment of *ca.* 47%. The $n_{ARC} \approx 1.57$ or 1.81 is neighboring the value of 1.69 and hence they also enhance ΔT_{sol} significantly but with smaller marginal increments. The insufficient enhancements of ΔT_{sol} are obtained by using 30 wt% TEOS ARC, because the overcoats offer low RI-tuning range (from 1.47 to 1.57) which is inadequate to meet the requirement for improving thermochromic properties of the VO₂ substrate, but it might be suitable for other RI requirements considering low n_{ARC} . The typical transmittance spectra of VO₂ with or without depositing the concentrated Si-Al based ARC (**Figure 6.3(c)**) reveal the noticeable increasing of T_{lum} and a blue shift of the intersecting points of the transmittance at low and high temperatures, which may contribute to the improvement of ΔT_{sol} .^[33]

Figure 6.3 (a) RI (at $\lambda=550$ nm) of the concentrated Si-Al and 30 wt% TEOS-based ARC change as a function of ARC annealing temperature. The red dashed segment indicates the abrupt increment of n_{ARC} . (b) n_{ARC} of either TEOS-based (black plot) or Si-Al based (blue plot) ARC offer various influences on ΔT_{sol} . The original ΔT_{sol} of bare VO₂ thin film substrates for TEOS-based ARC (left horizontal black-dashed line) is 4.6%, while that for Si-Al based ARC (right horizontal blue-dashed line) is 4.3%. Dash-dotted green line denotes to $\sqrt{n_{VO_2(low)}}$ at $\lambda=550$ nm (calculated from Ref.^[22]). (c) Blue shift of the intersecting points is indicated on the transmittance spectra of continuous VO₂ thin films with or without the Si-Al based ARCs

6.3.2 Improving T_{lum} and ΔT_{sol} of VO₂ nanocomposites with RI-tunable ARC

6.3.2.1 Characterization of VO₂ nanoparticles and nanocomposites

The XRD patterns of commercial VO₂ nanopowder (**Figure 6.4(a)**) reveal the characteristic crystallographic diffraction peaks of VO₂(M) crystals (JCPDF #82-661) with Scherrer crystallite size of 19.39 nm, which implies the good

formation of a crystal lattice that is one of the criteria for acquiring outstanding nanothermochromism.^[25] The high XRD peak intensity suggests the high degree of crystallinity of VO₂ nanoparticles, which plays an important role in the phase transition properties of VO₂. According to low magnification SEM image (**Figure 6.4(b)**) and DLS analysis (the inset of **Figure 6.4(b)**), VO₂-NP present a wide size distribution (by volume) from 10 nm to 500 nm when they are dispersed in pure DI water (1 wt%) without stabilizer. This may be due to the particle agglomeration when the surface potential of *ca.* −39.7 mV is not enough to restrict the combination of neighboring nanoparticles. The average particle size is approximately 100 nm with two peaks appearing at *ca.* 20 nm and *ca.* 80 nm, which could be correlated to the averaged lateral and longitudinal dimensions of ellipsoidal nanoparticles respectively as displayed in **Figure 6.4(c)**. Meanwhile, high magnification SEM image (**Figure 6.4(c)**) shows VO₂-NP mixing with 5–7 nm width VO₂ nanofibers, which may contribute to the small size part in the DLS plot (the inset of **Figure 6.4(b)**). With the stabilizer of PVP K30, nanoparticles can be uniformly dispersed and encapsulated in the polymer matrix (**Figure 6.4(d)**).

Figure 6.4 (a) XRD patterns of VO₂ commercial nanopowder (black) are associated with typical crystallographic peaks of VO₂(M) crystals (red). SEM images show: (b) the commercial VO₂-NP with the inset of particle size distribution (by volume) according to

DLS analysis; (c) the morphologies of VO₂-NP and nanofibers; (d) 1 wt% VO₂-NP well-dispersed in the PVP K30 polymer matrix

6.3.2.2 The effects of ARC compositions

Figure 6.5 The effects of the concentrations of (a) Si-Al and (b) TEOS based ARC on thermochromic properties of VO₂ nanocomposites

