Adaptive solar modulation of thermochromic VO₂ toward high-performance energy-efficient smart windows

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UNIVERSITY**

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**ADAPTIVE SOLAR MODULATION OF THERMOCHROMIC
VO₂ TOWARD HIGH-PERFORMANCE ENERGY-EFFICIENT
SMART WINDOWS**

KE YUJIE

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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SMART WINDOWS**

KE YUJIE

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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

2019

Statement of Originality

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

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Supervisor Declaration Statement

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

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Authorship Attribution Statement

This thesis contains material from 5 papers published in the following peer-reviewed journals where I was the first or co-first authors.

In Chapter 1, the “Background: Building Energy Consumption” is published as:

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The contributions of the co-authors are as follows:

- Dr. Y. Long provided the initial project direction and edited the manuscript drafts.
- I co-designed the content with Dr. Y. Long.
- I prepared the manuscript drafts. I drafted the sections of “1 Introduction”, “2.3 Metamaterials”, “2.5 Liquid Crystals”, and “2.6 Discussion and Comparison to VO₂”, as well as the entire sections of “3 Integrated Techniques” and “4 Conclusion and Perspective”. I also collect literature and help the drafting of “2.1 Hydrogel”, “2.2 Ionic Liquids”, and “2.4 Perovskites”.
- C. Zhou drafted the section “2.1 Hydrogel”, “2.2 Ionic Liquids”, and “2.4 Perovskites”.
- The manuscript was revised by Dr. Y. Long Prof. S. H. Chan, C. Zhou, Y. Zhou, and S. Wang.

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- Dr. Y. Long and Prof. Y. Gao provided the initial project direction and edited the manuscript drafts.
- I co-designed the content with Dr. Y. Long, Prof. Gao, and Prof. Y. Cui.
- I drafted the sections of “Introduction”, “Nanocomposites Based on VO₂ Crystals”, “Porous VO₂ Films”, “Grid VO₂ Films”, “Biomimetic VO₂ Patterning”, and “Conclusion and Perspectives”.
- Prof. Y. Cui drafted the sections of “Intrinsic Point Defects”, “Elemental Doping”, “Impacts of Strain on τ_c ”, “Multifunctional Antireflection Coating”, and “Energy Efficiency”
- C. Liu, Z. Chen, N. Wang, L. Zhang, Y. Zhou assisted in collecting and classifying literature.
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- I co-designed the study with Dr. Y. Long, Prof. I. Abdulhalim and I. Balin.
- I performed all the laboratory work at the School of Materials Science and Engineering. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing, and Simulation.
- I. Balin conducted the 3D FDTD simulation and analyzed the data.
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- I performed all the laboratory work at the School of Materials Science and Engineering. I also analyzed the data.
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- I co-designed the study with Dr. Y. Long.
- I performed all the laboratory work at the School of Materials Science and Engineering. I also analyzed the data.
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- Y. Yin and X. Wen conducted the 3D FDTD simulation and analyzed the data.
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- I co-designed the content with Dr. Y. Long, Prof. Gao, and Prof. Y. Cui.

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Abstract

Smart windows are promised with a significant contribution to the economization of building energy consumption. Such windows can dynamically modulate the indoor solar irradiation, leading to energy-saving for architectural heating and cooling systems. Development of smart windows can mainly be categorized as electro-, thermo-, and photo-stimulated optical response changes. Among them, thermochromic smart windows that change the optical properties in response to the temperature are highly competitive due to the low cost, passivity, and rational stimulus-response.

Vanadium dioxide (VO_2) is a promising candidate for thermochromic smart window application due to its reversible phase transition near the room temperature, accompanied with huge optical properties change. It can be transparent to the near-infrared solar irradiation at low temperature, while shield it at high temperature. However, challenges remain in VO_2 -based thermochromic smart windows, including the intrinsic yellow-brown color, the relatively low solar energy modulation (ΔT_{sol}) and visible transmittance (T_{lum}). This thesis is dedicated to improve these shortages and promote the performance of VO_2 -based thermochromic smart windows, resulting in three effective methods.

The photonic crystals were introduced to improve the undesirable yellow-brown color. The Silica/ VO_2 (SiO_2/VO_2) core/shell two-dimensional (2D) photonic crystal is prepared and demonstrated to exhibit static visible light tunability and dynamic near-infrared (NIR) modulation. Three-dimensional finite difference time domain simulations predict that the transmittance can be tuned across the visible spectrum while maintaining good ΔT_{sol} of 11.0% and a T_{lum} of 49.6%. Though the experimental result is not as prominent, it proves that the color changes of VO_2 films are accompanied by NIR modulation, which is aligned with the simulation result. In produced samples, colors beyond the yellow-brown are observed, such as green, blue, and red, demonstrating the effectiveness of photonic crystals for tuning the color of VO_2 -based smart windows.

The localized surface plasmon resonance (LSPR) was introduced to promote the performance of the ΔT_{sol} and the T_{lum} . The phenomenon is demonstrated in tuning the absorption peak position of VO₂ to the region with dense solar energy, which was demonstrated on 2D patterned VO₂ nanoparticles. Colloidal lithography method was applied to prepare the 2D patterned VO₂-based nanocrystals, resulting in nanonet, nanodome, to nanoparticle arrays. LSPR and their application in thermochromic smart windows. The nanoparticle arrays exhibit tunable LSPR at different temperatures and the LSPR red-shift is observed with the increase of the particle size and the media reflective index. A competitive solar regulation efficiency ($\Delta T_{\text{sol}} = 13.2\%$) and a transmittance contrast at 2000 nm ($\Delta T_{\text{NIR}} = 44\%$) can be achieved.

Pairing reconfigurable metamaterials with the active LSPR was demonstrated to provide performance. A kirigami-inspired elastomer containing plasmonic vanadium dioxide was developed, exhibiting adaptive, broadband, and high-efficient optical modulation. The geometrical transition and the active LSPR function synergistically by manipulating ultraviolet-visible and near-infrared regions, respectively. A new mechanical-thermal energy-saving smart window was developed adopting such materials exhibits an unprecedented solar energy modulation ($\Delta T_{\text{sol}} = 37.7\%$). Fully thermal responsiveness is also achieved in such a system. Smart window based on such materials are promised better energy-saving ability than commercialized low-emissivity glasses in cities, such as Hong Kong and Houston.

Lay Summary

The growing world population and rapid modernization have led to increased energy demand, necessitating highly efficient energy use. Building energy usage accounts for up to 40% of the overall energy consumption in developed countries, which exceeds the energy consumed by the industry and transportation sectors. Building services including heating, ventilation and air conditioning (HVAC) are major components of building energy consumption, contributing approximately 50% of total building energy. Reducing the energy consumption of these services whilst maintaining building comfort levels is a significant challenge in sustainable development. Amongst all building components, windows are considered to be one of the least energy-efficient parts as there is always heat transfer in the opposite direction to that desired.

A window can regulate indoor solar irradiation in a ‘smart’ way, that is, by dynamically and reversibly tuning the solar radiation. Thermochromic smart windows is a kind of smart windows that is highly competitive due to the low cost, passivity, and rational stimulus-response.

The vanadium dioxide (VO_2) is widely investigated for smart window application. This is because it promises the ability to smartly block the solar irradiation in hot days, while let it goes indoor in cold days. However, problems of such materials remain in regarding achieve the practical applications. Thus, novel technologies are necessary to improve this problem.

In this thesis, the methods so-called “photonic crystals”, “Localized surface plasmon resonance”, and “kirigami-inspired structures” are investigated for VO_2 -based thermochromic smart windows. These methods are demonstrated to improve the unfavorable yellow-brown color or are able to promote the energy-saving ability.

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Table Captions

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Table 2.2 Summary of experimental and simulation results of VO₂-based thermochromic nanocomposites.

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Figure Captions

Figure 1.1 a) Proportion of building energy consumption compared with total energy consumption. The proportion of energy consumption of building services such as heating, ventilation, and air conditioning of total building energy consumption. b) Schematic of electrochromic, thermochromic and photochromic smart windows. The orange arrows indicate incident sunlight. Reproduced with permission.^[21] Copyright 2017, John Wiley & Sons.

Figure 2.1 a) Schematic of the atomic structures of the high-temperature metallic tetragonal phase R and the low-temperature insulating monoclinic phase M. The V-V distances in each crystal structure are highlighted. b) Band structures of the metallic R and insulating M phases of VO₂ depicted by molecular orbital diagrams. Reproduced with permission. Copyright 2011.^[7] American Chemical Society.

Figure 2.2 a-c) Structural models of composites embedded with nanocrystals in ellipsoids, spheres, and core-shell nanoparticles. Reproduced with permission. Copyright 2010 and 2011.^[34,35] American Institute of Physics. d) Scheme of the preparation procedure for the VO₂-SiO₂/PU composite. e,f) Photographs of flexible thermochromic films based on VO₂-SiO₂/PU composites with high (Sample I) and low (Sample II) VO₂ contents. Reproduced with permission. Copyright 2012.^[38] Royal Society of Chemistry. g) Illustration of the solar modulation behavior of the VO₂/PNIPAm-based composites. Reproduced with permission. Copyright 2015.^[41] Royal Society of Chemistry. h) Photographs of the films based on the pure IL-Ni-Cl complex (top row), VO₂ nanoparticles (medium row), and VO₂/IL-Ni-CL composite at 20 and 80 °C, respectively. Reproduced with permission. Copyright 2016.^[42] American Chemical Society.

Figure 2.3 a) Summary of the calculated thermochromic performance as a function of porosity and film thickness. $T_{\text{lum,low}}$ (visible transmittance of the porous VO₂ film at low temperature) and ΔT_{sol} are denoted by the red dotted lines and black solid lines, respectively. b) The porous morphology of a 147 nm-thick VO₂ film, as an example, from the top and

side view (inset). c) Optical properties of porous VO₂ films comparing with reference. Reproduced with permission. Copyright 2011.^[52] American Chemical Society. d-k) Schematic of the self-templating and assembly during the dual-phase transformation process, which includes four steps: (d) deposition of a homogeneous solution-based precursor on a substrate, (e) assembly of self-templated hydrous sphere arrays, (f) formation of hollow VO(OH)₃ spheres, and (g) formation of the honeycomb-nanostructured VO₂ film *via* the collapse of hollow spheres. (h-i) are the corresponding experimental demonstrations of steps (d-g). Reproduced with permission. Copyright 2017.^[53] American Chemical Society.

Figure 2.4. a) Simulation models of the grid films with square holes and circular holes in square lattices as well as the circular holes in a hexagonal arrangement. b) Summary of the calculated T_{lum} and ΔT_{sol} of the model with square holes in square lattice under various periodicity and square hole length. Reproduced with permission. Copyright 2015.^[61] The Optical Society. c) Schematic of the electrodeposition process based on ionic strength. d) Photograph of the sample which contains VO₂ NPs deposited on flexible grid Cu/PET film (left) and the optical microscopy image of the grid structure (right). Reproduced with permission. Copyright 2017.^[62] Royal Society of Chemistry. e) Illustration of the mesh printing method. Reproduced with permission. Copyright 2016.^[63] Royal Society of Chemistry.

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Figure 2.6. a) Schematic of the responsive polymer chain behavior below and above the LSCT. Reproduced with permission.^[86] Copyright 2016, Elsevier. b) Schematic diagram of the PNIPAm hydrogel smart window sandwich structure. Incident light (golden arrows) passes through the hydrogel below 32 °C, but is largely blocked above 32 °C. The insets i and ii are the 200 μm demonstration devices at 20 and 80 °C, respectively. c) Transmittance spectrum of 200 μm PNIPAm hydrogel thin film at temperatures varying from 20 to 60 °C. d) Optical properties T_{lum} , ΔT_{sol} , ΔT_{IR} , and ΔT_{lum} of 200 μm PNIPAm film at temperatures ranging from 20 to 60 °C. Reproduced with permission.^[40] Copyright 2014, Royal Society of Chemistry. e) Schematic diagram of the PNIPAm-VO₂ hybrid hydrogel smart window sandwich structure. f) UV-Vis-NIR transmittance spectra of pure PNIPAm hydrogel, VO₂ nanoparticles and VO₂-PNIPAm hybrid hydrogel at 20 and 80 °C. g) Durability test of 100 μm PNIPAm-VO₂ hybrid film with temperature variation between 20 and 80 °C. Reproduced with permission.^[41] Copyright 2015, Royal Society of Chemistry.

Figure 2.7 a) Schematic illustration of the octahedral-tetrahedral configuration change of ionic liquid-based complex system. The IL-Ni-Cl complex undergoes a phase transition from octahedral to tetrahedral above the LCST. b) Transmittance spectrum over the UV-Vis-NIR regions of pure IL-Ni-Cl film, VO₂ nanoparticles and VO₂/IL-Ni-Cl hybrid film at 20 and 80 °C. c) Demonstrations of pure IL-Ni-Cl film, VO₂ nanoparticle film and VO₂/IL-Ni-Cl hybrid film at 20 and 80 °C. Reproduced with permission.^[42] Copyright 2016, American Chemical Society. d) Schematic illustration of thermochromic optical transmittance change upon variation in temperature. e) Transmittance spectrum over the UV-Vis-NIR region of ionogel at various temperatures ranging from 15-60 °C. The insets are photographs of transparent, translucent and opaque states of the ionogel, respectively. f) Demonstration of ionogel films mixed with brilliant green, rhodamine B (RhB) and methyl orange organic dyes below and above the transition temperature, respectively. Reproduced with permission.^[100] Copyright 2017, American Chemical Society.

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Figure 2.9 a) Schematic illustration of the inverse temperature crystallization (ITC) process of perovskite materials: with increasing temperature, the perovskite crystals nucleate and grow. b) Absorption spectra of perovskite crystals obtained from inks at 60, 90 and 120 °C. c) Photographs of thermochromic prototype annealed at 25 °C (top) and 60 °C (bottom). d) Absorption spectra of the thermochromic prototype after annealing at the indicated temperature. e) Band edge alternation of the thermochromic prototype during heating and cooling cycles between 25 and 60 °C. The green circles represent the extrapolated maxima at 25 °C; the red spots represent the extrapolated minima at 60 °C. Reproduced with permission.^[125] Copyright 2017, American Chemical Society.

Figure 2.10 a) Schematic of the orientation-dependent optical behavior of cholesteric liquid crystalline materials. Reproduced with permission.^[57] Copyright 2017, John Wiley & Sons. b) Schematic of the smectic A (SmA) to chiral nematic (N*) phase transition in a cell containing the liquid crystals (LCs) and indium tin oxide (ITO) nanocrystals (NCs). The transition can be reversibly induced by either electric- or thermal-stimulus (b1), accompanying with distinct transparency change, demonstrated as the corresponding photographs (b2). c) Temperature-dependent transmittance spectra of the smart film consisting 5 wt% ITO NCs before and after 300 cycles. Inset of (c) is the photography of the meter-scale film. d) Temperature-resolved transmittance at 560 nm of smart films containing 0% and 5 wt% ITO NCs. Reproduced with permission. ^[61] Copyright 2017, Royal Society of Chemistry. e) Schematic of the VO₂-LCs composite film (e1) with four optical states under different stimuli (e2). f) Temperature-dependent spectra of the composite film containing 2.5 wt% W-doped VO₂. g) Electric-field-dependent of the

transmittance spectra of the composite film containing 2.5wt% W-doped VO₂ at 55 °C. Reproduced with permission.^[63] Copyright 2017, Royal Society of Chemistry.

Figure 2.11 a) Crystal structures of tetragonal (top) and monoclinic (bottom) VO₂. b) Summary of the spectral ranges that can be modulated by metamaterials, perovskites, ionic liquids, hydrogels, and VO₂. Reproduced with permission. Reproduced with permission.^[152] Copyright 2014, Nature Publishing Group. For the metamaterials, the potential spectral range is indicated since accurate data is not available. c) Summary of quality data on solar energy modulation ability (ΔT_{sol}) and visible transmittance reported for methods. Reproduced with permission.^[153] Copyright 2016, John Wiley & Sons.

Figure 3.1 Photographs of the produced vanadium precursors with a low (Left) and a high (Right) viscosity.

Figure 3.2 Solar energy spectrum and the analysis of solar energy distribution along the UV-Vis-NIR region. The figure is adaptive from online resources,^[6] Discover Ideas About Renewable Energy, Pinterest, <https://www.pinterest.com/pin/4574037099007741/>.