As illustrated in **Figure 6.5(a)**, the concentrated Si-Al based ARC (red bars) lead to detrimental effects on both ΔT_{IR} and ΔT_{sol} with negligible marginal increments of $T_{lum(avg)}$ and ΔT_{lum} . Similarly, if maintaining the same concentration of TEOS based ARC (purple bars) as used for continuous thin films, the AR effect only participates in increasing $T_{lum(avg)}$. This phenomenon implies that more AR is given to the VO₂(R) state at a higher temperature (*i.e.* 90 °C) instead of the VO₂(M) state at a lower temperature (*i.e.* 20 °C), thereby decreasing all energy modulation abilities including ΔT_{lum} , ΔT_{IR} as well as ΔT_{sol} (see the upper part of **Figure 6.5(b)**). This may be due to the fact that the VO₂ nanocomposites have overall lower RI as compared with continuous VO₂ films since the polymer matrix has a low RI. Therefore, the diluted formulations of sol-gel based ARC are required to accommodate the reduced overall composite RI of the substrate. As shown in the lower part of **Figure 6.5(a)** and **6.5(b)**, both diluted Si-Al (green bars) and 22 wt% TEOS ARCs (blue bars) have remarkable AR effects throughout the solar spectrum (250-2500 nm) and they reveal the strong capabilities to simultaneously enhance $T_{lum(avg)}$, ΔT_{lum} , ΔT_{IR} and ΔT_{sol} of VO₂ nanocomposites.

6.3.2.3 Optimization of nanothermochromic properties and anti-oxidation

As compared with continuous film substrates, VO₂ nanoparticles dispersed in the polymer matrix could offer both higher $T_{\text{lum(avg)}}$ (38.6% vs. 37.5%) and much larger ΔT_{sol} (15.7% vs. 4.3%) due to the ‘nanothermochromism’.^[25] As indicated in **Figure 6.6(a)** and **6.6(c)**, the nanothermochromic properties could be further enhanced by tuning the ARC heating temperature to acquire optimized combinations of T_{lum} and ΔT_{sol} . According to **Table 6.1**, increasing heating temperature ensures promoting T_{lum} at both low and high temperature, but the downward development of $\Delta T_{\text{lum/IR/sol}}$ with increasing temperature is due to larger enhancement of $T_{\text{lum/IR/sol}}$ at high temperature as compared with $T_{\text{lum/IR/sol}}$ at low temperature (referring to **Equation 6.2**). The maximized nanothermochromic combinations could be obtained at 100 °C ARC heating temperature for the diluted Si-Al encapsulated nanocomposites, while 22 wt% TEOS coated VO₂ shows the optimized results when it is maintained at room temperature without post ARC heat treatments. As displayed in **Figure 6.6(b)**, Si-Al based ARCs in the dilution form could effectively facilitate the enhancement of spectral transmittance ($T_{\text{lum/IR/sol}}$) at low temperature throughout the solar spectra, while the diluted TEOS-based ARCs present the large anti-reflection effects with the most focus on the visible-near IR region (**Figure 6.6(d)**).

Figure 6.6 Relationship between thermochromic properties and the ARC heating temperature of (a) diluted Si-Al or (c) 22 wt% TEOS based ARC; Spectral transmittance of the optimized VO₂ nanocomposites with (b) the diluted Si-Al ARC heated at 100 °C or (d) 22 wt% TEOS ARC maintained at room temperature (RT). The insets of (b) and (d) show the transparency differences before and after applying diluted Si-Al or 22 wt% TEOS ARC, respectively. Note: * denotes ARC without heat treatments before UV-Vis-NIR measurements.

As tabulated in **Table 6.1**, the highest ΔT_{sol} of 18.9% can be achieved with the optimized $T_{lum(low)}$ of 46.3% and $T_{lum(high)}$ of 41.4% by the application of diluted Si-Al based ARC with heating at 100 °C. The best combination of thermochromic properties generated by using 22 wt% TEOS based ARC shows ΔT_{sol} = 16.4% with maximized $T_{lum(low)}$ = 52.7% in the VO₂(M) state and $T_{lum(high)}$ = 48.7% at the VO₂(R) phase. The superior nanothermochromic results obtained with the employment of RI-tunable sol-gel based ARC have surpassed all the contemporary ARC-coated VO₂-based structures (red spots^[14–17,21] and yellow squares^[18–20] in **Figure 6.7**). It is also comparable to the recent best reported results ($T_{lum(avg)}$ = 42.8% and

$\Delta T_{\text{sol}}=22.3\%$) with fine crystallized VO₂ nanoparticles in the polyurethane matrix (no application of ARC).^[34]

Table 6.1 Optimization of thermochromic properties for VO₂ nanocomposite smart window applications by using RI-tunable sol-gel based ARCs.

VO ₂ Nanocomposite samples			T _{lum} (%)		ΔT_{lum} (%)	ΔT_{IR} (%)	ΔT_{sol} (%)
			20 °C	90 °C			
Sample C1 (w/ diluted Si-Al ARCs)	w/o ARC		39.9	37.3	2.6	30.8	15.7
		RT*	45.4	40.8	4.6	36.2	18.9
	w/ ARCs	100°C	46.3	41.4	4.9	36.0	18.9
		150°C	44.5	39.9	4.6	34.8	18.2
		200°C	45.2	41.6	3.6	31.4	16.3
		250°C	47.8	45.3	2.5	26.4	13.4
Sample C2 (w/ 22 wt % TEOS ARCs)	w/o ARC		47.3	44.9	2.4	27.0	13.6
		RT*	52.7	48.7	4.0	31.4	16.4
	w/ ARCs	100°C	51.3	47.8	3.5	29.4	15.3
		150°C	52.6	49.2	3.3	28.7	14.8
		200°C	52.1	49.1	3.0	27.5	14.1
		250°C	56.3	54.1	2.2	20.8	10.8

Note: * RT denotes ARCs without heat treatments before UV-Vis-NIR measurements.

Figure 6.7 Comparisons of current work with the contemporary studies of ARC-coated thermochromic VO₂ thin films (round^[14–17,21] and square^[18–20]) in terms of ΔT_{sol} and T_{lum} .

Figure 6.8(a) shows that without ARC, after heating at 120 °C for 15 min, the VO₂ nanocomposites entirely lose the thermochromic effects and this instability of VO₂ limits its smart window applications. The XRD patterns (**Figure 6.8(b)**) illustrate that the peak intensity of VO₂(M) phase decreased obviously after the heating treatment of bare nanocomposites, which implies poor crystallinity of VO₂ composites due to oxidation without the thermal-protection of RI-tunable ARC and therefore explains the disappearance of thermochromism in **Figure 6.8(a)**. The ARC can provide anti-oxidation encapsulation for VO₂, especially for the nanoparticles with high surface energy embedded in a composite form.

Figure 6.8 (a) Transmittance spectra and (b) XRD patterns of the bare VO₂ nanocomposites before and after heat treatments.

6.3.3 Extensive application of RI-tunable ARC on micro-patterning VO₂ films

Figure 6.9(a) demonstrates the effective AR brought by the diluted Si-Al based ARC, which are coated on top of micro-patterning VO₂ substrates (**Figure 6.9(c)** and **6.9(d)**). It is worth noticing that, prior to heating the ARCs (*i.e.* “w/ ARC-RT” in **Figure 6.9(a)**), $R(\lambda)$ at 20 °C is lower than $R(\lambda)$ at 90 °C in the UV and visible region, leading to $\Delta R_{\text{lum}} = -0.5\%$, while these 2 factors flip over and cause the increase of ΔR_{lum} (from -0.5% to 0.6%) and ΔR_{sol} (from -0.1% to 0.8%) after slowly heating the ARC to 100 °C (referring to “w/ ARC-100 °C” in **Figure 6.9(a)**). As aforementioned in Section 6.3.1, lower ΔR_{sol} ultimately leads to

a higher ΔT_{sol} . The diluted Si-Al ARC without heating (see “w/ ARC-RT” in **Figure 6.9(b)**) significantly boost ΔT_{sol} from 3.6% to 10.5% with a tremendous enhancement of T_{lum} about 2.5 times ($T_{\text{lum}}(20^\circ\text{C})$ from 16.8% to 44.4% and $T_{\text{lum}}(90^\circ\text{C})$ from 16.7% to 42.1%). Therefore, these results evidence that RI-tunable sol-gel based ARCs can be extensively applied to solve the intrinsic problems of VO₂ thereby amplifying the thermochromic performances of various VO₂ substrates.

Figure 6.9 (a) Spectral reflectance and (b) transmittance of micro-patterning VO₂ films without (“w/o ARC”) or with the diluted Si-Al based ARC before (“w/ ARC-RT”) and after (“w/ ARC-100 °C”) heat treatment. The optical microscope images of micro-patterning VO₂ films without (C) and with (D) Si-Al based ARCs.

6.4 Conclusions

The trade-off issue between improving T_{lum} and sacrificing ΔT_{sol} has been tackled by employing a novel RI-tunable sol-gel based ARC. VO₂ has a higher RI at low temperature than that at high temperature for most visible and near IR range, which causes high Fresnel reflection at the cold stage leading to intrinsically low solar modulation ability (ΔT_{sol}) of VO₂. The results prove that with the specific RI

of the sol-gel based ARC, more AR effect could be offered to the cold state as compared with the hot state, consequently enhancing ΔT_{sol} . The best performing combination of VO₂ nanocomposites with Si-Al based ARC could enhance $T_{\text{lum(avg)}}$ (from 39% to 44%) and ΔT_{sol} (from 15.7% to 18.9%) simultaneously by simply fine tuning the RI of ARC *via* annealing and concentration dilution. This RI tunable ARC could work on various VO₂ substrates, including continuous thin films, nanocomposites and micro-patterning VO₂ substrates. It provides a facile approach to obtain various RI of ARC materials without the optical design and complex materials selection work, which paves the way for the practical applications of VO₂-based thermochromic smart windows in real life as well as other optical applications.