Figure 3.3 a) is a simplistic model of Bragg's law to understand how X-ray diffraction happens in related with crystals; b) is the diagram how XRD machine implements the Bragg-Brentano geometry. The both of (a) and b) are reprinted from tutorial PPT titled "Self-User Training for X-Ray Diffraction SEF" from Massachusetts Institute of Technology (MIT), United States of America (USA).^[7]

Figure 3.4 XRD analysis for a polycrystalline sample. Reprinted from tutorial PPT titled "Self-User Training for X-Ray Diffraction SEF" from Massachusetts Institute of Technology (MIT), United States of America (USA).^[7]

Figure 3.5 The diagram to represent how AFM works. Reprint from PPT of course MS7070, Scanning Tunneling Microscopy (STM) & Molecular Self-Assembly, School of Materials Science and Engineering, Nanyang Technological University.^[8]

Figure 3.6 The diagram to illustrate the two types of imaging mode. Reprint from PPT of course MS7070, Scanning Tunnelling Microscopy (STM) & Molecular Self-Assembly, School of Materials Science and Engineering, Nanyang Technological University.^[8]

Figure 3.7 The diagram to represent how UV-vis-NIR spectrometer works. Reprint from user guide and tutorial for using the Cary 500, School of Materials Science and Engineering, Georgia Institute of Technology, USA.^[9]

Figure 3.8 The diagram to illustrate the electron beam interaction with materials. Reprint from the handbook titled “Properties of Electrons, their Interactions with Matter and Applications in Electron Microscopy”, Laboratory of Inorganic Chemistry, ETH Zurich, Switzerland.^[10]

Figure 3.9 The diagram to illustrate the mechanism how TEM works in analogy with optical microscopy. Reprinted from the tutorial PPT of a lecture titled “Samuel Roberts Noble Electron Microscopy Laboratory”, University of Oklahoma, USA.^[11]

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Figure 4.1 a) Diagram of the procedure to fabricate 2D SiO₂/VO₂ core/shell foils. a1-3) Fabrication of silica nanosphere MCC templates, and 4,5) preparation of SiO₂/VO₂ films. SEM images of 400 nm silica sphere MCC b) before and c) after the treatment in Piranha solution. And their calculated size distributions d) before and e) after the treatment. Average diameters are presented respectively.

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Figure 4.6 SEM images of the color changed samples using the different unit size of MCC, from a) 200 nm, b) 400 nm, c) 600 nm to d) 700 nm. Inserts are the corresponding cross-section view. TEM images of the 400 nm sample are shown in e) low and f) high magnification. Inset of (f) shows the illustration of produced VO₂/Silica sphere structures.

Figure 4.7. Photographs of prepared samples with a tag paper background under sunlight from a) the normal view and b) a tilted view of 45 degrees; c) photographs of these samples with a white wall background under sunlight; d) photographs of the same samples with tag paper background in the lab under a common incandescent lamp. A tilted view of 45 degrees is for (c) and (d). The captured photographs are exhibited without any post color processing. Simulated band structure of SiO₂/VO₂ photonic crystal is shown in e) Reflection (left) and transmission (right), period 600 nm; f) Reflection (left) and transmission (right), period 700 nm. The measured transmittance spectrums of g) color changed samples and h) prepared silica sphere MCCs. In (g) and (h), the transmittance

peaks and troughs are indicated by the solid and dashed arrows respectively. (i) And its insert is the data analysis charts for the trough and peak positions respectively as a function of the sphere diameter.

Figure 5.1 Effect of synthesis conditions on the morphology evolution. Route 1: nanoparticle arrays are prepared via short PE duration and low viscosity precursor; Route 2: nanodome arrays are produced, using high viscosity precursor that can stick on the tops of PS spheres; Route 3, nanonet arrays are fabricated by controlling the interval space between adjacent spheres via prolonging PE duration.

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Figure 5.3 SEM images of patterned VO₂ films. a-c) nanoparticle, d-f) nanonet, and g-i) nanodome arrays prepared using 160-, 490-, and 830-nm PS spheres from left to right, respectively. (a-f) are the top-views, while (g-i) are the tilted-views. The inset of (h) is high magnification tilted-view image of 490-nm periodic nanodome arrays on edge. Periodicities of the nanoparticle arrays are illustrated as yellow hexagons and measured to be 160, 490, and 830 nm for (a-c), respectively.

Figure 5.4 a) XRD analysis of VO₂ nanonet, nanoparticle, and nanodome arrays under room temperature. Characteristic peaks of monoclinic VO₂, (011), (200), and (220), are observed (JCPDS card no. 72-0514, space group: p21/c). All samples are demonstrated with monoclinic VO₂. b-e) Size distributions of the VO₂ nanoparticles fabrication via (b) 160, (c) 490, and (d) 830 nm PS sphere templates. e) the increasing relation of PS spheres diameters in templates with the size of prepared VO₂ nanoparticles. f,g) SEM images of the sample prepared using 490-nm MCC with PE duration of (f) 40 and (g) 80 s. h) Tilted SEM image of the nanodome sample on edge before annealing. i) SEM image of the 490 nm MCC annealed under 120°C for 1h.

Figure 5.5 Illustrations of VO₂ film morphological evolution, which mainly includes four sequential stages: a) the small nanoparticles, b) the large nanoparticles, c) the partially linked nanoparticles, and d) the nanonet array. VO₂ nanocrystals are indicated by blue color, while the green slats below them stand for the quartz substrates. The morphological evolution is verified experimentally by e-h) the corresponding SEM images. Patterned VO₂ nanocrystals are observed with the change from (e) the small particles to (f) the big nanoparticles, then (g) develop to the partially linked nanoparticles. Finally, (h) the nanonet array forms.

Figure 5.6 a) Calculated (dashed lines) and measured (solid lines) transmittance spectra of nanoparticle arrays with diameters of 67, 125, and 287 nm, respectively. All spectra are normalized for LSPR peak position comparison. Inset of (a) is the magnified spectra for the measured peaks, which indicated by the corresponding triangles. b) Experimental and simulated correlations of the LSPR peak positions (nm) and particle diameters. c-e) In-plane (x-y) electric-fields at VO₂-air interfaces of the VO₂ nanoparticle arrays with diameters of (c) 67, (d) 125, and (e) 287 nm at resonances of 1075, 1085, 1230 nm, respectively. f) Transmittance spectra of 67-nm VO₂ arrays in PEG, PVA, and PVP. Inset of (f) is the magnified spectra for the LSPR peaks pointed out by the triangles. g) Effect of the medium reflective index to LSPR peak position. h) Temperature-dependent LSPR tunability of the 67-nm VO₂ nanoparticle array in the temperature range from 20 to 100 °C. Extinction (A) is calculated via $A = -\log_{10}(\text{transmittance})$. i,j) are the hysteresis loops of the relative LSPR intensity and the LSPR peak position. The relative LSPR intensity relies on the normalized integrated area under curves.

Figure 5.7 (a) Illustration of the way to overlay VO₂ nanoparticle array foils, inserted photograph on left is the 1 layer sample. 2D nanostructured VO₂ nanocrystals are prepared with 1.2 mm in length. The inserted table of (a) is calculated thermochromic performance based on (b) the transmittance spectra at 20°C and 95°C. (c) Durability test for the double-layered sample. (d-e) The thermochromic performance comparisons of the double-layered sample in this work with (d) reported periodic VO₂ nanostructures, and (e) the best through

other methods. Data in (d) and (e) include honeycomb,^[50] 2D phononic crystals,^[23] periodic nanonets,^[51] truss network,^[28] biomimetic moth-eyed structure,^[48] anti-reflective multilayer,^[52] controlled porosity,^[53] VO₂ nanoparticles/transparent media composite,^[54] and doping.^[55]

Figure 6.1 Schematic of transmittance modulation methods based on a) reconfigurable metamaterials for UV-visible modulation, b) active LSPR for NIR modulation, and c) the integration of active LSPR and reconfigurable metamaterials for UV-visible-NIR modulation.

Figure 6.2 a) XRD pattern of the VO₂ NPs with identified planes based on the PDF card No. JCPDS# 82-661. b) A TEM image of quasi-sphere VO₂ NPs. c) The size distribution diagram. d) SEAD pattern with identified four rings corresponding to the (022), (210), (200), and (011) planes of monoclinic VO₂. e) The HRTEM image of a VO₂ NP on edge and the corresponding fast Fourier transition (FTT) image as the inset. The interplane spacing of 0.24 nm and (200) plane are indicated.

Figure 6.3 a) Illustration of the produced composite film consisted of well-dispersed VO₂ NPs in PDMS matrix. b) Transmittance spectra of the planar PDMS film at 20 (The black line) and 95 (The red line) °C, respectively. c) Photographs of the roll-up process of the yellow-brown composite film from figures on 1 to 6. b) Photographs of the VO₂-PDMS composite film under a stretch of 0%, 20%, 40%, 60%, 80%, and 100% from left to right. The film is observed being elongated in a uniaxial direction and no distinct fracture is observed during the process, demonstrating the VO₂-PDMS film is stretchable.

Figure 6.4 a) Temperature-dependent extinction spectra of VO₂-PDMS composite under an increasing temperature from 20 to 100 °C. b) The hysteresis loop of extinction intensity at 1260 nm (0.98 eV) during a heating and cooling process. c) Transmittance spectra of the composite films with different VO₂ concentrations at 20 and 95 °C, respectively.

Figure 6.5 a) Transmittance spectra of the samples under different dispersion conditions. The spectra are normalized for the convenience of LSPR position comparison. b) Experimental LSPR positions on the sample #1-4 corresponding to Figure 2d and calculated results on two VO₂ NPs with a gap varied from 20 to 200 nm. Inset is the illustration of the gap (*d*). c) Simulated configuration transition of a VO₂ NP in PDMS matrix under an increasing strain, illustrated by four simulated stress contours under the strains of 0%, 33%, 67%, and 100%. d) Illustration of the gap (*d*) between two VO₂ NPs. e) Calculated extinction spectra of two VO₂ NPs in PDMS matrix with a gap of 20, 40, 100, 150, and 200 nm, respectively. c) Electric fields (*x-y*) of two VO₂ NPs in PDMS with a gap of 20, 100, and 200 nm. The extinction peak positions are observed with a blue-shift under increase of the gap (*d*).

Figure 6.6 a) Normalized transmittance spectra of the composite film under strains of 0%, 33%, 67%, and 100%. b) Experimental and simulated LSPR positions under the strains. c) Simulated configuration transition of a VO₂ NP in PDMS matrix under an increasing strain, illustrated by four simulated stress contours under the strains of 0%, 33%, 67%, and 100%. d) Calculated extinction spectra of the stretched VO₂-PDMS film based on the model illustrated in (c).

Figure 6.7 a) Photography of the curved designs prepared by tailoring the VO₂-PDMS films, including “lion”, “butterfly”, and “flowers”. b,c) Kirigami designs and their configurational transitions under stretch. b) Illustration of the design with alternant parallel lines cuts and the photography of its configurations under an in-plane axial strain from 0% to 100%. c) Illustration of the design with perpendicular crossed lines cuts and the photographs of its 2D-to-3D configurations transitions under out-plane stress. c) Illustration of the kirigami design with alternant parallel lines cuts. The geometry is identified as the red arrows in a magnified unit cell. d) Illustration of the kirigami design with perpendicular crossed lines cuts. The geometry is identified as the red arrows in a magnified unit cell as the image on right.

Figure 6.8 a) Measured uniaxial stress-strain curves of the planar PDMS, the planar VO₂-PDMS composite, and the kirigami VO₂-PDMS films with the design in figure 3b. b) Mechanical property analysis of stress, strain, Young's modulus, and toughness. c) d) Measured uniaxial stress-strain curves of the planar VO₂-PDMS composite films with nominal VO₂ concentration of 0.75%, 1.50%, and 22.5%, respectively. e) Mechanical property analysis of stress, strain, Young's modulus, and toughness.

Figure 6.9 a) SEM simulated strain distributions of the kirigami VO₂-PDMS film and the magnified strain contour on a cut tip area as the inset. b) Transmittance spectra of kirigami-patterned VO₂-PDMS film under strains of 0%, 33%, 67%, and 100%. c) Normalized transmittance contrasts in the wavelength range from 250-2500 nm. The black histogram indicates the contrast of kirigami-patterned composite film under 0% and 100%. The red histogram represents the contrast of composite film under a temperature of 20 and 90 °C.

Figure 6.10 a) Illustration of an energy-saving smart window that adaptively reduces the indoor solar energy irradiation under elevated temperature. b) The photograph of the house model for the smart window demo. c) The configuration transition of the smart window model under increasing temperature. The fully thermal responsive system is applied, which fabricated based on kirigami-patterned VO₂-PDMS film. d) Transmittance spectra of the film at (state 3) 20 °C with noncompact configuration (strain of 100%), (state 2) 20°C with compact configuration, and (state 1) 95 °C with compact configuration. e) Cycling test of the film switching between state 1 and 3. The transmittance at 1260 nm is recorded. f) Calculated ΔT_{sol} , T_{lum} , and $\Delta T_{1260 \text{ nm}}$ of the film in state 1-3 and the reference film based on planar VO₂ and PDMS, respectively. g) Comparison of this work with the best-reported experiment and simulation works regarding the T_{lum} and ΔT_{sol} .^[25, 28, 33-46] The trend lines of experiment and simulation results are indicated as the blue and orange lines, respectively. Reported methods are classified and denoted using difference colors on the right of (g).

Figure 6.11. a) Schematic of the building model. Size of the building model is 10.56 m × 10.56 m × 2.6 m × 2 stories. Two windows (1.2 m × 1.5 m) are evenly arranged for each orientation of each floor to average out the effects of orientation. The window to wall ratio

of the model is 13%. Insert form presents the air condition information applied for simulation. b,c) Simulation results of building heating and cooling energy. b) Calculated energy consumptions per year for the material applied in Houston (US), Hong Kong (China), and Madrid (Spain), respectively, comparing to the base and low E glasses. c) Comparison of the monthly energy consumption of the material and base glasses applied in Houston. d,e) Simulation results of building heating and cooling energy of films based on kirigami-LSPR, LSPR, and kirigami, respectively. d) Calculated energy consumptions per year for the materials applied in these three cities. e) Monthly energy conservation of the materials in Houston. The energy conservation of the materials is calculated based on the reduction of the energy consumption of the materials to the bare glasses.

Figure 7.1 Illustration of the design of the SiO_2/VO_2 core/shell 2D photonic crystals and the simulated transmittance spectra with statically visible and dynamically infrared modulated for smart window deployment.

Figure 7.2 a) Illustration of preparation of 2D VO_2 nanoparticle arrays through the colloidal lithography method. b) Temperature-dependent extinction spectra, indicating the switch-on behavior of active LSPR. c) The LSPR position changes in related to the VO_2 NPs diameter and the medium reflective index. Insert are the SEM images of prepared VO_2 NPs with corresponding particle diameter.

Figure 7.3 a) The schematic of the synthetic effect of the reconfigurable transition of kirigami-inspired structures and the active LSPR of VO_2 NPs, targeting the adaptive, broadband, and high-efficient solar modulation. b) The schematic smart window with functional layer based on such materials, which block the solar energy in hot days while permitting the solar energy in hot days.

Abbreviations

2D	Two-dimension/dimensional
3D	Three-dimension/dimensional
ARC	Antireflection coating
ATO	Sb-doped SnO ₂
AZO	Al-doped ZnO
CLETS	Co-based ligand exchange thermochromic system
CTAV	Cetyltrimethylammonium vanadate
CTAB	Cetyltrimethyl ammonium bromide
CVD	Chemical vapor deposition
DOS	Density of states
DFT	Density functional theory
EMT	Effective medium theory
FDTD	Finite difference time domain
FOS	Fluorooctyl triethoxysilane
FTO	F-doped SnO ₂
HPC	Hydroxypropyl cellulose
HCL	Hydrochloric acid
HCP	Hexagonal-close-packed
IL-Ni-Cl	Ionic liquid-nickel-chlorine
IR	Infrared
LCA	Life cycle assessment
LCST	Lower critical solution temperature
LSPR	Localized surface plasmon resonance
MCC	Monolayer colloidal crystal
MIT	Metal-insulator transition
M/R	Monoclinic/rutile
NIR	Near-infrared
NLETS	Nickel-based ligand exchange thermochromic system
NP	Nanoparticle

N ₂ H ₄	Hydrazine
PBG	Photonic bandgap
PC	Photonic crystals
PDMS	Polydimethylsiloxane
PE	Plasma etching
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PNIPAm	Poly-N-isopropylacrylamide
PS	Polystyrene
PU	Polyurethane
PVP	Polyvinylpyrrolidone
RhB	Rhodamine B
RI	Refractive index
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscope
SiO ₂	Silica
SPR	Surface plasmon resonance
STM	Scanning tunnelling microscopy
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilicate
UV	Ultraviolet
VCl ₂	Vanadyl dichloride
VO ₂	Vanadium dioxide
T_{lum}	Average visible transmittance
ΔT_{sol}	Solar energy modulation
τ_c	Phase transition temperature

Chapter 1*

Introduction

This chapter starts from the background of building energy and the promising role of the smart window toward the energy reduction. The development of a smart window is mainly classified as three directions: the electrochromism, the thermochromism, and the photochromism. We briefing the advantages of thermochromism and point out the scientific challenges in this field. The objectives and scope of the thesis are introduced targeting the improvement or solutions of the problems. Finally, we present the overview contents and detail the funding and outcomes.