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Chapter 7

Discussion and Future Work

The threads of this dissertation are drawn together. The implications and impacts of the findings, and the outstanding questions for future work will be presented. In the implications and impacts section, the hypotheses raised in Chapter 1 will be discussed again to understand the extent of target fulfillment. The possible future opportunities will be highlighted in the second section of this chapter with the suggested strategies.

7.1 General Discussion

In conclusion, this thesis exploits three types of vanadium dioxide (VO_2)-based nanostructures, which achieve the main objective of enhancing both T_{lum} and ΔT_{sol} . The intrinsic limitations of conventional VO_2 thin films are predominately caused by the inherently high-refractive index (RI) of VO_2 ,^[1] which is tackled by the three simple and straightforward approaches from the different angles. Firstly, the $\text{VO}_2/\text{Si-Al}$ nanocomposites (**Figure 7.1(a)**) have realized the concept of “nanothermochromism” and overcome the limitations of the VO_2 thin films by incorporating VO_2 nanoparticles ($\text{VO}_2\text{-NP}$) in the transparent Si-Al gel matrix.^[2] With the optimized 10% solid content, increasing the thickness of nanocomposites improves the ΔT_{sol} to 12% with a high $T_{\text{lum(avg)}}$ of *ca.* 60%. Next, the “touching-hole” design in the VO_2 nanogrid simulations (**Figure 7.1(b)**) reveals this potential to boost T_{lum} to around 80% with an excellent retention of ΔT_{sol} about 14%.^[3] In practice, the facile “reduction-oxidation (red-ox) free” ionic-strength induced electrochemical method materializes the VO_2 grid-patterning (**Figure 7.1(b)**) on the flexible polymer foils.^[4] The fill factor (FF) has been well-controlled by controlling the deposition time. The experiment results reveal the similar relationship between FF and VO_2 grids’ modulation abilities as compared with the simulation data (**Figure 7.1(b)**). In addition, this new approach also provides an alternative one-step solution for obtaining the grid-patterned structures of different dimensional nanomaterials, which might be important for the nano-manufacturing. Lastly, by tuning the RI of the sol-gel based anti-reflection coatings (ARC) *via* heating the coatings or adjusting the ARC concentrations, the thermochromic performance of VO_2 continuous thin films, nanocomposites and micro-patterned substrates (**Figure 7.1(c)**) can be further improved with the maximized ΔT_{sol} . In this conclusive chapter, the main findings of each attempt are summarized in the following sections, which effectively facilitate the real life applications of thermochromic smart windows.

Figure 7.1 Summary figures for each results chapter: (a) Chapter 4: VO₂/Si-Al nanocomposites compose of small size VO₂-NP encapsulated in Si-Al gel matrix for achieving “nanothermochromism”; Reproduced with permission from Reference [2]. Copyright 2013, Elsevier Inc. (b) Chapter 5: “Touching-hole” design of the simulated VO₂ nanogrids and VO₂-NP grid-patterning obtained by ionic strength induced electrodeposition reveal the similar tendencies of the relationship between FF and modulation abilities. dramatically increase T_{lum} with the retention of large ΔT_{sol} ; Reproduced with permission from Reference [3] (Copyright 2015, Optical Society of America) and [4] (Copyright 2016, The Royal Society of Chemistry). (c) Chapter 6: RI-tunable sol-gel based ARC further enhance both the T_{lum} and ΔT_{sol} of various VO₂-based substrates, including continuous thin films, nanocomposites and periodic micro-patterned films.

7.1.1 Discussion to the hypothesis #1 – VO₂/Si-Al Nanocomposites

In Chapter 4, the application of the cost-effective and scalable bead-milling method successfully leads to the substantial reduction of VO₂ particle size from the commercially-available micro-size (greater than 100 nm) to 10-20 nm, which fulfills the requirement of “nanothermochromism”.^[2] The mechanical attrition preserves the crystal structure of VO₂-NP, which helps to secure the intrinsic thermochromic properties of VO₂. The milled VO₂-NP with a dimension of approximately 20 nm were uniformly dispersed in the Si-Al gel matrix by vortex mixing, and the PVP component in the gel facilitates the de-agglomeration of the particles in the matrix of composites. It is of interest that the Si-Al gel forms an encapsulation layer of VO₂ in order to moderate the surface energy of the nanoparticles.

The optimization of the nanothermochromic properties has been done with the consideration of two factors: the VO₂-NP solid content and the thickness of nanocomposite foils casted on the glass substrate.^[2] Increasing either of them shows the ability of enhancing ΔT_{sol} , while the more VO₂ nanofillers leads to the darker appearance of the nanocomposite smart windows with a lower visible transparency. In general, increasing the foil thickness demonstrates more premium properties-improvement effects than adding more loading of VO₂-NP, because the former can induce the more pronounced increment of ΔT_{sol} from almost 0% (if thickness=1.0 μm) to 12.0% (if thickness=3.0 μm) with less side-effect on T_{lum} (approximately from 80% to 60%) as compared with the later. It is worth to notice that the loading of solid particles is capped as 10%, otherwise the bulk VO₂ aggregations (with weak thermochromic effects) will form and break the homogeneity of the nanoparticles dispersion, resulting in the undesirable deteriorations of both ΔT_{sol} and T_{lum} . In this case, with the optimal composite conditions of 10% VO₂-NP loading and 3.0 μm foil thickness, the high T_{lum} ($T_{\text{lum}}(20\text{ }^{\circ}\text{C})=63.7\%$ and $T_{\text{lum}}(90\text{ }^{\circ}\text{C})=54.4\%$) and the large ΔT_{sol} of 12% have been

obtained, which surpasses some of the contemporary results of pure VO₂-NP based thermochromic nanocomposites.^[5,6]

7.1.2 Discussion to the hypothesis #2 – VO₂ grid-patterning: simulations and experiments

As an alternative of VO₂ patterning structures (other than the high aspect ratio ‘moth-eye’ nanostructures), a new concept of VO₂ “nanogrids” has been studied in a computational way with the considerations of three structural models. The Finite Difference Time Domain (FDTD) parameter optimizations have been performed in a systematic manner to reveal the hole size/shape, FF, thickness and periodicity effects on the thermochromic properties. Regardless of the hole and lattice shape, increasing the size of nanoholes show the dramatic enhancement of T_{lum} , which ensures that the design of nanogrids is able to obtain the high transparency smart windows. The FF dominates the transmittance in the full solar spectrum (T_{lum} , T_{IR} and T_{sol}) and indicates a proportional relationship, whereas the transmittance differences (ΔT_{lum} , ΔT_{IR} and ΔT_{sol}) may decrease marginally with increasing FF, which could be compensated by increasing the structural thickness to ensure the enough solid content of VO₂. It is worth to highlight that the thickness effects on enhancing ΔT_{sol} is restricted at 160 nm in the case of continuous thin films, while the upper-limit can be extended up to 400 nm (referring to the turning point in **Figure 7.2(a)**) if adopting the new concept of nanogrids. Reducing periodicity and increasing FF at the same time lead to the “touching-hole” structure (**Figure 7.1(b)**) when the radius is identical to half of the periodicity. As a result, the superior T_{lum} around 80% is attained with the remarkably high ΔT_{sol} of 14% (**Figure 7.2(b)**). Therefore, the design of “touching-hole” nanogrids opens up a new concept for VO₂-based thermochromic films with the features of high transparency and notable energy-saving efficiency.

Figure 7.2 (a) Thickness effects on the VO₂ continuous thin films (dashed black line) and perforated nanogrid films (solid red line). (b) Periodicity effects reflected on T_{lum} and ΔT_{sol} of nanogrid films. Adapted from Reference [3]. Copyright 2015, Optical Society of America.

Furthermore, the VO₂ grid-patterning concept has been physically embodied by developing a novel electrodeposition approach, which is based on controlling the ionic strength in the proximity of the working electrode to directly depositing (not forming upon deposition) VO₂-NP on the conductive grid area of electrode (**Figure 7.3**). The applied moderate electrical potential increases sharply the ionic concentration at the interface of electrode/dispersion and prompts the irreversible selective deposition of the intact VO₂-NP from their aqueous dispersions without involving the conventional red-ox reactions. Specially, the copper electrode is selected as the deposition substrate, because the copper ions are more stable in the aqueous solutions as compared with the high-valence metallic ions, and applying the moderate potential (0.05 V) in a short time (20 s) is enough to generate a flux of copper ions for causing the local aggregation of VO₂-NP rapidly. Meanwhile, the massive deposition on the planar Cu demonstrates a good coating-to-substrate adhesion, which implies the good durability of the VO₂-NP grid-patterned smart foils that are deposited in the same way. By utilizing this new method, the line-width, thickness and FF of free area can be actively controlled *via* the precise control of deposition time, and the growth of deposited line highly depends on the diffusion rate of copper ions. The relationships of FF and modulation abilities show the similar trends as predicted by the simulations. The smaller FF leads to a greater

enhancement of ΔT_{sol} , and the ΔT_{lum} , ΔT_{IR} and ΔT_{sol} obtained by the experiments are slightly higher than the computed results. In the aspect of T_{lum} , the best-performing VO₂-NP grid deposits achieve 143% T_{lum} improvement of the best continuous thin film results, which is obtained by the simulations. Also, the near-infrared (NIR) switching efficiency is as large as 53%, which is superior to the contemporary report of VO₂ periodic porous structure. Electrodepositing the relatively diluted dispersion (0.5 wt%) for a short time (20 s) provides $T_{\text{lum(avg)}}$ of 57.7% and ΔT_{sol} of 10.5%, which is comparable to the best results of the periodic porous films.^[7]

Furthermore, this new electrochemical method has successfully been applied to deposit various nanomaterials, such as gold nanoparticles (0D), carbon nanotubes (1D) and graphene oxide nanosheets (2D), directly from their suspensions with the retention of the original crystallinity and materials' properties. Therefore, the new concept is prospective to provide a simple and straightforward route towards the future designing of novel nanomaterials-containing devices.