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1.1 Background: Building Energy Consumption

The growing world population and rapid modernization have led to increased energy demand, necessitating highly efficient energy use.^[1, 2] Building energy usage accounts for up to 40% of the overall energy consumption in developed countries, which exceeds the energy consumed by the industry and transportation sectors (Figure 1.1a).^[3-5] Building services including heating, ventilation and air conditioning are major components of building energy consumption, contributing approximately 50% of total building energy (Figure 1.1a).^[3] Reducing the energy consumption of these services whilst maintaining building comfort levels is a significant challenge in sustainable development.^[6, 7] Amongst all building components, windows are considered to be one of the least energy-efficient parts as there is always heat transfer in the opposite direction to that desired.^[8, 9]

In recent times, smart windows have received considerable attention because of their potentially significant contribution to the economization of building energy consumption.^[10-16] A window can regulate indoor solar irradiation in a ‘smart’ way, that is, by dynamically and reversibly tuning the transmittance of ultraviolet (UV), visible, and infrared (IR) solar radiation.^[17-20] Development of smart windows can mainly be categorized as electro-, thermo-, and photo-stimulated optical response changes (Figure 1.1b).^[21-25] Among them, smart windows based on thermoresponsive materials are highly competitive due to their unique characteristics: (1) low cost, arising from their simple configuration resulting in low fabrication and maintenance costs, especially compared to electrochromic smart windows which are composed of electrolyte, electrodes, require an additional power system and other features (Figure 1.1b); (2) passivity, with their automatic response to temperature cutting down the need for switch systems, for example electrical control requiring external energy and human manipulation; and (3) rational stimulus-response, with regulation by indoor temperature rather than UV-triggered optical modulation in photochromic materials.

Figure 1.1 a) Proportion of building energy consumption compared with total energy consumption. The proportion of energy consumption of building services such as heating, ventilation, and air conditioning of total building energy consumption. b) Schematic of electrochromic, thermochromic and photochromic smart windows. The orange arrows indicate incident sunlight. Reproduced with permission.^[21] Copyright 2017, John Wiley & Sons.

1.2 Problem Statement

Vanadium dioxide (VO_2) is the most studied material for thermochromic smart window due to its reversible phase transition near room temperature, which undergoes a metal-insulator transition at the critical temperature (τ_c) of 68°C , accompanied with huge transmittance contrast in the IR range and negligible change in the visible range.^[26] The integrated luminous transmittance (T_{lum}) and the integrated solar energy modulation (ΔT_{sol}) are two key parameters to assess performance, for which calculation methods can be found in previous reports.^[21, 26] Extensive efforts have been put into optimizing T_{lum} and ΔT_{sol} by nano/micro-scale engineering, including porosity, nanocomposites, biomimetic design, grids, and multilayers.^[27, 28] However, challenges regarding pure VO_2 -based smart windows still remain regarding the following aspects:

- (1) the relatively high τ_c intrinsic yellow-brown color;
- (2) low resistance to oxidization;
- (3) more importantly, the unfavorable combination of low T_{lum} and ΔT_{sol} , which are less than 50% and 20%.

1.3 Objectives and Scope

The objective of projects in the thesis as well as in my doctoral academic life is to improve the VO₂-based thermochromic smart window. More specifically, the objectives are:

- (1) to improve the intrinsic yellow-brown color of VO₂-based smart windows and, more importantly;
- (2) to promote the thermochromic performance, the combination of T_{lum} and ΔT_{sol} .

Methods are applied by engineering the photonics and plasmonics in patterned VO₂ nanostructures as well as introducing the adaptive reconfiguration structures.

From a scientific scope, the thesis starts from materials to optical and mechanical properties as well as the potential applications. The thesis focuses on the VO₂-based thermochromic smart windows and is extended to the concepts of stimuli-responsive materials, the nano/microscale fabrication, photonic crystals (PCs), localized surface plasmon resonances (LSPR), kirigami-inspired mechanical metamaterials, and the architectural energy consumption.

1.4 Dissertation Overview

This thesis is dedicated to promoting the performance of VO₂-based thermochromic smart windows, which are concluded as following chapters.

Chapter 1 introduces the background of building energy consumption, the importance of smart window, and the energy-saving thermochromic smart windows. Then it followed with the statement of problems, objectives, and scope as well as a brief summary of the entire doctoral thesis.

Chapter 2 introduces the phase transition and the optical properties of VO₂, following by the comparison with other potential materials for the thermochromic smart window,

including temperature-responsive hydrogels, thermal-sensitive ionic liquid, reconfiguration metamaterials, thermochromic perovskite, orientation-tunable liquid crystals. Besides, the advances of VO₂-based thermochromic smart windows are summarized.

Chapter 3 discusses the experimental methodology details and the basic principle of characterization techniques. These details include material preparation, the calculation method of T_{lum} and ΔT_{sol} , and the related simulation methods.

Chapter 4 presents the VO₂-based photonic crystals for thermochromic smart window applications to improve the undesirable yellow-brown color. The SiO₂/VO₂ core/shell 2D photonic crystal is prepared and demonstrated to exhibit static visible light tunability and dynamic near-infrared (NIR) modulation. Three-dimensional (3D) finite difference time domain (FDTD) simulations predict that the transmittance can be tuned across the visible spectrum while maintaining good solar regulation efficiency ($\Delta T_{sol}=11.0\%$) and high solar transmittance ($T_{lum}=49.6\%$). Though the experimental result is not as prominent, it proves that the color changes of VO₂ films are accompanied by NIR modulation, which is aligned with the simulation result.

Chapter 5 discusses the controlled preparation of 2D patterned VO₂-based nanocrystals with tunable morphologies, from nanonet, nanodome, to nanoparticle arrays and their application in thermochromic smart windows. The nanoparticle arrays exhibit tunable LSPR at different temperatures and the LSPR red-shift is observed with the increase of the particle size and the media reflective index. A competitive solar regulation efficiency ($\Delta T_{sol} = 13.2\%$) and a transmittance contrast at 2000 nm ($\Delta T_{NIR} = 44\%$) can be achieved.

Chapter 6 discusses the method pairing reconfigurable metamaterials with the active LSPR. We develop a kirigami-inspired elastomer containing plasmonic vanadium dioxide (VO₂), exhibiting adaptive, broadband, and high-efficient optical modulation. The geometrical transition and the active LSPR function synergistically by manipulating ultraviolet-visible and near-infrared regions, respectively. We also investigate an active LSPR control via stretch-induced local dielectric changes which is mitigated on kirigami metamaterials due to their unique strain distributions. We further demonstrate a new mechanical-thermal energy-saving smart window adopting such materials exhibits an unprecedented solar

energy modulation ($\Delta T_{\text{sol}} = 37.7\%$). Fully thermal responsiveness is also achieved in such a system.

Chapter 7 summaries each project, including (1) 2D SiO₂-VO₂ Photonic Crystals for Smart Windows, (2) 2D patterned VO₂ Nanostructures for Smart Windows, and (3) Pairing Plasmonic VO₂ with Kirigami Metamaterials for Smart Windows. In conclusion, a successful improvement on the yellow-brown color is achieved on (1) 2D photonic crystals of SiO₂-VO₂. Promotions of the combination of T_{lum} and ΔT_{sol} are achieved on both the (2) 2D patterned VO₂ and (3) the integration of reconfiguration structures with the active LSPR. Moreover, perspectives on the challenge and the future work are suggested.

1.5 Findings and Outcomes

The findings and outcomes are summarized with specific emphasis on the novelty. To our knowledge, these findings are reported for the first time by us in our related publications. They are classified and concluded mainly from 4 aspects, including (1) the material preparation, (2) optical properties, (3) the performance promotion of smart windows, and (4) new concepts.

(1) Materials preparation.

1a. The successful preparation of 2D patterned VO₂-SiO₂ core-shell nanostructures.

1b. The controlled preparation of 2D patterned VO₂ nanoparticle and nanodome arrays.

(2) Optical properties.

2a. Demonstration the tunable PBGs in 2D patterned VO₂-SiO₂ core-shell nanostructures.

2b. Identification the thermal-responsive as well as the size- and media-dependent LSPR in VO₂ nanoparticles.

2d. Demonstration of a new method to actively control the LSPR via stretch-induced local dielectric changes.

(3) The performance promotion of smart windows

3a. Achieved ΔT_{sol} of 13.2% in the 2D patterned VO₂ nanoparticles, surpassing the best result in reported periodic VO₂ nanostructures.

3b. Achieved ΔT_{sol} of 37.7% and T_{lum} of 35.2% in the method by integrating the active LSPR with kirigami-reconfiguration structures, outperforming the best reports based on a multilayer, porosity, composite, grid, and biomimetic structure.

(4) New Concepts.

4a. Introducing the photonic crystals for color changes in smart window applications.

4b. Investigating the active LSPR of VO₂ in smart window applications, including size-, media-, temperature-, and strain-induced controls for promoting the performance (ΔT_{sol} and T_{lum}).

4c. Integrating the active LSPR with kirigami-inspired metamaterials for promoting the performance (ΔT_{sol} and T_{lum}).

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Chapter 2*

Literature Review

In this chapter, we introduce the background of the phase transition of VO_2 . Recent progress on VO_2 -based smart windows is summarized, including the method of composite films using the responsive and non-responsive matrix, the porous structures as well as the grid and biomimetic methods. We further outline the emerging thermochromic materials such as the temperature-responsive hydrogel, thermal-sensitive ionic liquid, reconfiguration metamaterials, thermochromic perovskites, and the orientation-tunable liquid crystals. Finally, we compare the VO_2 with these emerging materials to illustrate the advantages and disadvantages of VO_2 for thermochromic smart windows.

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2.1 Vanadium dioxide (VO₂)

In recent years, both monoclinic (M) and rutile (R) phase vanadium dioxide (VO₂) has aroused great attention as a promising candidate for smart windows owing to the reversible metal-to-insulator transition (MIT) at a critical temperature of 68 °C (341 K).^[1, 2] In fact, VO₂(M/R) is also a widely studied material in physical chemistry and condensed-matter physics because of its specific phase-transition features.^[3-5]

The low-temperature insulating phase has a monoclinic structure (M, space group P2₁/c, $a_M = 5.75$ Å, $b_M = 4.52$ Å, $c_M = 5.38$ Å, $\beta = 122.6^\circ$).^[1, 2] When the temperature is above 68 °C, this low-temperature insulating phase transforms to the high-temperature metallic phase, which displays a tetragonal structure (R, space group P4₂/nm, $a_R = b_R = 4.55$ Å, $c_R = 2.86$ Å) (Figure 2.1a).^[3] The vanadium atoms occupy the lattice point of the body-centered cubic structure and are located at the centers of the tilted VO₆ octahedra, which exhibit local Jahn-Teller distortions.^[6] Four of the six oxygen atoms in the VO₆ octahedra are located closer to the vanadium atom, and the V-O bond distances are 1.922 and 1.933 Å, respectively. Chains of edge-sharing VO₆ octahedra have a corner-sharing arrangement with other VO₆ octahedra and are arranged linearly along the crystallographic *c*-axis, with a V-V distance of ~2.85 Å.^[7] During the phase transition, the vanadium atoms move along the V-V direction, resulting in the pairing and tilting of VO₆ octahedra in this direction.^[8] Compared with the metallic phase, the unit cell of the insulating phase is doubled, and two distinct sets of long and short V-V distances (3.12 Å and 2.65 Å) exist as a result of the new positions of the vanadium atoms.

To fully describe the phase-transition process of VO₂(Monoclinic/Rutile), a molecular picture based on relatively simple crystal-field theory is typically considered, as first proposed by Goodenough in 1971.^[9] In brief and as shown in Figure 2.1b, in the tetragonal phase, a wide π bond and a narrow π^* anti-bond are formed between the V⁴⁺ and O²⁻ $d\pi$ orbitals, and a $d_{//}$ nonbond is formed between adjacent V⁴⁺ orbitals along the crystallographic *c*-axis. Although the energy band of tetragonal VO₂ is approximately 2.5 eV, the unfilled π^* and $d_{//}$ bands partially overlap, and the Fermi level falls at the point

where the π^* and $d_{//}$ bands overlap, giving it metallic characteristics. When the temperature decreases, the tilting of the VO_6 octahedra enhances the π overlap between the V^{4+} and O^{2-} orbitals, thereby elevating the anti-bonding π^* level, whereas the $d_{//}$ bonds interact strongly in V-V pairs and then split into $d_{//}$ bonding and anti-bonding components. A band gap of ~ 0.7 eV is formed between the π^* and $d_{//}$ bands, leading to the formation of a semiconducting phase. Although this model exhibits several discrepancies from the experimental data, it can nevertheless qualitatively explain the nature of the phase transition in VO_2 .

A fierce debate over the driving force of the VO_2 phase transition has persisted for several decades, with respect to whether the electron-electron correlation is strong enough to localize the electrons by forming a Mott-Hubbard insulator (Mott model) or whether structural distortions alone can induce the insulating phase (Peierls model).^[10-14] Wentzcovitch *et al.* revealed a distorted monoclinic ground state to be in good agreement with the experimental findings and a nearly open gap with respect to charge excitations; thus, they believed that VO_2 may be more band-like than correlated.^[14] This result was supported by Cavalleri *et al.*, who employed ultrafast spectroscopy to construct a time-domain hierarchy between the structural and electronic effects and found that the initiation of the metallic phase formation was prompted by hole photodoping into the valence band of the insulator phase; therefore, the phase transition could be retarded with respect to hole injection and exhibits a bottleneck time scale.^[15-17] Baum *et al.* used four-dimensional (4D) ultrafast electron microscopy to study the phase transition of VO_2 initiated by near-infrared excitation.^[18] Their results suggest that the transition from the insulating phase to the metallic phase initially involves the expansion of the primary V-V bond with local displacements (on femtosecond and picosecond timescales), followed by long-range shear rearrangements (on a nanoseconds timescale and at the speed of sound), revealing a structural pathway and non-concerted transformation mechanism.

Figure 2.1 a) Schematic of the atomic structures of the high-temperature metallic tetragonal phase R and the low-temperature insulating monoclinic phase M. The V-V distances in each crystal structure are highlighted. b) Band structures of the metallic R and insulating M phases of VO₂ depicted by molecular orbital diagrams. Reproduced with permission. Copyright 2011.^[7] American Chemical Society.

2.2 Progress in VO₂-Based Thermochromic Smart Windows

2.2.1 Elemental Doping

Elemental doping is a process that intentionally introduces another element (s) into a pure material to modify its electrical or optical properties. For VO₂, elemental doping is one of the conventional strategies to tailor its τ_c and optical properties. The effects of repeated doping elements are summarized in Table 2.1. The electronic phase transition in VO₂ is proposed to be accompanied by a (nearly) simultaneous structural phase transition between the VO₂(R) and VO₂(M) phase. If the energy barrier across the phase transition could be lowered by doping, τ_c would decrease. Accordingly, the selection of the doping element is commonly based on two aspects: increasing the carrier concentration to accelerate the electronic phase transition, or introducing distortion into the atomic structure to assist the structural phase transition.

Table 2.1 Elemental doping effects on the thermochromic performance of VO₂ thin films

Group	Dopant	Doping level	$T_{lum}(\%)$	$\Delta T_{sol}(\%)$	$d\tau_c/dx$ (°C/at.%)	Ref.
IA	H	3%	\	\	-38	[19]
	Li	3%	\	\	-43	[20]
	Na	3%	\	\	-49	[20]
	K	3%	\	\	-94	[20]
IIA	Be	3%	\	\	-58	[21]
	Mg	5%	82.1	4.8	-3	[22]
	Ca	1.3%	\	7.6	\	[23]
	Sr	9.6%	54.3	5.0	\	[23]
	Sr	6.8%	50.3	6.5	\	[23]
	Ba	8.3%	\	7.5	\	[23]
IIIA	B	\	\	\	-83	[24]
VIIA	F	2.93%	48.7	10.7	-11.3	[25]
Transition Metal	W	2%	45.1	6.9	-20	[26]
	Mo	2%	\	\	-11	[27]
	Nb	2%-3%	\	\	-7.8	[28]
	Zr	9.8%	60.4	14.1	-0.4	[29]
	Ti	1.1%	53	17.2	0	[30]
Rare	Tb	4%	65.9	4.6	-1.5	[31]
Earth	La	4%	50.1	10.3	-1.1	[32]
Co-Doping	Mg+W	4% Mg + 2% W	81.3	4.3	-5.5	[22]
	F+W	2.1% F + 1.8% W	\	\	-17.4	[33]
	Zr+W	8.5% Zr + 0.6% W	56.4	12.3	-1.3	[29]

Note: “\” means data not available.

2.2.2 Composite Films based on VO₂

In the continuous VO₂ thin films, the thickness needs to be increased to overcome the insufficient ΔT_{sol} , but at the cost of depressing the T_{lum} . A promising way to tackle the trade-off between ΔT_{sol} and T_{lum} is by fabricating nano thermochromic composite, which can be achieved by embedding VO₂-based nanoparticles in a dielectric matrix. The reported simulated and experimental results concerning VO₂-based nanocomposites are summarized in Table 2.2. The VO₂ composite films were demonstrated recently to be fabricated through technologies, such as the inkjet printing.^[34,35]

This concept was first developed by Li *et al.*, who demonstrated *via* calculations based on effective medium theory (EMT) that a system composed of well-dispersed VO₂ nanoparticles (reflective index of ϵ_p) in a dielectric host has advantages over continuous thin films.^[36,37] Dilute composites composed of three types of VO₂ nanoparticles (spheres, ellipsoids, and core-shell) embedded in a dielectric matrix were considered (Figure 2.2a-c) and the aspect ratio m is defined as a/c to describe the spheroidal geometry in the calculation.

Over the past decade, many methods for preparing VO₂ nanoparticles with fine crystallinity have been explored and implemented, followed by dispersion in various host materials, for practical applications of nanothermochromics. These host materials are classified as non-responsive or responsive matrixes, depending on if they display distinct optical modulation during heating. Polyurethane (PU) has been widely studied as a host material for VO₂-based thermochromic composites. The incorporation of pure VO₂ nanocrystals with PU was achieved by Chen *et al.*, with excellent thermochromic properties observed.^[38] Embedding doped VO₂ nanoparticles into the PU matrix also achieved superior nanothermochromic properties. The primary reason for doping other elements into VO₂ nanoparticles is to reduce the τ_c from ~ 70 °C to around room temperature. Upon substituting V atoms with F,^[25] Mg,^[39] W or Zr atoms,^[29] both VO₂(M) and VO₂(R) lattice structures are distorted due to structural defects induced by the dopants. The motivation for employing core-shell structures is to protect VO₂ nanoparticles from oxidation and

maintain the outstanding nanothermochromic properties. The SiO_2 shell can act as a protective layer to restrain oxygen diffusion and prevent thermodynamically unstable VO_2 from being oxidized. Gao *et al.* successfully prepared VO_2 - SiO_2 core-shell nanocrystals and integrated them in a PU matrix to produce flexible thermochromic foils.^[40] The fabrication process is described in Figure 2.2d. VO_2 nanoparticles were sequentially treated by PVP and tetraethyl orthosilicate (TEOS) to obtain silica shells. The composite was cast on a polyethylene terephthalate (PET) substrate. As shown in Figure 2.2e-f, the films with high (Sample I) and low (Sample II) VO_2 content display excellent flexibility. Alternatively, Long's group adopted a transparent Si-Al gel as the host material. They utilized mechanical attrition (bead-milling) to obtain VO_2 nanoparticles without using a heating source.^[41] Besides, the group of He has successfully prepared $\text{SiO}_2/\text{TiO}_2/\text{VO}_2$ three-layered hollow nanospheres and applied them to multifunctional smart windows,^[42] demonstrating energy-saving, antireflection, and self-cleaning functionalities that is similar to the films consisted of VO_2 and SiO_2 multilayers.^[43,44]

Though numerous advancements in VO_2 -based non-responsive composites have improved the thermochromic performance, the best T_{sol} is still below 30%, which is limited by the spectral range that VO_2 can modulate. Solar energy is dense in the visible range, but VO_2 cannot regulate in this region due to the limited difference of the optical constants in the spectrum range of 400 to 800 nm between its rutile and monoclinic phases. Incorporating a thermoresponsive host material with VO_2 has been proven to be a promising way to overcome this limitation. Recently, Zhou *et al.* applied a thermoresponsive matrix to a VO_2 -based composite for solar energy modulation.^[45, 46] Pure poly-N-isopropylacrylamide (PNIPAm) is transparent below the lower critical solution temperature (LCST) and becomes translucent when the temperature increases, accompanied by a change in the NIR transmittance. Figure 2.2g illustrates the formation of the laminated VO_2 /hydrogel hybrid thin film and the mechanism to regulate solar energy at a different temperature. In a different work, Jin's group combined VO_2 nanoparticles with a thermochromic ionic liquid, which typically increases the absorbance during heating over the range of 650 to 750 nm rather than over the whole visible range as the hydrogel does.^[47] In the experiment, an ionic

liquid-nickel-chlorine (IL-Ni-Cl) complex was observed to undergo a gradual color change from colorless to blue during heating. The VO₂/IL-Ni-Cl composite demonstrated outstanding optical regulation properties (ΔT_{sol} of 26.5%) and maintained good transparency (T_{lum} of 50%). More interestingly, the films exhibited a distinct color change from brown at 20 °C to green at 80 °C, which was believed to be a synergistic effect of the color variations in pure VO₂ and pure IL-Ni-Cl films (Figure 2.2h). This method provides an alternative way to simultaneously improve the unfavorable brownish-yellow color of VO₂ and achieve good solar energy modulation. They then applied similar methods to cobalt(II)- and nickel(II)-based ligand exchange thermochromic systems CLETS and NLETS and similar results were obtained.^[48, 49]

Table 2.2 Summary of experimental and simulation results of VO₂-based thermochromic nanocomposites.

Category	Matrix		Embedded nanocrystals		T_{lum} (%)	ΔT_{sol} (%)	Ref.	
			Types	Dopant \ structures				
Simulation	Non-responsive	\	spheroidal VO ₂ particles		67.0	20.0	[36]	
		\	VO ₂ -based core-shell structures		59.0	20.9	[37]	
Experiment	Non-responsive	PU	VO ₂		45.6	22.3	[38]	
			VO ₂ and Sb-doped SnO ₂		51.4	11.7	[50]	
			Doped VO ₂	F	48.7	10.7	[25]	
				Mg	54.2	10.6	[39]	
				Zr	60.4	14.1	[29]	
				W+Zr	56.4	12.3	[29]	
				W	56.0	12.7	[38]	
				Ti	53.0	17.2	[30]	
				Core-shell structure	VO ₂ -SiO ₂	27.8	13.6	[40, 51]
			V _x W _{1-x} O ₂ -SiO ₂		50.6	14.7	[52]	
			Si-Al gel	VO ₂	59.1	12.0	[41]	
			PDMS	VO ₂	85	\	[53]	
			TiO ₂	VO ₂	61.2	14.6	[54]	
			Responsive	PNIPAm	VO ₂	62.6	34.7	[42, 43]
				HPC	Doped VO ₂ W	56.0	36.0	[55]
				IL-Ni-Cl	VO ₂	55.2	26.5	[47]
				CLETS	VO ₂	59.2	20.8	[48]
				NLETS	VO ₂	71.0	18.2	[49]

Note: “—” means unchanged; “↓” means decrease; “\” means data not available.

Figure 2.2 a-c) Structural models of composites embedded with nanocrystals in ellipsoids, spheres, and core-shell nanoparticles. Reproduced with permission. Copyright 2010 and 2011.^[36,37] American Institute of Physics. d) Scheme of the preparation procedure for the VO_2 - SiO_2 /PU composite. e, f) Photographs of flexible thermochromic films based on VO_2 - SiO_2 /PU composites with high (Sample I) and low (Sample II) VO_2 contents. Reproduced with permission. Copyright 2012.^[38] Royal Society of Chemistry. g) Illustration of the solar modulation behavior of the VO_2 /PNIPAm-based composites. Reproduced with permission. Copyright 2015.^[41] Royal Society of Chemistry. h) Photographs of the films based on the pure IL-Ni-Cl complex (top row), VO_2 nanoparticles (medium row), and VO_2 /IL-Ni-CL composite at 20 and 80 °C, respectively. Reproduced with permission. Copyright 2016.^[42] American Chemical Society.

2.2.3 Porosity in VO₂ film

The introduction of air-filled nanopores, which are considered to be a secondary component in VO₂ films, has been proven to be an effective method to improve the thermochromic performance, especially the T_{lum} . Gao *et al.* calculated the spectral transmittance of a nanoporous VO₂ film on a fused-silica-glass substrate with variable porosity and thickness by employing the optical-admittance recursive method, which is based on the optical-admittance function.^[56] Based on the calculation, they plotted a useful diagram that correlates the thermochromic performance, including ΔT_{sol} and visible transmittance of porous VO₂ films at low temperature ($T_{\text{lum, low}}$), with the thickness and porosity of the film (Figure 2.3a). Optimizing thermochromic performance is demonstrated up to a ΔT_{sol} of 20% with a $T_{\text{lum, low}}$ of 45%. They suggested that ΔT_{sol} could be enhanced without a decrease in $T_{\text{lum, low}}$ because of the depression of the porosity-derived reflection. The progress of simulation and experimental of porous VO₂ films are summarized in Table 2.3.

Incorporating removable additives into the vanadium precursor has been demonstrated to be a facile way to fabricate porous VO₂ films. Gao *et al.* pioneered the porous films and successfully produced nanoporous thermochromic VO₂ films by a polymer-assisted deposition method.^[57] The pores in the final films are formed from PVP degradation and shrinkage of the gel films during high-temperature annealing (Figure 2.3b). These air-filled pores had feature sizes much smaller than the visible wavelength lower the low optical constants (Figure 2.3c), resulting in high luminous transmittance, $T_{\text{lum}} = 43.3\%$, and solar modulation, $\Delta T_{\text{sol}} = 14.1\%$.

A spontaneous self-templating and assembly process during dual-phase transformation was successfully applied by Liu *et al.* to prepare porous VO₂ structures.^[58] In the experiment, an aqueous vanadium precursor including vanadyl dichloride (VCl₂), hydrazine (N₂H₄), hydrochloric acid (HCl), and PVP was spin-coated on a quartz substrate and then dried under nitrogen (Figure 2.3d). These spheres self-assembled into a close-packed structure at the colloid-substrate interface when saturation was reached in the hydrous colloids

(Figure 2.3e). After that, the hollow sphere structures developed at 300 °C and then collapsed and crystallized to VO₂ during annealing at 500 °C (Figure 2.3f-g). These processes have been demonstrated experimentally (Figure 2.3h-k). By optimizing the experimental conditions, a high transmission (95.4% at 700 nm) was achieved, accompanied by $\Delta T_{\text{sol}} = 5.5\%$, for a honeycomb VO₂ film with a thickness of 65 nm.

Table 2.3 Summary of porous VO₂ films

Category	Preparation method		Structure	Pore size	ΔT_{sol} (%)	T_{lum} (%)	Ref.
Simulation	\		Random porosity	Nano	20	45	[57]
	PVP		\	Nano	14.1	43.3	[57]
	Incorporating removable additive	CTAV	Hierarchical porous structure	Nano/micro	\	46.5	[59]
		CTAB	\	Nano	\	\	[60]
		PEG	\	Nano	\	\	[61]
		SDS	\	Nano	\	\	[62]
Experiment	Process control	Freeze-drying	\	Nano	14.7	50.0	[63]
		Sintering in CO ₂ atmosphere	\	Nano	2.2	35.9	[64]
	Self-assembly	Dual-phase transformation	Quasi-honeycomb	Nano	5.5	\	[58]
		Crystallographic orientation control	nanonet	Nano	\	\	[65]

Note: “\” means data not available.

Figure 2.3 a) Summary of the calculated thermochromic performance as a function of porosity and film thickness. $T_{lum, low}$ (visible transmittance of the porous VO₂ film at low temperature) and ΔT_{sol} are denoted by the red dotted lines and black solid lines, respectively. b) The porous morphology of a 147 nm-thick VO₂ film, as an example, from the top and side view (inset). c) Optical properties of porous VO₂ films comparing with reference. Reproduced with permission. Copyright 2011.^[57] American Chemical Society. d-k) Schematic of the self-templating and assembly during the dual-phase transformation process, which includes four steps: (d) deposition of a homogeneous solution-based precursor on a substrate, (e) assembly of self-templated hydrous sphere arrays, (f) formation of hollow VO(OH)₃ spheres, and (g) formation of the honeycomb-nanostructured VO₂ film *via* the collapse of hollow spheres. (h-i) are the corresponding experimental demonstrations of steps (d-g). Reproduced with permission. Copyright 2017.^[58] American Chemical Society.

2.2.4 Grid and Biomimetic VO₂ Films

Films based on grid-structured VO₂ have attracted increasing interest due to the great potential of structure-induced thermochromic enhancements, including but not limited to increased transmittance, antireflection, and localized surface plasmon resonance (LSPR).

Previous studies, including simulation and experimental works, are summarized and classified in Table 2.4.

The group of Long demonstrated that nanogrid structure is able to significantly enhance the T_{lum} without deteriorating ΔT_{sol} and demonstrated by 3D finite difference time domain method to numerically optimize a number of parameters, including structural models, cavity size, periodicity, film thickness, and fill factor.^[66] In the simulation, three structural models are calculated: square holes in square lattices, circular holes in square lattices, and circular holes in a hexagonal arrangement (Figure 2.4a). The thermochromic performance of square holes in square lattices is summarized in Figure 2.4b. Moreover, a competitive thermochromic performance ($T_{\text{lum}} = 76.5\%$ and $\Delta T_{\text{sol}} = 14.0\%$) was demonstrated on hexagonal-packed circular cells of VO_2 with a radius of 80 nm, the periodicity of 160 nm, and thickness of 300 nm.

Table 2.4 Summary of grid-structured VO_2 films.

Category	Preparation method	Structure	ΔT_{sol} (%)	T_{lum} (%)	Ref.
Simulation	\	Grid	14.0	76.5	[66]
		Nanoparticle array	\	\	[69]
Experiment	Electrodeposition	Micro-grid	13.9	38.4	[67]
	Mesh printing	Micro-patterned	14.9	43.3	[68]
	Nanosphere lithography	Nanonet	7.9	\	[70]

Note: “\” means data not available.

Grid VO_2 films with periodicity in microscale are processable,^[71] and the same group has applied the electrodeposition method to successfully assemble the VO_2 NPs to electrodes by tuning the ionic strength (Figure 2.4c).^[67] The flexible thermochromic film was produced by depositing the VO_2 NPs on to grid Cu/PET substrates, in which the NPs assembled along the grid Cu electrodes (Figure 2.4d). An optimized ΔT_{sol} of 13.9% and T_{lum} of 38.4% were demonstrated. Another facile method, the mesh printing method was reported by Lu *et al.* to prepare micropatterned $\text{VO}_2/\text{Si-Al}$ gel composites by mounting a mesh above a glass substrate with controllable distance (Figure 2.4e).^[68] Films *via* the

method display competitive performance which up to a ΔT_{sol} of 14.9% under a T_{lum} of 43.3%.

Figure 2.4 a) Simulation models of the grid films with square holes and circular holes in square lattices as well as the circular holes in a hexagonal arrangement. b) Summary of the calculated T_{lum} and ΔT_{sol} of the model with square holes in square lattice under various periodicity and square hole length. Reproduced with permission. Copyright 2015.^[66] The Optical Society. c) Schematic of the electrodeposition process based on ionic strength. d) Photograph of the sample which contains VO₂ NPs deposited on flexible grid Cu/PET film (left) and the optical microscopy image of the grid structure (right). Reproduced with permission. Copyright 2017.^[67] Royal Society of Chemistry. e) Illustration of the mesh printing method. Reproduced with permission. Copyright 2016.^[68] Royal Society of Chemistry.

The usual properties of biomimetic structures have attracted great research interest, especially in light manipulation and the design of high-performance optics. Moth-eye nanostructures can efficiently eliminate reflection because the sub-wavelength nipple array generates a continuous refractive index gradient between the air and the medium, effectively reducing the refractive index gap at the air-medium interface (Figure 2.5a-b).^[72]

^{73]} Taylor *et al.* introduced the moth-eye structures to thermochromic VO₂-based intelligent glazing.^[74] In their simulation, the VO₂-coated nipple arrays were designed to be hexagonal-close-packed (HCP) on a glass substrate (Figure 2.5c). The thermochromic performances were calculated by numerically optimizing these dimensions using the 3D FDTD method and are plotted in Figure 2.5d. As shown in Figure 2.5d, structures with heights lower than 500 nm are preferred, as these structures are reflective, especially in visible and dense solar energy regions. A decent thermochromic performance of $T_{\text{lum}} = 59.9\%$ combined with $\Delta T_{\text{sol}} = 19.4\%$ was revealed at point C in Figure 2.5d. VO₂ films with moth-eye structures were successfully prepared by Qian *et al.* by coating VO₂ onto fused silica substrates with moth-eye structures that were pre-fabricated *via* nanosphere lithography (Figure 2.5e-f).^[75] They found that the T_{lum} increases with decreasing periodicity, and moreover, the sample with a periodicity of 210 nm simultaneously enhanced T_{lum} and ΔT_{sol} over those of the planar sample. Future research can be directed at reducing the periodicity, which may be a challenge for the fabrication of sub-100 nm patterns.

Figure 2.5 a) Photograph of the compound eyes of *Calliphora*. b) The antireflection structures on the surface of its ommatidium. Reproduced with permission. Copyright 2003.^[73] Nature Publishing Group. c) A three-dimensional illustration of the VO₂-coated nipple arrays used in the simulation and d) the calculated ΔT_{sol} map based on the FDTD parameter search. Reproduced with permission. Copyright 2013.^[74] The Optical Society. e) Produced moth-eye nanostructured VO₂ films containing f) the individual nipple structure of VO₂-coated silica. Reproduced with permission. Copyright 2014.^[75] American Chemical Society.