Figure 7.3 Schematic summary of Chapter 5 from the proof-of-concept of the ionic-strength induced electrodeposition of VO₂-NP to the physical implementation of VO₂ grid-patterning on the flexible Cu-grid/PET substrates, finally revealing a large increase of T_{lum} together with the good retention of the NIR-switching ability.

7.1.3 Discussion to the hypothesis #3 – RI-tunable ARC applied on various VO₂-based substrates

The purpose of this ARC design is to offer more anti-reflection (AR) effect to the low-temperature semiconducting state of VO₂-based substrates for

maximizing ΔT_{sol} , which has been proven by applying a single layer of the Si-Al based ARC on top of VO₂ nanocomposites. Both R_{lum} (at both low and high temperature) and ΔR_{sol} can be substantially diminished by 50% and more if the ARC are applied at not higher than 100 °C. The dramatic decrease of ΔR_{sol} evidences that the RI-tunable ARC exhibit the greater AR effects at the cold state as compared to the hot state, which is consistent with the hypothesis stated in Chapter 1. With heating the concentrated Si-Al and TEOS based ARC at different temperature, a wide-range of RI-tunability can be achieved from 1.47 to 1.92 at $\lambda=550$ nm (in accordance to the peak position of solar irradiance). With the assistance of the known spectral RI of VO₂ continuous films, the theoretical maximum reduction of Fresnel reflection has also been confirmed experimentally, because the ΔT_{sol} of bare films (4.3%) is increased to the highest achievable value of 6.3% (the enhancement by 47%) especially when n_{ARC} is tuned to the approximate $\sqrt{n_{\text{VO}_2(\text{low})}}$. Therefore, this implies that by simply searching for an optimal heating temperature of these RI-tunable ARC, the wide-range RI-tunability is able to facilitate the further improvement of the thermochromic properties of various VO₂-based substrates.

When the ARC are applied on the VO₂-based composites, the composition of the ARC solutions needs to reduce due to the existence of the low-RI in the common polymer-based matrix. Therefore, the best-performing ARC and conditions for the VO₂-NP (embedded in PVP) nanocomposites are the 50% diluted Si-Al ARC heated at 100 °C for increasing both $T_{\text{lum(avg)}}$ by *ca.* 14% (from 38.6% to 43.9%) and ΔT_{sol} by *ca.* 20% (from 15.7% to 18.9%). This results combination has surpassed all the contemporary ARC-coated VO₂ structures summarized in Chapter 2 (referring to **Table 2.4** and **2.5**). In the same time, the thermal stability of VO₂ nanocomposites has also been strengthened, which will prolong the lifespan of the thermochromic smart coatings in the practical application.

Furthermore, this RI-tunable overcoat has also applied on the micro-patterned VO₂ films and the results show that the Si-Al based ARC can boost

three times of ΔT_{sol} and twice of T_{lum} when the heating induces the flip-over of ΔR from negative to positive. This also evidences that the RI-tunable ARC concept is generally applicable to solve the intrinsic high reflection issue of not only the planar films or composites, but also the uneven patterned films, thereby realizing the goal of maximizing ΔT_{sol} .

7.2 Outstanding Questions/Future Work

7.2.1 Ionic-strength induced VO₂ deposition to incorporate doping elements

For the practical application in thermochromic smart windows, the τ_c (68 °C) of VO₂ materials should be lowered to, preferably, room temperature (20 °C-30 °C). As one of the most efficient strategies, the elemental doping of VO₂ has been extensively adopted to reduce the τ_c value and modify the hysteresis loop width. It has been reported that the τ_c value could be lowered by doping with high valence cationic ions, *e.g.* W⁶⁺, Ta⁵⁺, Mo⁶⁺, and Nb⁵⁺.^[8] Among these cations, W⁶⁺ was demonstrated to be one of the most effective cationic ions to reduce the τ_c value of VO₂. Extensive research efforts have been devoted to the study of W-dopant on the thermochromic properties of VO₂ films, including WO₃-doping by sol-gel process,^[9] WCl₆-doping,^[10] and formation of V_{1-x}W_xO₂ (0<x<0.76%)^[11] nanocomposites, which indicated the successful improvement of phase change quality can be realized through the addition of a W-dopant. By the combination of first-principle calculations and synchrotron radiation X-ray absorption spectroscopy, researchers demonstrated the mechanism of W-doping in reduction of τ_c value.^[12] The local atomic structure of W-dopant is intrinsically tetragonal-like symmetric structure, exhibiting a concentration dependent evolution with the distortion, repulsion, and stabilization due to the interaction between the doped W atoms and VO₂ lattices across the phase transition (**Figure 7.4**). It is revealed that the symmetric W core drives the nearby asymmetric monoclinic VO₂ lattice to the formation of rutile-like VO₂ nuclei, which lowers the thermal energy barrier for the phase transition.