2.3 Comparison with Other Materials for Thermochromic Smart Windows

2.3.1 Other Potential Materials

2.3.1.1 Temperature-Responsive Hydrogels

Hydrogels are networks of hydrophilic polymer chains with an aqueous rich environment which renders broadly tunable chemical and physical properties. The first hydrogel was demonstrated in 1894.^[76] Nowadays, hydrogels have been applied in different areas, including tissue engineering,^[77, 78] drug delivery systems,^[79, 80] cell cultures,^[81, 82] biological implants.^[83]

Recently, thermochromic hydrogels, a special category of hydrogels, have attracted considerable attention as a candidate for energy-efficient smart window applications. The extensively studied thermochromic hydrogels include polyampholyte hydrogel (PAH),^[84] poly(N-isopropylacrylamide) (PNIPAm),^[40, 41, 85, 86] and hydroxypropyl cellulose (HPC).^[55] Significantly, thermochromic hydrogels undergo a hydrophilic to hydrophobic transition (Figure 2.6a): when the temperature is below the lower critical solution temperature (LCST), intermolecular hydrogen bonds are prevalent between the polymer chains and surrounding water molecules; once the temperature increases above the LCST, intermolecular hydrogen bonds are broken and the intermolecular hydrogen bonds, then polymer chains collapse, resulting in phase separation and polymer aggregation.^[87, 88] The aggregated polymer clusters reduce the transparency of the hydrogel by scattering incident light.^[89-91] A polymer chain volume reduction of over 90% can be observed following the phase transition separation.^[92]

This LCST characteristic makes thermochromic hydrogels promising candidates for energy-efficient smart windows. One of the most common configurations for hydrogel-based smart windows is the sandwich structure, where the thermochromic hydrogel is sandwiched between two pieces of the glass substrate (Figure 2.6b). Zhou *et al.* reported pure PNIPAm hydrogel based smart window, which has suitable LCST at $\sim 32\text{ }^{\circ}\text{C}$,^[45] the

LCST phase transition was found to affect a relatively large spectral range of light transmittance, as illustrated in Figure 2.6c. Specifically, a drastic transmittance contrast in response to temperature was observed from 250-1800 nm, while the temperature effect on transmittance after 1800 nm was relatively negligible. The difference in transmission was mainly due to the aggregation of polymer chains once the temperature is above LCST.^[88, 93] The temperature-dependent optical properties of 200 μm PNIPAm hydrogel thin film is displayed in Figure 2.6d, including T_{lum} , ΔT_{sol} , calculated infrared modulation (ΔT_{IR}), and integrated visible light modulation (ΔT_{lum}). Below LSCT, the transparency of the PNIPAm hydrogel film was maintained well in both the visible light region and the NIR region. However, as the temperature increased above the LSCT, a significant drop of transmittance was observed throughout the entire spectrum. When the temperature was increased to 60 °C, T_{lum} fell to 60% and T_{IR} was reduced significantly to only 19.3%. Due to the rapid decrease of both T_{lum} and T_{IR} , a continuously decreasing T_{sol} was observed (from 83.3% to 9.4%). The result was that the 200 μm PNIPAm hydrogel thin film was observed to change from transparent at room temperature to opaque above 35 °C (Figure 2.6bi and 2.6bii). The PNIPAm could be further embedded within a silica-alumina-based gel matrix for 3D printing process.^[94] The PNIPAm has also be incorporated with ferrocene-based materials for electro-/thermo-dual responsive materials that have potential for smart windows.^[95] Another example is a PAH-based smart window,^[84] which, instead of being transparent at low temperature was designed to be opaque at cold temperatures to retain indoor heat, which may be applicable particularly for winter nights.

Further explorations have been reported by Long *et al.* on hybrids of hydrogel with inorganic VO₂ particles.^[46] PNIPAm-VO₂ hybrid thin film was sandwiched between two pieces of the glass substrate (Figure 2.6e), with a demonstration of this film at room temperature and 35 °C shown in Figures 3ei and 3eii, respectively. The transmittance spectrum of the pure hydrogel, pure VO₂ nanoparticles and the VO₂/hydrogel hybrid at 20 and 80 °C are shown in Figure 2.6f. Compared with pure hydrogel, ΔT_{sol} of the hybrid material was significantly improved, especially in the NIR region where an enormous ΔT_{IR} of 22.2% was observed. The PNIPAm-VO₂ hybrid film also showed constant T_{lum} and ΔT_{sol} ,

as demonstrated by repeated heating and cooling of a 100 μm film between 20 and 80 $^{\circ}\text{C}$ for 20 cycles (Figure 2.6g). Furthermore, compared with pure VO_2 nanoparticles the hybridized system demonstrated higher luminous transmittance at both room temperature and elevated the temperature. The same research group also applied less noxious HPC hydrogel to thermochromic foils that were responsive near room temperature by compositing with tungsten-doped VO_2 .^[55]

Figure 2.6 a) Schematic of the responsive polymer chain behavior below and above the LSCT. Reproduced with permission.^[93] Copyright 2016, Elsevier. b) Schematic diagram of the PNIPAm hydrogel smart window sandwich structure. Incident light (golden arrows) passes through the hydrogel below 32 $^{\circ}\text{C}$, but is largely blocked above 32 $^{\circ}\text{C}$. The insets i and ii are the 200 μm demonstration devices at 20 and 80 $^{\circ}\text{C}$, respectively. c) Transmittance spectrum of 200 μm PNIPAm hydrogel thin film at temperatures varying from 20 to 60 $^{\circ}\text{C}$. d) Optical properties T_{lum} , ΔT_{sol} , ΔT_{IR} , and ΔT_{lum} of 200 μm PNIPAm film at temperatures ranging from 20 to 60 $^{\circ}\text{C}$. Reproduced with permission.^[45] Copyright 2014, Royal Society of Chemistry. e) Schematic

diagram of the PNIPAm-VO₂ hybrid hydrogel smart window sandwich structure. f) UV-Vis-NIR transmittance spectra of pure PNIPAm hydrogel, VO₂ nanoparticles and VO₂-PNIPAm hybrid hydrogel at 20 and 80 °C. g) Durability test of 100 µm PNIPAm-VO₂ hybrid film. Reproduced with permission.^[46] Copyright 2015, Royal Society of Chemistry.

2.3.1.2 Thermal-Sensitive Ionic Liquid

The ionic liquid is defined as salt in a liquid state without any decomposition or vaporization. In contrast to ordinary solvents like water, ionic liquid consists of ions and short-lived ion pairs instead of neutrally charged molecules. It has been considered the solvent of the future.^[96] Walden reported the first room-temperature ionic liquid in 1914;^[97] since then there has been ongoing interest in ionic liquid research and diverse potential applications have been described, including cellulose processing,^[98, 99] nuclear fuel processing,^[100] solar thermal energy systems,^[101, 102] and batteries.^[103, 104]

The ionic liquid-based complex film, a mixture of transition metal compounds and an ionic liquid, has received considerable attention as a promising candidate for energy-saving smart windows due to its ability to modulate solar radiation absorption. Current research in this field is mainly focused on thermochromic ionic liquids, which property is based on an octahedral-tetrahedral configuration change of transition metal complexes assisted by interaction with donor solvent molecules. More specifically, octahedral complexes are formed at low temperatures, while the complexes become tetrahedral at high temperatures, leading to the light transmittance variation (Figure 2.7a).^[47] The chromic variation is caused by a change in energy difference between t_{2g} and e_g orbitals through the configuration transformation.^[105] In the tetrahedral configuration, the energy gap between t_{2g} and e_g orbitals is much smaller than that in the octahedral complexes; hence, resulting in a strong absorption at higher temperature and favorable thermochromic response.

Ionic liquid-based complex materials display high sensitivity and efficiency to temperature change. For example, Wei *et al.* reported a thermochromic system of dissolved [bmim]₂NiCl₄ in C_nOH_{min}⁺-based ionic liquids.^[106] In this nickel(II)-based ionic liquid

system, the enthalpy and entropy changes during the octahedral-tetrahedral configuration transformation were just 30-40 kJ mol⁻¹ and 140-160 J mol⁻¹K⁻¹, respectively, leading to a promising low energy requirement that was fully achievable by exposure to sunlight. However, the solar modulation ability of pure ionic liquid-based composite systems has been insufficient for use in energy-efficient smart window applications due to the narrow modulation spectrum range. To address this issue, both inorganic and organic approaches have been developed.

The inorganic approach hybridizes an ionic liquid-based complex system with VO₂ nanoparticles. For example, Zhu *et al.* reported a composite film made up of VO₂ nanoparticles and IL-Ni-Cl complexes.^[47] The pure IL-Ni-Cl displayed a significant transmittance contrast mainly in the 500-800 nm spectral range, resulting in limited modulation ability in the context of the full solar energy spectral range of 250-2500 nm (Figure 2.7b). However, the composite of IL-Ni-Cl and VO₂ significantly broadened the modulation range and thereby promoted solar energy regulation, which was attributed to the combination of IL-Ni-Cl visible light modulation (500-800 nm) as well as VO₂ nanoparticle modulation of NIR (700-2500 nm) (Figure 2.7b). As illustrated in Figure 2.7b, compared with the pure IL-Ni-Cl, the VO₂ hybridized materials demonstrated significantly wider solar regulation ability covering a broad range from 500 to 2500 nm. A ΔT_{sol} up to 26.5% was achieved when such a composite system was heated to 80 °C. Meanwhile, the T_{lum} at high temperature was maintained at a high level of 43.9%. A color change was observed in the composite from light brown at 20 °C to dark green at 80 °C, which was attributed to the combination of IL-Ni-Cl changing from transparent to blue whilst VO₂ remained yellow-brown (Figure 2.7c). Recently, they also revealed similar thermochromic properties based on the incorporation system with VO₂ and IL-Br-Cl.^[107]

The organic approach hybridizes an ionic liquid-based complex system with thermochromic hydrogels, also known as ionogels or ion gels.^[108] Besides the configuration transformation of ionic liquid-based complex systems, an LCST-type phase transition occurs between the polymer chains and ionic liquids at elevated temperatures, leading to a remarkably distinguishable difference in optical transmittance (Figure 2.7d).

At low temperature, the polymer chains and ionic liquid form a homogeneous network that has high transparency. Upon heating, this uniform distribution of polymer chains and the ionic liquid is no longer stable, resulting in the formation of ionic liquid-rich domains, a scattering of incident light and a change in optical transmittance.^[109] Figure 2.7e represents the transmittance spectra of ionogel at various temperatures ranging from 15 to 60 °C. As the temperature of ionogel was increased, the 300-2200 nm spectral range is affected. As Lee *et al.* reported, when the ionogels were heated above the LCST, up to 80% luminous modulation (ΔT_{lum}) could be achieved via an observable color change to white (insets of Figure 4e).^[110] Below the LCST, the T_{lum} was maintained at 87%. Furthermore, the exact LCST could be manipulated from below zero to over 100 °C just by varying the composition of the ionic liquid. The ionogel system demonstrated high stability, maintaining solar modulation performance after 5000 heating-cooling cycles. Additionally, as shown in Figure 2.7f, this ionogel has been successfully adapted with various organic dyes, increasing its competitiveness for commercial smart windows.

Figure 2.7 a) Schematic illustration of the octahedral-tetrahedral configuration change of ionic liquid-based complex system. The IL-Ni-Cl complex undergoes a phase transition from octahedral to tetrahedral above the LCST. b) Transmittance spectrum over the UV-Vis-NIR regions of pure IL-Ni-Cl film, VO₂ nanoparticles and VO₂/IL-Ni-Cl hybrid film at 20 and 80 °C. c) Demonstrations of pure IL-Ni-Cl film, VO₂ nanoparticle film and VO₂/IL-Ni-Cl hybrid film at 20 and 80 °C.

Reproduced with permission.^[47] Copyright 2016, American Chemical Society. d) Schematic illustration of thermochromic optical transmittance change upon variation in temperature. e) Transmittance spectrum over the UV-Vis-NIR region of ionogel at various temperatures ranging from 15-60 °C. The insets are photographs of transparent, translucent and opaque states of the ionogel, respectively. f) Demonstration of ionogel films mixed with brilliant green, rhodamine B (RhB) and methyl orange organic dyes below and above the transition temperature, respectively. Reproduced with permission.^[110] Copyright 2017, American Chemical Society.

2.3.1.3 Reconfiguration Metamaterials

Metamaterials refer to engineered composite materials with properties that are not found in nature. These properties are not derived from the source materials themselves but from their artificially constructed structures.^[111, 112] Various applications of metamaterials have been developed, including antennae,^[113, 114] absorbers,^[115, 116] and cloaking.^[117, 118] Metamaterials are also regarded as one competitive candidate for energy-efficient smart window applications.

In order to achieve thermal responsiveness for energy-efficient smart window applications, metamaterials could either be constructed from thermoresponsive materials,^[119] or from origami-inspired metamaterials^[120-122] attached to materials that respond to environmental temperature change, resulting in the metamaterial configuration changing spontaneously. Tang *et al.* pioneered a thermoresponsive origami-inspired structure (also known as kirigami) that could be buckled out of the plane to reflect or transmit light in response to a minor change of local temperature.^[123] The so-called kiri-kirigami structure was characterized by patterned notches inserted into both sides of the sheet (Figure 2.8a). These notches acted as geometrical imperfections of the kirigami structure so that only certain desirable tilting orientations could be achieved. Furthermore, the tilting orientation was fully programmable by adjusting the design of notches, as demonstrated in Figure 2.8b. By integrating the thermally shrinkable tape (black) onto the patterned notches (Figure 2.8c), a self-foldable bilayer structure formed, relying on the mismatched deformation between the thermally shrinkable tape and the kiri-kirigami metamaterial to spontaneously self-tilt

upon thermal activation. Upon heating from 24 to 65 °C, the tilting orientation changed until it reversed (Figure 2.8c). By integration with a reflective coating, the configuration could change such that it reflected sunlight at elevated temperature and directed sunlight indoors at low temperature.

To evaluate the performance of this kiri-kirigami material, a testing space was designed with dimensions of 5200 mm (L) x 3400 mm (W) x 2300 mm (H), containing three windows, 2300 mm (L) x 580 mm (W) (Figure 2.8d), each with reflective, thermoresponsive metamaterial structure (Figure 2.8e). Figure 2.8f shows the illumination performance of the base model without the kiri-kirigami smart windows installed, and Figure 2.8g shows the illumination performance of the proposed model with the kiri-kirigami smart windows. Taking an average day as the example, it was observed that direct penetration of sunlight decreased dramatically with the kiri-kirigami window. According to the simulation, using the kiri-kirigami smart windows throughout the year would result in a total saving of 47% and 26% of electricity for cooling and lighting, respectively.

Figure 2.8 a) Schematic illustration of kiri-kirigami structure with notches on both sides. The upper part (green) has reversed patterned notches compared with the lower part (yellow). b) Optical images of the deformed kiri-kirigami structure with identical design to (a) upon uniaxial stretching. c) Experimental demonstrations of thermal activation and orientation switch of kiri-kirigami paper

metamaterials at various temperatures. d-g) Simulation of building energy consumption while kiri-kirigami metamaterials are applied as the thermoresponsive building envelope. Schematic illustration of the stimulation space, (d) without (base model) and (e) with kiri-kirigami (proposed model) smart windows. Performance in the stimulation space of the (f) base model and (g) proposed model at noon. Reproduced with permission.^[123] Copyright 2016, John Wiley & Sons.

2.3.1.4 Thermochromic Perovskite

Perovskites are materials with an identical crystal structure to calcium titanium oxide. Among thousands of complex structures, perovskites stand out with numerous interesting properties including chemically manipulatable optical and electrical properties.^[124-126] There has been tremendous recent scientific interest into the development and application of perovskites, especially for photovoltaics,^[127, 128] lasers,^[129] LED devices,^[130, 131] and photoelectrolysis.^[132, 133]

The general formula of perovskite is ABX_3 , in which anion X is bonded to both larger cation A (positioned at cornered) and smaller cation B located at the center of the unit cell (Figure 2.9a). For thermochromic smart window application, the thermoresponsive behavior of halide perovskites is based on their unusual crystallization behavior, also known as inverse temperature crystallization (ITC).^[134] Unlike the majority of substances, the solubility of perovskites decreases as the solution temperature increases, resulting in single crystal cell nucleation and growth of perovskite single crystals (Figure 2.9a). As the temperature increases, perovskite crystals gradually precipitate, accompanied by an absorbance band gap shift and optical property change.

It is the halogen constituent that determines the crystallization temperature of halide perovskites; therefore, introducing more than one halide constituent can enable further control of the thermochromic behavior of halide perovskite solutions. Pioneering work on perovskites for smart window applications was by Bastiani *et al.*, using a bi-constituent $MAPbBr_{3-x}I_x$ perovskite solution.^[135] As the solution temperature was varied from 25-

120 °C, the color changed from yellow to black due to the different precipitation rates of black iodine-based perovskite and orange bromide-based perovskite. The solubility of iodine-based perovskite drops much more rapidly than that of the other, therefore x increases with increasing temperature in the precipitates. Upon temperature elevation to 120 °C, the iodine-based perovskite dominated and the color turned black. During the thermochromic process of halide perovskite solution, the absorption spectrum varied significantly. The mainly affected spectral range was 250-780 nm, which includes visible light and part of the UV region. Similar phenomena associated with halide perovskite materials have also been reported in other papers.^[136, 137] This light modulation is due to the absorption of photons by transition metal ions from the precipitate, which is affected by precipitate size and composition.^[138] Figure 2.9b shows the absorption spectrum of perovskite crystals at three different temperatures. As the temperature was increased, a red-shift of the absorption edge was observed. Figures 2.9c and d show the thermochromic smart window prototype produced by Bastiani *et al.* and its absorption spectrum after annealing at the indicated temperature. At 60 °C, the absorption maximum of the prototype (Figure 2.9d) matched well with the absorption maximum of the perovskite powder (Figure 2.9b). However, when the prototype was heated to 90 °C, the absorption maximum position was observed with a red-shift to the edge of the visible region (780 nm) compared with the powder sample. Additionally, the stability of this system requires further exploration since the band edge displayed variations over several cycles of 25-60 °C heating and cooling (Figure 2.9e). Sarkar *et al.* reported the reversible thermochromic behavior of thin film to dehydrate methylammonium lead iodide.^[139] With increasing temperature from 25 to 60 °C, the film demonstrated a significant absorption enhancement caused by a shift in the absorption maximum from ~400 to ~500 nm, accompanied by a distinct color variation from transparent to dark orange.

Recently, Yang *et al.* demonstrated a thermochromic smart window based on a fully reversible structural phase transitions of inorganic halide perovskite caesium lead iodide/bromide.^[140] At low temperature, the non-perovskite phase with high transparency (81.7% visible transparency) is exhibited; while due to the elevated temperature, the

crystals are transferred into perovskite phase, which is deeply colored with much lower transparency (35.4% visible transparency). The group of Gao recently demonstrated a lead-free halide perovskite with temperature-dependent bandgap modulation, displaying good potential for thermochromic smart windows.^[141]

Figure 2.9 a) Schematic illustration of the inverse temperature crystallization (ITC) process of perovskite materials: with increasing temperature, the perovskite crystals nucleate and grow. b) Absorption spectra of perovskite crystals obtained from inks at 60, 90 and 120 °C. c) Photographs of thermochromic prototype annealed at 25 °C (top) and 60 °C (bottom). d) Absorption spectra of the thermochromic prototype after annealing at the indicated temperature. e) Band edge alternation of the thermochromic prototype during heating and cooling cycles between 25 and 60 °C. The green circles represent the extrapolated maxima at 25 °C; the red spots represent the extrapolated minima at 60 °C. Reproduced with permission.^[135] Copyright 2017, American Chemical Society.

2.3.1.5 Orientation-Tunable Liquid Crystals

Liquid crystals (LCs) represent the new class of material, which is intermediate between the conventional liquid and crystalline solids and may flow like a liquid while the

molecules are well-oriented in a crystal-like way.^[142] Most liquid crystals are made of organic compounds. They are characterized by the anisotropy of optical, electrical, and mechanical properties.^[143] These properties are responsive to a variety of stimuli, including the temperature, electric field, light etc., which make LCs broad interesting in applications.
[144-146]

Optical properties of LCs highly rely on the orientation of anisotropic molecules. The thermochromism of LCs is achieved by tuning the orientation in response to temperature stimulus.^[147] In a sandwich configuration smart window, LC molecules can be tuned in a number of orientation between two glass slides. Figure 2.10a shows three typical orientations of LCs and the corresponding optical states that affect the incident light perpendicular to the glass slide. When the molecules are assembled in helical structures and parallel to the slides (planar orientation), the incident light is reflected (reflective state). A light scattering state form when the helical structures are randomly tilted in a focal conic orientation. The LCs perform to be transparent when the molecules extend perpendicular to the slides (homeotropic alignment). In scattering and reflective states, the reflection band is determined by the incident angle of light, the pitch of LCs, and the refractive index of materials.

Thermochromic films based on orientation transition of LCs have been demonstrated as a good candidate for energy-efficient smart windows. Akifumi *et al.* reported the thermal-induced transmittance-to-diffraction states of the holographic polymer-LC composite.^[1488] The group of Yang has produced a series of thermochromic films based on the polymer-LCs composites. In these works, they produced a coexistent system containing polymer-stabilized and polymer-dispersed LCs.^[149] Films based on the system were observed higher transparency at low temperature and a narrow thermal hysteresis (less than 2 K) in 42 °C. To further decrease the NIR irradiation, they introduced the inorganic nanocrystals (NCs) with strong NIR absorption, such as ITO ^[150] and CSxWO₃,^[151] to the polymer-LC composite. For example, they developed a dual-response film containing well-dispersed ITO NCs and LC droplets in phase-separated polymer network (Figure 2.10b).^[150] The LC could be changed reversibly from focal conic to homeotropic orientations by either thermal

or electrical field stimuli (Figure 2.10b1). In this case, the transition here was also suggested as a smectic (SmA) to chiral nematic (N*) phase transition. The film was observed changes from opaque to transparent appearances during the transition (Figure 2.10b2). On the film with 5 wt% ITO, it was demonstrated with a low NIR transmittance (~15%) from 1400 to 2500 nm as well as a huge transmittance contrast at 400 nm up to ~70% between at 300 and 308 K (Figure 2.10c). The introduction of ITO NCs also slightly decreased the transition temperature (Figure 2.10d), which was explained as the effect of ITO NCs residue in the LC domain after the phase transition. It is worthy to mention that these films are easily processable and were successfully produced in meter scale by a roll-to-roll method (inset of Figure 2.10c).

The hybrid film was studied by Liang et al. by combining the electrochromic LC with the thermochromic VO₂.^[152] In the experiment, W-doped VO₂ (W-VO₂) NCs and LCs were homogeneously dispersed in the phase-separated polymer framework (Figure 2.10e1). The electrochromic of LCs and thermochromic of W-VO₂ NCs were maintained after combination and could work independently, which made the stimulus-responsive film display four optical states under different stimuli: low temperature/no electrical field, high temperature/no electrical field, low temperature/electrical field, and high temperature/electrical field (Figure 2.10e2). For example, the film with 2.5 wt% W-VO₂ displayed decreasing transmittance in the NIR spectrum range under an increasing temperature from 25 to 55 °C (Figure 2.10f). The transmittance (400-2500 nm) was further decreased by increasing the applied voltage from 0 to 35 V with a significant depression in the visible range (Figure 2.10g). The optimized ΔT_{sol} was achieved up to 34.6%, which is comparable to the hydrogel/VO₂ hybrid.

Figure 2.10 a) Schematic of the orientation-dependent optical behavior of cholesteric liquid crystalline materials. Reproduced with permission.^[62] Copyright 2017, John Wiley & Sons. b) Schematic of the smectic A (SmA) to chiral nematic (N*) phase transition in a cell containing the liquid crystals (LCs) and indium tin oxide (ITO) nanocrystals (NCs). The transition can be reversibly induced by either electric- or thermal-stimulus (b1), accompanying with distinct transparency change, demonstrated as the corresponding photographs (b2). c) Temperature-dependent transmittance spectra of the smart film consisting 5 wt% ITO NCs before and after 300 cycles. Inset of (c) is the photography of the meter-scale film. d) Temperature-resolved transmittance at 560 nm of smart films containing 0% and 5 wt% ITO NCs. Reproduced with permission.^[66] Copyright 2017, Royal Society of Chemistry. e) Schematic of the VO₂-LCs composite film (e1) with four optical states under different stimuli (e2). f) Temperature-dependent spectra of the composite film containing 2.5 wt% W-doped VO₂. g) Electric-field-dependent of the transmittance spectra of the composite film containing 2.5wt% W-doped VO₂ at 55 °C. Reproduced with permission.^[68] Copyright 2017, Royal Society of Chemistry.

2.3.2 Comparison of VO₂ with Other Materials

Considering the huge potential impact of emerging materials on the traditional VO₂ in thermochromic smart window applications, it is of great interest to compare emerging thermoresponsive materials to the conventional VO₂ material.^[2, 153] This section begins with a brief introduction to VO₂, followed by a comparative discussion on the advantages and disadvantages of each material in terms of ΔT_{sol} , T_{lum} , transition temperature, and durability.

VO₂ undergoes a reversible monoclinic to rutile crystal transition at the τ_c of 68 °C.^[154, 155] Below τ_c , VO₂ displays a distorted rutile structure, characterized as atomic zigzag chains consisting of vanadium ions with interlaced V-V distances of 3.19 and 2.60 Å. Above τ_c , it presents a tetragonal rutile phase with V⁴⁺ ions at the corner and center positions with a V-V distance of 2.85 Å along the c-axis (Figure 2.11a).^[154] The transition induces an abrupt optical transmittance change mainly in the IR spectral range, which has made VO₂ attractive for smart window applications.^[67] Another important advantage of pure VO₂-based thermochromic film is that it works “silently”.^[156] compared to the pronounced color changes of most electrochromic and photochromic smart windows,^[157, 158] The color, transparency, and T_{lum} remains constant due to its negligible variation in the visible range in response to temperature. Nevertheless, there remain intrinsic shortfalls of VO₂ that hamper its practical applications. The following section is to compare the pros and cons of emerging thermoresponsive materials with VO₂. We summarize the achievement and discuss remaining challenges by categories as in Table 2.5.

Firstly, the pure VO₂ system displays a limited ΔT_{sol} that is commonly lower than 20% with an acceptable T_{lum} of 50%.^[159] This is largely attributed to the negligible optical modulations in the visible range, where nearly half of the solar energy exists (Figure 2.11b). However, emerging materials such as hydrogels display excellent control within both the NIR and visible ranges (Figure 2.11b), giving to significantly enhanced performance in solar energy regulation. For example, PINIPAm-based thermochromic films were demonstrated to have an optimized ΔT_{sol} of ~26% upon a T_{lum} above 70%,^[45] which

surpassed the best reported VO₂-based thermochromic films, including those produced with controlled porosity,^[57, 63] nano thermochromism,^[37, 38, 41, 50] moth-eyed nanostructure, antireflective overcoating,^[74, 75] as well as doping^[31, 160, 161] and nanogriding methods (Figure 2.11c).^[66] The hybrid combining VO₂ and PNIPAm also displayed a high level of performance that could not be achieved by the pure VO₂ system (Figure 2.11c).^[46] Thermochromic perovskite and reconfigured metamaterials have also demonstrated visible light control but the quantitative optical calculations are missing and more researches are needed in those two categories. It is reasonable to consider these materials as promising candidates for solar energy modulation.

Secondly, the transition temperature range of emerging thermoresponsive materials is suitable and easily processable. The τ_c (68 °C) of typical VO₂ is too high for smart window applications. Although methods such as doping can reduce the τ_c , these methods are commonly achieved *via* crystallographic engineering and are accompanied by some sacrifice of thermochromic properties.^[22, 162] On the other hand, all the reported hydrogels, thermoresponsive perovskites, and reconfigured metamaterials show suitable transition temperatures, starting from 25 °C. In addition, their different transition mechanisms offer more freedom to modify their transition temperatures with the potential not to jeopardize their optical performance. For example, the heat-shrinkable tapes determine the transition temperature range while contributing little to the optical properties of programmable kirigami metamaterials.^[123] These tapes can be changed according to specific circumstances.

Finally, durability must also be considered in real applications. A challenge of VO₂ is its weak resistance to oxidization,^[40, 163] and emerging thermoresponsive materials have not yet demonstrated sufficient durability. For example, thermoresponsive perovskite displayed an obvious band gap variation within less than 10 heating-cooling cycles.^[135] Although a few emerging thermoresponsive materials studies have considered their durability, these tests were far from adequate for real applications. It is believed that improvements to prolong durability are necessary for all these emerging thermoresponsive materials.

Figure 2.11 a) Crystal structures of tetragonal (top) and monoclinic (bottom) VO_2 . b) Summary of the spectral ranges that can be modulated by metamaterials, perovskites, ionic liquids, hydrogels, and VO_2 . Reproduced with permission. Reproduced with permission.^[164] Copyright 2014, Nature Publishing Group. For the metamaterials, the potential spectral range is indicated since accurate data is not available. c) Summary of quality data on solar ΔT_{sol} and visible transmittance reported for methods. Reproduced with permission.^[165] Copyright 2016, John Wiley & Sons.

Table 2.5. Summary of achievements and remaining challenges by categories.

Category		Achievement		Challenge	
Thermal-responsive materials		Modulated solar spectrum (250-2200 nm) / nm	Transition temperatures / °C	Appearance changes during transitions	
	Hydrogels	250-2200	32	Transparent-to-white	Liquid phase that requires rigorous encapsulation
	Ionic liquid	500-800	\	Transparent-to-colorful	Liquid phase that requires rigorous encapsulation and a narrow spectrum of solar modulation
	Metamaterials	200-2200	55-65	\	For kirigami-based metamaterials, hollow space is essential for the operation and facile fabrication of structure in small-scale (less observable) is preferable
	Perovskites	400-700	25-90	Colorful-to-colorful	Liquid phase that requires rigorous encapsulation, the stability improvement is necessary, and a narrow spectrum of solar modulation
	Liquid crystals	400-2200	29-33	Transparent-to-white	The liquid phase of scattering state (chiral nematic, N*, phase) that requires rigorous encapsulation

Note: “\” means data not available.

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Chapter 3

Experimental Methodology

In this chapter, we discuss the chemicals, preparation methods, and the characterization methodologies used in the projects. In the preparation methods, we present the preparation of vanadium precursors and the assembly method for colloidal templates. Because these two methods are relatively complex and attribute to both the projects in chapter 4 and 5. Besides, calculation methods of ΔT_{sol} and T_{lum} are described in detail since it is the key parameters through the whole these. Other experiment details beyond are included in the experimental sections in each chapter. Moreover, we briefly discussed the mechanism of characterization technologies, including the SEM, TEM, XRD, UV-Vis-NIR, and AFM. These technologies play a significant role in the projects in the thesis as well as for the material characterization of cutting-edge researches in nano/micro scales.

3.1 Chemicals

Vanadium pentoxide (V_2O_5 , 99.6%, Alfa, Aesar), hydrogen peroxide (H_2O_2 , 30%, Sigma-Aldrich), PDMS gel (SYLGARD 184, Dow Corning), methanol (CH_4O , 95%, Aik Moh Pet Ltd), vanadium dioxide nanoparticles (VO_2 NPs, Jincheng, China), ml hexane (Aik Moh, Singapore), ethanol (C_2H_6O , 95%, Aik Moh Pet Ltd), propyl alcohol (C_3H_8O , 99%, Sigma-Aldrich), sodium dodecyl sulfate (SDS, 99%, Sigma-Aldrich), dodecanol ($C_{12}H_{26}O$, 99%, Sigma-Aldrich), and plain silica spheres with diameters of 200nm, 400nm, 600nm and 700nm (5%, Microsphere-Nanospheres), oxalic acid (99.99%, Alfa Aesar), and polystyrene spheres with average diameters of 164 nm, 485 nm, 640 nm, 834 nm (PS spheres, 10%, Sigma-Aldrich) were used as received.

3.2 Preparation and Method

3.2.1 Preparation of Vanadium Precursors

Generally, low viscosity vanadium precursor was prepared by mixing 182mg V_2O_5 powder with 15ml H_2O_2 in 90°C for 1h, then 400mg oxalic acid is added to reduce the vanadium and turn the solution to blue color. High viscosity precursor was synthesized via mixing 182mg V_2O_5 powder with 15ml H_2O_2 at 20 °C until a homogeneous clear yellow solution is formed. The high viscosity precursor is ready for usage after aging for several days. Prepared low- and high-viscosity precursors are captured in Figure 3.1. The reaction of V_2O_5 powder with H_2O_2 release heat strongly, which should be done in a big flask.

Figure 3.1 Photographs of the produced vanadium precursors with a low (Left) and a high (Right) viscosity.

3.2.2 Interfacial Assembly Method for the Preparation of Monolayer Colloidal Crystals Templates

An interfacial self-assembly method is applied that is similar to reported methods.^[1-5] Close-packed monolayer PS spheres were prepared via an interface method. In brief, 0.2 wt% PS/SiO₂ sphere dispersion in a 1: 1 by volume mixture of deionized (DI) water: ethanol was dropped slowly on the water/air interface. The PS/SiO₂ spheres on the top surface of the glass slide spread out onto the water-air interface, carrying by the water/ethanol solution and the PSs pack automatically, forming an irradiance film on the interface. The film is further compacted and pushes to one side of the petri dish by the introduction of SDS (wt. 0.2%), due to the competitive roles of SDS molecules with PSs to the fixed interfacial area. The colloidal crystals can be transferred onto the quartz substrate, displaying a structure-induced green color. The produced templates are consisted

of hexagonal-closed-packed (HCP) PSs. This character of a hexagonal array of templates is well maintained on the produced VO₂ nanocrystals. After that, the plasma etching or cleaning process was applied to further shape the template morphology or tune the hydrophobic surface to hydrophilic. Detail conditions vary in different projects and were given in the experiment sections in each following section.

3.2.3 Calculation Method for Solar Energy Modulation (ΔT_{sol}) and Visible Transmittance (T_{lum})

The integral luminous transmittance, T_{lum} (380-780 nm), and luminous modulation, ΔT_{lum} , are calculated by equations (1 and 2):

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

$$\Delta T_{lum} = T_{lum,95^\circ C} - T_{lum,25^\circ C} \quad (2)$$

where $T(\lambda)$ denotes spectral transmittance, $\varphi_{lum}(\lambda)$ is the standard luminous efficiency function of photopic vision in the wavelength range of 380–780 nm. Solar transmittance, T_{sol} (250-2500 nm), and solar modulation, ΔT_{sol} are calculated via equations (3 and 4):

$$T_{sol} = \frac{\int_{250}^{2500} \varphi_{sol}(\lambda) T(\lambda) d\lambda}{\int_{250}^{2500} \varphi_{sol}(\lambda) d\lambda} \quad (3)$$

$$\Delta T_{sol} = T_{sol,95^\circ C} - T_{sol,25^\circ C} \quad (4)$$

where $\varphi_{sol}(\lambda)$ is the solar irradiance spectrum for air mass 1.5 illustrated as the solar energy distribution spectrum in Figure 3.2, corresponding to the sun standing 37° above the horizon with 1.5-atmosphere thickness, corresponds to a solar zenith angle of 48.2°. The final average result is calculated from three repeated experiments, and the uncertainties are calculated from the standard deviation of the three experiments.