Figure 7.4 Models and theoretical calculations of W-doping VO_2 . Models of local structure distortions of three representative doped concentrations (a) 0.54%, (b) 0.95%, and (c) 2.38%. The white area displays the local structure evolutions around W atoms. The variations of average W-W distances and $[\text{WO}_6]$ octahedral geometries are shown in the left top and bottom panel, respectively. (d) The relaxed structure projected along $[010]$ axis and (e) the corresponding spatial redistribution of charge density of W doped VO_2 with about 0.6% concentration; $|\Delta R|$ ($|\Delta R| = |R_{\text{distorted}} - R_{\text{previous}}|$) based on calculation results give a distinct pattern of doped effects. The blue and red isosurfaces correspond to charge densities of $0.005 \text{ e}/\text{\AA}^3$ and $-0.005 \text{ e}/\text{\AA}^3$, respectively. (f) A schematic diagram of concentration scaled influences of W dopants in VO_2 , in which shows the low concentration with isolated dopants and the high concentration with interactional dopants. Reproduced with permission from Reference ^[12]. Copyright 2012, Nature Publishing Group.

Electrochemical method represents a very efficient, feasible technique in the preparation of thin films on the electrode surface. As demonstrated in Chapter 5, we employed a copper (grid) electrode that was electrochemically oxidized under well-controlled conditions to generate a flux of copper ions. The latter increased the ionic strength and therefore reduced the repulsion forces between the negatively charged $\text{VO}_2\text{-NP}$. The electro-deposited film is composed of the original metal-insulator transitional (MIT) $\text{VO}_2\text{-NP}$, maintaining their nanothermochromic

properties. This universal ionic strength induced VO₂ thin film electrodeposition method could be further used for the W-doping VO₂ process. The tungsten nanoparticles could be deposited on fused silica by mesh printing, which would serve as the working electrode. In very acidic solution (*e.g.* H₂SO₄), the following reaction would take place for the anodic oxidation of tungsten (grid) electrode,^[13]

The formed positively charged WO₂²⁺ ions could cause the ionic strength change around the electrode surface, which acts as an inducer for the electrodeposition of negatively charged VO₂-NP. The W-doping VO₂ thin films would be achieved by further heating treatment. In principle, this one electrochemical step induced simultaneous W-doping and VO₂ thin film deposition is simple and feasible, which might improve the VO₂ phase change quality, and eventually the reduction of τ_c value.

Besides the τ_c value, other limitations of using thermochromic VO₂ smart windows should also be overcome, including dark color with low transmittance and low solar modulation capability, which are related to optical constants, micro-/nano-structure and film thickness.^[8] These drawbacks could also be resolved by element doping, *e.g.* fluorine (F),^[14] Mg,^[15] and Ti.^[16] It might be applicable that by multiple-doping method the synergistic effect of different dopants would result in improvement of thermochromic VO₂ films properties, such as reduced τ_c , enhanced T_{lum} and ΔT_{sol} , and favorable color.

7.2.2 Conductive and flexible Ag grid for ionic-strength induced VO₂ deposition as electro-thermochromic devices

As demonstrated in Chapter 5, Cu grid was employed as the substrate electrode for the ionic strength induced VO₂ nanoparticles deposition, which was chosen to illustrate the applicability of this new concept. From a practical point of view, other electrodes, *e.g.* Ag, may also serve as the good candidate due to its high thermal and electrical conductivity, flexibility and optical transparency.^[17–19] Especially, Ag electrode could function as film heaters, which yields rapid and effective heating at a relatively low input voltage.^[20,21] With an input voltage, heat is generated on the Ag nanowires electrode, which is subsequently transferred to the VO₂ nanoparticles thin films. The heat absorption by VO₂ nanoparticles thin films caused its metal–insulator phase transition (MIT), which is reflected by the gradual optical transmission decrease in the infrared region with the increased input voltage.^[22] Instead of using glass substrate for the deposition of Ag nanowires, a better choice might be using transparent and flexible Ag conductive grid on the heat-sensitive substrates. Recently, a simple method was reported to obtain transparent and flexible Ag conductive grid by using Ag nanoparticles aqueous dispersions in an evaporative lithography process, which is directly performed onto flexible plastic substrates.^[23] As demonstrated in **Figure 7.5(A)**, a droplet of Ag nanoparticles solution is dropped on top of a metallic mesh, and subsequently, the solution spreads over the mesh and the plastic substrate. A transparent Ag nanoparticles grid is formed after the flow of the Ag nanoparticles solution towards the wires of the mesh. The Ag nanoparticles are then tailored to self-sinter upon the exposure to HCl vapors, due to the polyacrylic acid on the surface of Ag nanoparticles. The conductive Ag grid yielded by this process, shown in **Figure 7.5(B)**, possess a very low sheet resistance ($9 \Omega \text{ sq}^{-1}$) and high transparency (>75%).

Figure 7.5 A) Schematic presentation of the fabrication process to obtain a transparent and conductive Ag grid. Reproduced with permission from Reference ^[24]. Copyright 2011, Royal Society of Chemistry. B) The photographs of formed Ag grid, a) 10×, and b) 50×.

By exploiting the conductive, flexible, effective heating Ag grid as the substrate and employing the ionic strength induced VO₂ deposition method developed in Chapter 5, one can achieve the efficient and feasible VO₂ modification on Ag grid, which could act as a novel electro-thermochromic smart film and the properties could be easily adjusted by the applied potential on the substrate.

7.2.3 Controllable and patterned VO₂ hybrid prepared by 3D printing

In Chapter 5, we demonstrated the numerical optimizations using parameter search algorithms through a series of first FDTD simulations on nano-gridded, VO₂-based perforated films with taking account of film thickness, geometrical design of nano-holes and cells as well as periodicity and FF. The nano-sized opening would improve the transmission of short-wavelength visible light, while the abundant volume of VO₂ retained in the pattern maintains the good long-wavelength NIR modulation abilities of the films. The best-performing theoretical combination of 79% T_{lum} and 14% ΔT_{sol} are superior to other theoretical works such as biomimetic nanostructuring,^[1] nanothermochromism,^[25] and nanoporous

structuring.^[26] As a follow-up of this FDTD simulation, a micro-gridded VO₂ structure was fabricated by using screen-printing meshes with high controllability in film thickness, periodicity and concentration (**Figure 7.6**).^[27] Comparing to continuous films, the micro-patterned VO₂ possesses enhanced T_{lum} value due to the open grid and also ΔT_{sol} value due to a thick sample layer.

Figure 7.6 Schematic representation of the screen-printing meshes method for the preparation of periodic VO₂ films. The mesh is mounted on top of a glass substrate with a distance D . VO₂ nanoparticles dispersion is dispersed onto the glass pane using a pipette, whereby it immediately spreads across the mesh thread upon contact due to capillary forces. Inset: Enlarged picture of top view and side view showing the contact between the mesh and solution. Reproduced with permission from Reference ^[27]. Copyright 2016, Royal Society of Chemistry.

Besides the screen-printing meshes method, another feasible method that could form the micro-patterned VO₂ films might be 3D printing.^[28] One of the most important features in 3D printing is that one can get an object with the exact configurations designed at the first place using computer based software (.STL file). By using VO₂ powders as the source materials, micro-patterned VO₂ structure with high controllability in film thickness, shape, size, and periodicity could be eventually realized with the 3D printing. Not confined to the powder form, a combination of VO₂ nanoparticles with hydrogels (e.g. poly-*N*-isopropylacrylamide (pNIPAM)),^[29] which has a lower critical solution temperature

(LCST) of 32 °C) exhibiting low enough viscosity might be printed into micro-patterned structures rather than a continuous film. These configuration, composition and properties controllable methods might open new and promising directions of VO₂ based thermochromic materials for smart window applications.

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APPENDIX

Table A. 1 Adhesion tests of VO₂-NP deposits on Cu substrates according to American Standard Testing Method (ASTM) D 3359-09 Cross-Cut Tape Test

No. of ASTM D 3359-09 tape test	Percent area removed
<p>Making the required cuts before applying the tape</p>	<p>Not applicable</p>
<p>After the 1st time of removing 3M # 600 tape</p>	<p>6.7%</p>
<p>After the 2nd time of removing 3M # 600 tape</p>	<p>7.7%</p>

<p>After the 3rd time of removing 3M # 600 tape</p>	<p>8.3%</p>

Figure A. 1 C 1s XPS peaks of MWCNT deposited under different potential (0.2-2 V) as comparing with the peaks of the commercial MWCNT dispersion (dip coated). Reproduced with permission from Reference ^[1]. Copyright 2016, The Royal Society of Chemistry.

Figure A. 2 Raman spectra of GO deposited under different potentials (0.2-1.0 V) as comparing with the commercial GO sample (dip coated). The inset table shows the corresponding intensity ratios between D and G bands. Reproduced with permission from Reference [1]. Copyright 2016, The Royal Society of Chemistry.

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