Figure 3.2 Solar energy spectrum and the analysis of solar energy distribution along the UV-Vis-NIR region. The figure is adaptive from online resources,^[6] Discover Ideas About Renewable Energy, Pinterest, <https://www.pinterest.com/pin/4574037099007741/>.

3.3 Characterization

3.3.1 X-ray Diffraction

Crystal phases are identified by the ordered arrangement of atoms. These periodic arrays serve as scatters and thus can diffract light. X-ray is also scattered incoherently when they interact with matter. This behavior can be depicted by Bragg's law:

$$\lambda = 2 d_{hkl} \sin \theta \quad (5)$$

where λ is the wavelength length of incident light and θ is the incident angle. Illustrating as Figure 3.3, d_{hkl} denotes the space between the planes. Constructive interference occurs when Bragg's law meets. To fulfill this geometry, a typical XRD is designed as Figure 3.3. The incident angle, ω , is defined between the incident beam and the specimen.

Figure 3.3 a) is a simplistic model of Bragg's law to understand how X-ray diffraction happens in related with crystals; b) is the diagram how XRD machine implements the Bragg-Brentano geometry. The both of (a) and b) are reprinted from tutorial PPT titled "Self-User Training for X-Ray Diffraction SEF" from Massachusetts Institute of Technology (MIT), United States of America (USA).^[7]

In reality, a polycrystalline sample contains innumerable of crystallites with random orientation. Thus, all possible diffraction peaks can be detected (Figure 3.4). To every set of planes, there should be a certain quantity of crystallites that are properly oriented to diffract. The produced result is a continuous line with specific peaks. The result information includes the peak position, intensity, and width. Then the result can be matched to the data in crystalline phase library to make an identification. XRD can help to determine the composition of a sample, unit cell lattice parameters, crystal structure and so on.

Considering the sample of thin films in this report, a Shimadzu XRD-6000 Thin Film XRD with a Cu K- α radiation was used for all samples. The 2θ mode is applied, which is fixing the tube position while tuning the sample holder and detector. The measurement is executed under 40 kV and 30mA. Produced samples were used for measurement without any pre-treatment.

Figure 3.4 XRD analysis for a polycrystalline sample. Reprinted from tutorial PPT titled “Self-User Training for X-Ray Diffraction SEF” from Massachusetts Institute of Technology (MIT), United States of America (USA).^[7]

3.3.2 Atomic Force Microscopy (AFM)

AFM is designed to measure the topology of the sample surface. This technology represents high resolution in mild working condition. Its resolution can reach 15-40 nm in the lateral and 0.1 nm in the vertical. The working circumstance can be in air, liquid or vacuum. And the surface can be either conductive or insulated. Figure 3.5 illustrates the typical structure of an AFM. The key components are the cantilever, tip, laser, and quadrant photodetector. The principle of AFM relies on measuring the deflection of the cantilever of known spring constant, due to tip-surface interaction forces. The laser as an information carrier can be collected by quadrant photodetector for analysis.

Figure 3.5 The diagram to represent how AFM works. Reprint from PPT of course MS7070, Scanning Tunneling Microscopy (STM) & Molecular Self-Assembly, School of Materials Science and Engineering, Nanyang Technological University.^[8]

For imaging, a sample by AFM, most common modes are contact mode and tapping mode. (Figure 3.6) For the contact mode, the tip is keeping in contact with the sample. Hard surface is preferred and high resolution can be achieved. But damages happen easily for tip and sample surface when a rough surface is applied. Tapping mode can reduce the possibility of damages while maintaining a good resolution. In such case, the cantilever is oscillating, thus tip is touching surface gently and frequently. Tapping mode is commonly used for biological samples and soft materials.

In this report, surface topology of samples was by AFM (DI-3100, Bruker) with a commercial silicon probes. It requires the surface roughness of the sample not more than 2 μm . A tapping mode is applied to all samples. Produced samples were used directly, and measurement was done at room temperature in air.

Figure 3.6 The diagram to illustrate the two types of imaging mode. Reprint from PPT of course MS7070, Scanning Tunnelling Microscopy (STM) & Molecular Self-Assembly, School of Materials Science and Engineering, Nanyang Technological University.^[8]

3.3.3 UV-Vis-NIR Spectrophotometer

The principles of spectroscopic analysis rely on passing light of a given wavelength through a specimen and measuring the percentage of the light absorbed or reflected. In a UV-vis-NIR spectrophotometer, light range from ultraviolet, visible to near infrared can be measured. Showing as Figure 3.7, the light starts from the source, then being split by dispersion device. Two slits located before and after the dispersion device can refine the light. The light passed the exit slit display single wavelength. After passing the sample, the remaining part of the light is collected by the detector. The wavelength of incident light is controlled by the dispersion device and exit slit. Samples can be liquid or solid depending on the type of sample holder.

In this report, a UV-vis-NIR spectrophotometer (Cary 5000, Agilent Ltd) is used. The heating stage is attached to the thin film sample holder. The range of measurement is 175 nm to 3300 nm. For samples tested, the transmittance spectrums were measured in the range from 250nm to 2500nm. Thin film sample holder with an aperture diameter of 0.5 cm is used for all measurement. All samples are measured at 20°C and 95°C.

Figure 3.7 The diagram to represent how UV-vis-NIR spectrometer works. Reprint from user guide and tutorial for using the Cary 500, School of Materials Science and Engineering, Georgia Institute of Technology, USA.^[9]

3.3.4 Transmission Electron Microscopy (TEM)

The electron-matter interactions generate a variety of signals, which carry on structural and chemical information of materials and can be collected. These interactions are generally illustrated as Figure 3.8. They are systemically classified as the elastic and the inelastic interactions. Elastic interactions happen when the energy of electrons maintain the same after the interaction. These interactions include the electrons are deflected by Coulomb interaction with materials. While in the case of the inelastic, energy transfer from the incident electrons to the materials. Electron energy significantly reduced after the interaction. These interactions generate X-rays or secondary electrons, Auger electrons and so on. In the respect of analytical electron microscopy, inelastic interactions are predominantly utilized.

Figure 3.8 The diagram to illustrate the electron beam interaction with materials. Reprint from the handbook titled “Properties of Electrons, their Interactions with Matter and Applications in Electron Microscopy”, Laboratory of Inorganic Chemistry, ETH Zurich, Switzerland.^[10]

TEM is designed to collect the direct beam. Comparing to SEM, TEM can reach a higher resolution and requires higher accelerating voltage, which can increase the intensity of the direct beam. For TEM, the specimen can not be too thick to block the electrons.

The mechanism of a TEM is analogous as it of optical microscopy, as shown in Figure 3.9. Both of them contain an “illumination” source, condenser lens, objective lens, and a projector. The main difference is “illumination source”. TEM uses electrons, while optical microscopy utilizes visible light. The electrons source requires TEM to utilize electron-magnetic (EM) fields rather the glasses for all lens. These electron-magnetic lens can changes trajectory of the electron, and focal length by the varying current. Also, the final image of TEM is displayed on a fluorescent screen instead of being observable directly by eyes. Moreover, a high vacuum inside the cambers is essential for TEM operation.

Here, the samples were characterized using either the TEM JEOL 2010 HR on an accelerating voltage of 200kV. It equipped with a LaB6 electron source. The resolution can

reach 2.3 Å in point and 1.4 Å in line. Samples for TEM were prepared by scraping the film from foils and transfer to the copper grid.

Figure 3.9 The diagram to illustrate the mechanism how TEM works in analogy with optical microscopy. Reprinted from the tutorial PPT of a lecture titled “Samuel Roberts Noble Electron Microscopy Laboratory”, University of Oklahoma, USA.^[11]

3.3.5 Scanning Electron Microscope (SEM)

SEM is designed to image the materials in submicron scale by collecting the interacted electrons, then interpreting them into morphological information. A typical SEM contains several parts showing as Figure 3.10. The electron gun at top produces a stream of monochromatic electrons. Then, the condenser aperture eliminates high-angle electrons and condenses electron beam. The scan coils control the condensed electron beam to sweep in a defined frequency. This procedure ensembles the work mode of television. Followed objective aperture focuses the scanning beam onto the selected area of the sample. Once the electron beam strikes the sample, interactions occur. The information carried by interactions can be collected by detectors. The commonly used detectors are back scattering electron (BSE) detector and secondary electron (SE) detector. The detected information combining with instrument setting is analysis by the software to composite the final image. High vacuum is required. So the sample strictly has to be solid. On the other hand, the sample also required to be conductive. For insulators and some semiconductors with bad conductivity, coating by a conductive layer is necessary before imaging. The common coating materials are silver, gold, and platinum. The resolution of SEM is usually than 5.0 nm.

For the SEM used in this report, there are FESEM 6340 and FESEM 7600. The resolution is 3.0 nm for the former one and 1.5 nm for the later. All samples are coated by gold before imaging. SE detector is used for all imaging.

Figure 3.10 The diagram to illustrate the mechanism how SEM works. Reprinted from the tutorial PPT of lecture MENA3100 in University of Oslo, Norway.^[12]

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Chapter 4*

2D SiO₂-VO₂ Photonic Crystals with Statically Visible and Dynamically Infrared Modulation for the Smart Window Application

In this chapter, we discuss the integration of 2D photonic structures, widely used for generating photonic band gaps (PBG) in a variety of materials, with the temperature dependent phase change of vanadium dioxide (VO₂). VO₂ possesses thermochromic properties, whose potential remains unrealized due to an undesirable yellow-brown color. Here, a SiO₂/VO₂ core/shell 2D photonic crystal is demonstrated to exhibit static visible light tunability and dynamic near-infrared (NIR) modulation. Three-dimensional (3D) finite difference time domain (FDTD) simulations predict that the transmittance can be tuned across the visible spectrum while maintaining good solar regulation efficiency ($\Delta T_{sol}=11.0\%$) and high solar transmittance ($T_{lum}=49.6\%$). Experiments show that the color changes of VO₂ films are accompanied by NIR modulation. This work presents a novel way to manipulate VO₂ photonic structures to modulate light transmission as a function of wavelength at different temperatures.

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4.1 Introduction

Photonic crystals are a significant class of chronotropic materials.^[1] Accurate color modulation across the full visible range has been achieved with photonic crystals based on many binary components including ZrO_2 ,^[2] ZnS ,^[3] TiO_2 ,^[4] where coherent optical diffraction generates Photonic Bandgaps (PBG) that can be tuned to selectively forbid the propagation of specific wavelengths to produce distinct structural colors. For colloidal photonic crystals the synthesis-structure-property relationship, with periodicity down to the sub-micron range, is well understood.^[5-8]

Incorporation of intelligent architectural windows, or “smart windows”, is a promising approach to reduce the energy consumption of buildings, which contributes up to 40% of the world’s energy usage.^[9] Generally, these windows operate by blocking a large fraction of the sunlight on hot days, while transmitting solar energy in cold weather.^[10] Through temperature-responsive solar energy modulation, thermochromic smart windows are a key component of green buildings that have been extensively studied in recent years.^[11,12]

Vanadium dioxide (VO_2) is a thermochromic material that changes its optical behavior at a critical transition temperature (T_c) of 341K (68°C),^[13,14] where an insulator-to-metal phase transition is accompanied with abrupt decrease in the Infrared (IR) transmittance while maintaining transmittance in the visible range.^[15] In this manner, VO_2 -based thermochromic windows can largely block solar energy inflow at high temperatures without compromising brightness.

However, VO_2 -based smart windows face several obstacles, such as high T_c , relatively low visible transmission (T_{lum}), limited solar modulation (ΔT_{sol}), and an unfavorable brown color. Numerous methods have been proposed to solve the first three issues, including chemical doping,^[16] together with the fabrication of porous,^[17] composite,^[18-20] multi-layered,^[21,22] and gridded structures.^[23,24] In contrast, modification of its intrinsic brown-yellowish color was less studied, and while dopants can induce color changes these improvements have been limited or accompanied by sacrificing solar modulation performance (Table 4.1).

Table 4.1 Summary of Color-Improved VO₂ film and Their Thermochromic Properties

	Types	Color Change	ΔT_{sol}	T_{lum}	T_c
Doping	Sr ^[25]	Light Yellow	↓	↑	↓
	Zr ^[26]	Light Yellow	↑	↑	↓
	W-Zr ^[26]	Light Yellow	↑	↑	↓
	Zn ^[27]	Light Yellow	\	↑	\
	F ^[28]	Light Yellow	↓	-	↓
	Mg ^[29]	Light Yellow	↓	↑	↓
	W ^[30,31]	Green/Blue	↓	↓	↓
Composite	Au NPS in VO ₂ Matrix ^[32]	Green/Blue	\	-	↓
	Core-Shell VO ₂ @TiO ₂ ^[33]	Grey/Light Blue	↓	↑	\
	Combination of VO ₂ Layer with Organic Solar Cell ^[34]	Green/Blue	↓	↓	-

Note: "↑" means "increased"; "↓" means "decreased"; "-" means "unaffected" and "\" means "data not available".

The two-dimensional photonic crystal is one of the most promising structures, that demonstrates conspicuous structural color, and because it contains less VO₂ compared to 3D structures,^[4,35,36] static absorption in the VO₂ layer is minimized.^[37,38] Inspired by the color modulation of photonic structures and the viability of emerging preparation techniques, VO₂/SiO₂ photonic films were prepared to tune the color of reflected and transmitted light for thermochromic applications at various wavelengths. Hexagonal-close-packed SiO₂/VO₂ core/shell 2D photonic crystal is predicted by 3D finite difference time domain (FDTD) simulations to exhibit tunable structural colors and distinct solar energy modulation abilities, that was subsequently confirmed experimentally for VO₂ foils. While previous research focused on the IR light modulation of photonic crystal films that simultaneously achieve visible static modulation and near-IR (NIR) dynamic modulation. In this study, a novel approach is presented for manipulating the light transmission of VO₂-based foils at different wavelengths.

4.2 Experimental Methods

4.2.1 Chemicals

Vanadium pentoxide (V_2O_5 , 99.6%, Alfa, Aesar), hydrogen peroxide (H_2O_2 , 30%, Sigma-Aldrich), methanol (CH_3OH , 95%, Aik Moh Pet Ltd), ethanol (C_2H_5OH , 95%, Aik Moh Pet Ltd), propyl alcohol (C_3H_7OH , 99%, Sigma-Aldrich), dodecanol ($C_{12}H_{25}OH$, 99%, Sigma-Aldrich), sodium dodecyl sulfate (SDS, 99%, Sigma-Aldrich), and plain silica spheres with diameters of 200nm, 400nm, 600nm and 700nm (5%, Microsphere-Nanospheres), were used as received.

4.2.2 Assembly of Monolayer SiO_2 Nanospheres

The MCCs were produced using a modified interface assembly method described previously (Figure 4.1a1-3).^[39-41] The silica spheres were rendered hydrophobic by refluxing in specific alcohols. The optimized alcohols are different for the silica spheres with different sizes to assist the formation of high-quality templates. Based on the experiment results, the optimized alcohols/silica-size (nm) matches are $C_{12}H_{25}OH/200$ nm, $C_3H_7OH/400$ nm, $C_2H_5OH/600$ nm, $CH_3OH/700$ nm. Besides, the optimized experiment conditions are different for different alcohols. The reflux temperature/duration are $190\text{ }^{\circ}C/4$ h for $C_{12}H_{25}OH$, $75\text{ }^{\circ}C/20$ h for C_3H_7OH , $70\text{ }^{\circ}C/20$ h for C_2H_5OH , and $60\text{ }^{\circ}C/20$ h for CH_3OH . The hydrophobicity of silica spheres was precisely controlled to obtain floating on the air/water interface without aggregation to multilayers. The modified silica spheres were washed and re-dispersed at 1 wt% in a 1:1 by volume mixture of deionized (DI) water: ethanol. For interface assembly, a 1 cm^2 hydrophilic square glass was placed at the mid-bottom of a Petri dish to which DI water was added carefully to a level slightly higher than the upper glass surface without submersion. Subsequently, the silica microspheres dispersion was dropped slowly onto the glass surface to disperse freely and self-assemble as a floating monolayer that was close-packed by pushing to one side of the Petri dish through the addition of several drops of SDS solution (2 wt%). The 2D close-packed silica

MCC was easily picked up by the hydrophilic quartz glass substrate. After overnight heat treatment at 100°C, the MCC templates were stored in a desiccator for further use. The hydrophilic quartz glasses were prepared by immersion in piranha solution ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2=3:1$ in volume) at 90°C for 15 mins, followed by washing several times in DI water and ethanol.

4.2.3 Preparation of VO_2 films

The vanadium oxide precursor was prepared through the dissolution of vanadium pentoxide powder in hydrogen peroxide at 90°C.^[16] This stock solution was aged for two weeks before use. In this paper, the precursor concentration was a variable parameter. The standard precursor was fixed as 182 mg V_2O_5 dissolved in 15 ml H_2O_2 . The silica MCCs were immersed in Piranha solution at 90°C for 10 mins to eliminate the grafted organic chains and turn the surface hydrophilic, where no obvious decreasing in silica sphere diameter observed (Figure 4.1b-e).

Figure 4.1 a) Diagram of the procedure to fabricate 2D SiO_2/VO_2 core/shell foils. a1-3) Fabrication of silica nanosphere MCC templates, and 4,5) preparation of SiO_2/VO_2 films. SEM images of 400 nm silica sphere MCC b) before and c) after the treatment in Piranha solution. And their calculated size distributions d) before and e) after the treatment. Average diameters are presented respectively.

These templates were cleaned several times with DI water, then were processed through a sol-gel infiltration method by immersion in the vanadium oxide precursor and dip-coating at a specific withdrawal speed (Figure 4.1a4).^[42] After drying at room temperature, the 2D SiO₂/VO₂ photonic crystals were prepared via annealed at 550°C for 2h under the protection of argon gas with a ramping speed of 1°C/min (Figure 4.1a5).

4.2.4 Characterization

The 2D photonic crystal morphology was characterized using field-emission scanning electron microscope (FESEM, JEOL JSM-6340F) at an accelerating voltage of 5 kV, and transmission electron microscopy (TEM, JEOL JEM2010) at an accelerating voltage of 200 kV. TEM samples were prepared by scraping the film from the glass substrates and transferred to copper grids with ethanol. The crystal phases were identified using the thin film glancing angle X-ray diffraction (XRD, Shimadzu XRD-6000) with Cu K- α X-rays. The transmittance spectra were measured from 250nm to 2500nm using UV-vis-NIR spectrophotometry (Cary 5000, Agilent Ltd) as a function of temperature (heating stage, Linkam PE120). Please refered the details to section 3.1.

4.2.5 Optical Spectrum Simulation

3D FDTD simulations were performed using commercial software (FDTD solution, Lumerical Inc. Vancouver, Canada). The optical constants of the materials were selected for operation across the spectral range 300 nm to 2500 nm. The dielectric dispersion profiles of the materials were fitted by the multi-coefficient model that relies on an extensive set of basis functions. To calculate the frequency dependent transmittance, PML (perfectly matched layer) boundary conditions were set for the z-direction, and Bloch boundary conditions were applied to the x and y directions of the simulation region. For computation, SiO₂/VO₂ core/shell 2D colloidal crystals were supported on the glass, the entire system suspended in air/vacuum, and the incident beam modeled as a plane wave propagating along the z-axis. Field monitors were placed at fixed z positions below the SiO₂/VO₂ core/shell 2D photonic crystal film surface to detect the transmitted beam

intensity. The other parameters were set as follows: a simulation time of 100 fs with an auto-shutoff parameter of 10^{-5} , a mesh accuracy of 5 (i.e., 22 mesh points per wavelength), and mesh refinement algorithm set to “conformal variant 1” allowing for a nonuniform mesh over the FDTD domain. For the initial validation of FDTD algorithm reliability for the specific use case presented in the paper, the transmission of a flat film (110 nm thickness) of VO₂ was simulated and the results are consistent to the previous report.^[39]

4.3 Results

4.3.1 Concept and Simulation Results

The process of designing photonic crystal based VO₂ foils is illustrated in Figure 4.2a. For example, the window shows the desired appearance (such as red, blue, and green) via selectively reflecting light with certain color. By selectively blocking visible light in the vicinity of the PBG, both transmittance and reflectance can be tuned, and the foil color adjusts precisely to meet the required functionality. Simultaneously, these foils maintain IR transmission at low temperature, but strongly attenuates IR transmission at high temperature, as necessary for thermochromic smart glasses.

The 2D SiO₂/VO₂ core/shell photonic crystal structure is depicted in Figure 4.2b, where a 20 nm VO₂ film homogeneously coats the SiO₂ nanospheres. The whole structure is considered as one unit, with the sphere diameters varying from 400 nm, 500 nm, 600 nm to 700 nm, that are hexagonally close-packed monolayers on a glass substrate. Ideally, the assemblage is wholly 2D in the “x-y” plane of the glass substrate with no vertical “z” extension. These films can be therefore termed 2D photonic crystal because the close-packed VO₂ shells create a contiguous surface.

Figure 4.2 a) Illustration of how photonic VO₂ smart window works; b) illustration of designed structures for simulation; and c) simulated transmittance spectrum, where transmittance peaks and troughs are indicated by the solid and dashed arrows respectively. The colorful background in c) denotes the visible spectrum from 370 nm to 770 nm.

The normal incidence transmission spectra for these films were calculated at high and low temperatures using FDTD simulation (Figure 4.2c). At low temperature, NIR transmittance exceeds the visible because of the intrinsic strong absorption of VO₂.

Independent of temperature, the photonic crystal structure permits statical tuning of the transmission color across most of the visible range, such that the main transmission peak (denoted with solid arrows) blue-shifts gradually from 680 nm to 390 nm as the SiO₂/VO₂ sphere diameter decreases from 700 to 400 nm (Table 4.2). Strong diffraction correlates

with the transmittance valleys where strong scattering causes low transmittance. The main transmittance valleys blue shift almost linearly from 920 nm to 570 nm (denoted with dashed arrows), and reaches the visible range when the sphere diameter decreases to 500nm. These transmission spectrum behaviors specific to 2D photonic crystal structures have not been reported previously for VO₂ structures.

The trough in transmission spectra can be explained because the monolayer of SiO₂/VO₂ spheres behaves as a two dimensional (2D) diffraction grating. This trough in transmitted intensity is tentatively interpreted as a Rayleigh – Wood anomaly related to higher order diffraction. When higher order diffracted waves propagate at a grazing angle with respect to the normal, they may efficiently couple to surface modes, and due to overall energy conservation, this coupling causes an attenuation of the transmitted intensity, thus causing color changes in the transmitted spectra.^[43-45] On the other hand, temperature dependent metal-insulator transition of VO₂ means all films can dynamically modulate NIR transmission. Simulations confirmed that the NIR transmission can be dynamically tuned by temperature (Figure 4.2c and Table 4.2). Around 70% transmittance contrast at 2500 nm can be observed for all films. For the optimal sphere diameter of 600 nm, it shows ΔT_{sol} is as high as 11.0% while maintaining T_{lum} at 49.6%.

Table 4.2 Optical properties obtained for FDTD simulated films.

Unit Size	Peak Position (nm)	Trough Position (nm)	T_{lum} (%)	Contrast at 2500 nm	ΔT_{sol} (%)
400	410	570	21.1	66.7	12.2
500	500	670	37.7	70.5	10.8
600	570	760	49.6	71.2	11.0
700	680	920	37.9	72.0	10.1

Notes: Main transmittance peaks and troughs, which are indicated by solid and dashed arrows respectively in Figure 4.2c, are selected and their positions are concluded as “Peak Position” and “Trough Position”.

4.3.2 Produced Monolayer Colloidal Crystals of SiO₂ Nanospheres

The MCC templates were found to be homogeneous by SEM (Figure 4.3a). For example, the 400 nm silica spheres are hexagonally close-packed monolayers supported on the quartz substrate. All the films are highly transparent, turning slightly semitransparent when larger silica spheres are used (the upper image, Figure 4.3b). Under an incandescent lamp in the lab, the films showed high uniform and size-dependent iridescence (the lower image, Figure 4.3b). To our knowledge, it is the first time that high-quality closed-packed monolayer of silica spheres assemble without the assistance of Langmuir-Blodgett trough.

Figure 4.3 a) SEM images of prepared MCC templates using silica sphere with a diameter of 400nm; b) photo images of prepared silica MCCs with a normal view (top) and images under fluorescent lamp light (bottom). Samples from left to right are quartz glass, 200 nm, 400 nm, 600 nm, and 700 nm diameters respectively, and the size of the samples is 1.5×1.5 cm for all. SEMs images of samples processed at steps of c) before annealing, d) after annealing at 200°C for 2h, and e) at 550 °C for 2h respectively. f) XRD result of prepared films.

The 400 nm silica MCC was by dip-coated in the standard vanadium precursor at a withdrawal speed of 7 mm/min and the morphology evolution during heat treatment was recorded. SEM observation of 2D colloidal crystals before annealing, after annealing at

200°C for 2h, and 550°C for 2h, is shown in Figure 4.3c-e. As shown in the inset of Figure 4.3c, the initial infiltrated precursor uniformly covered the upper half of the MCC but did not penetrate into the lower spaces between the silica spheres and the quartz substrate because the sol-gel precursor has high viscosity. At higher annealing temperatures, the coated precursor tends to aggregate around the spheres (Figure 4.3d, e). After treatment at 550°C for 2h, the precursor crystallizes as VO₂ with rutile (Figure 4.3f) either as nanoparticles attached to the upper half of silica spheres or intercalated between the spheres. This indicates that aggregation occurs during annealing, and may be triggered by high thermal stress between the VO₂ film and the SiO₂ spheres.

4.3.3 Effects of Precursor Concentration and Dip-Coating Speed

The infiltrated precursor has to fully coat the silica sphere in order to replicate the simulated SiO₂/VO₂ structure. However, as discussed above, the standard precursor was unable to penetrate into the bottom half of silica spheres (Figure 4.4). For infiltration at sub-micron scales, the interfacial interaction between the precursor and spheres has to be considered,^[46] as either the pore hydrophilicity of the silica spheres or the high viscosity can reduce penetration of the precursor solution. Since the MCC templates have been rendered hydrophilic by the piranha solution, viscosity of the precursor is likely the dominant factor. Therefore, at the higher precursor concentration, the greater viscosity, lead to excessive coverage of VO₂ on the silica spheres, a flattened surface morphology, and deviation from ideal 2D spherical photonic structures (Figure 4.4d).

The effect of dip coating speed on the amount of coated precursor as well as the final morphology of films was studied (Figure 4.5). Higher withdrawal speeds favor more complete coverage of silica sphere MCC, and increasing withdrawal speed is similar to that with increasing concentration. Lower concentration and dip coating speeds promote sphere coverage but with lower VO₂ loadings. The optimal parameters for fabrication were a 1.33 relative concentration and a dip-coating speed of 4 mm/min.

Figure 4.4 SEM images of samples using precursors with a concentration of a) 1, b) 1.33, c) 1.67 and d) 2 in relative to the standard vanadium precursor. The withdrawal speed of dip-coating is 1mm/min and used MCC is 400 nm for all samples.

Figure 4.5 SEM images of samples prepared by dip-coating with speed of (a) 1, (b) 7mm/min, and (c) 17mm/min. The 400 nm MCC template and standard precursor were used for all samples.

4.3.4 Effects of SiO₂ Sphere Diameter

MCC templates prepared by silica spheres with various diameters, 200 nm, 400 nm, 600 nm, and 700 nm were used. The morphology of the samples was characterized using SEM (Figure 4.6). Noticeably, the type of MCC templates also significantly affected the

morphology of the final films. The 200 nm sample can be described more like a double-layered structure, with a thick VO₂ layer above the silica MCC layer, while the 700 nm sample resembles 2D photonic crystal structure with silica spheres capped by a thin VO₂ layer. To further understand the microstructure of the fabricated films, 400 nm samples were characterized by TEM, then compared with the designed structure. Consistent with SEM results, the prepared films demonstrated HCP close-packed monolayer filled with VO₂ nanocrystals (Figure 4.6e). The VO₂ crystals form nanoparticles attached to the surfaces of the silica spheres. To better compare the experiment with simulation, the diagram of designed and produced units are illustrated as an inset of Figure 4.6f. The main differences can be summarized as follows: (i) The VO₂ layers do not fully encapsulate the silica spheres due to poorer film coverage of the lower part of the spheres. (ii) VO₂ crystals are formed as individual particles rather than as continuous films due to large thermal stress between spheres and VO₂ films. So other approaches are proposed to form a continuous VO₂/silica core-shell structure, such as atomic layer deposition (ALD),^[47] chemical vapor deposition (CVD),^[48] or spray deposition.^[49-51]

Figure 4.6 SEM images of the color changed samples using the different unit size of MCC, from a) 200 nm, b) 400 nm, c) 600 nm to d) 700 nm. Inserts are the corresponding cross-section view. TEM images of the 400 nm sample are shown in e) low and f) high magnification. Inset of (f) shows the illustration of produced VO_2 /Silica sphere structures.

4.3.5 Optical Properties and Analysis

The sample appearance was captured in several circumstances (Figure 4.7). For a given sample, the appearance (transmittance, absorption, and reflectance) varied as a function of light source, background, and observation angle.^[1,52] For example, the reflected light color of the 700nm sample is light brown (Figure 4.7a) and it turns to distinct green in Figure

4.7b and Figure 4.7d. Meanwhile, the 400nm sample shows as red in Figure 4.7b but the iridescence changes to red-brown in Figure 4.7d. The observed color is affected by many factors including but not limited to material properties and surroundings.

As sphere size increases, the color changes from dim yellow-brown color through red-brown, bluish to greenish from a normal viewing angle under outdoor conditions (Figure 4.7a), and becomes more pronounced when viewed at larger tilt angles (Figure 4.7b,c) or under incandescent light (Figure 4.7d). Color variation with viewing angle and the incident light source was a distinct characteristic of each 2D opal crystal that displayed PBG in the visible range.^[1] These color changes are of practical importance because architectural windows are viewed from various angles in daily life. The experimental result can be fully explained by angle-resolved simulations (Figure 4.7e,f) with the iridescence proving the viability of color modulation in VO₂ based photonic thermochromic films.

Figure 4.7e,f shows the simulated band structures for the SiO₂/VO₂ photonic crystal for unpolarized light with the angle of incidence scanned from the -50 to 50 degrees. A flat band of energy can be observed at the vicinity of 0.47 μm wavelength for reflection and 0.54 μm wavelength for transmission (period 600 nm, Figure 4.7e). Similarly, a flat energy band appears in the vicinity of 0.52 μm wavelength for reflection and 0.57 μm wavelength for transmission (period 700 nm, Figure 4.7f). Since the human vision wavelength range is from about 400 to 700 nm, these flat bands are determining the color perception of the reflected and transmitted light. Specifically, the reflected light is blue for 600 nm period and green for 700 nm period, in correspondence with observed colors (Figure 4.7b-d).

These films also maintain a highly dynamic NIR modulation and show large light contrast between low temperature and high temperature (Figure 4.7g). At low temperature, semi-conductor VO₂ films are relatively transparent for NIR light, while at high temperature, metallic VO₂ largely blocks the IR light. The optical properties of fabricated films are calculated and presented in Table 4.3. The 400 nm and 600 nm samples are demonstrated with 50.4% and 54.5% contrast at 2500 nm, which are comparable to, or surpass, the best reported VO₂ films.^[38,53] However, although the ΔT_{IR} remains relatively high for all five samples, the low ΔT_{sol} is due to the high ΔT_{lum} . This relative low ΔT_{sol} is different from that predicted by FDTD simulation and may be due to incomplete VO₂

coverage of the silica spheres to form a SiO_2/VO_2 core/shell structure. Moreover, the VO_2 coating thickness was not uniformly 20 nm as controlling the synthesis of monoclinic VO_2 in sub-20 nm nanocrystals is challenging.^[54,55] The simulated vanadium dioxide photonic crystal has a vertical periodicity relative to the glass plane, and hexagonally packed SiO_2/VO_2 colloidal crystal in the substrate plane. These two parameters are crucial for quantitative matching of experimental and calculated results. The optical results presented verify the possibility of these color changing films in smart window application.

Figure 4.7 Photographs of prepared samples with a tag paper background under sunlight from a) the normal view and b) a tilted view of 45 degrees; c) photographs of these samples with a white wall background under sunlight; d) photographs of the same samples with tag paper background in lab under common incandescent lamp. A tilted view of 45 degrees is for (c) and (d). The captured photographs are exhibited without any post color processing. Simulated band structure of SiO_2/VO_2 photonic crystal is shown in e) Reflection (left) and transmission (right), period 600 nm; f) Reflection (left) and transmission (right), period 700 nm. The measured transmittance spectrums of g) color changed samples and h) prepared silica sphere MCCs. In (g) and (h), the transmittance peaks and troughs are indicated by the solid and dashed arrows respectively. (i) And its insert is the

data analysis charts for the trough and peak positions respectively as a function of the sphere diameter.

The 2D photonic structure allows the VO₂ films to exhibit PBGs in both visible and NIR ranges. This is confirmed by the transmittance spectrum in Figure 4.7g, where distinct troughs are seen for 400 nm, 600 nm, 700 nm samples as denoted with dashed arrows. As to the 200 nm sample, its optical behavior is similar to the plain VO₂ film, which is partially explained by the double-layered structure of 200 nm sample, with a thick VO₂ layer above the silica MCC layer (Figure 4.6a), and because of strong materials intrinsic absorption from 250 to 300 nm as shown in red line (Figure 4.7g). The PBG becomes more distinct with the increasing size of MCC template used is consistent with their morphology evolution, wherein from double layers to a photonic crystal structure. To further elaborate these troughs, they are compared with measured transmittance spectra of silica sphere MCCs (Figure 4.7h), which is consistent with the previous report.⁵⁶ The broad trough in the NIR range, and a sharp one in the visible range corresponding to the first and second order Bragg diffraction calculated of an HCP crystal. The first and the second order diffraction can be calculated by $\lambda_{\max} = 2Dn_{\text{eff}}$ and $\lambda_{\max} = Dn_{\text{eff}}$ respectively with D being the lattice parameter (D is fixed to $0.866d$ for an HCP packing), and N_{eff} being the effective refractive index.^[6, 56] The effective refractive index is calculated in good approximation as follows:

$$n_{\text{eff}} = f_{\text{SiO}_2} \cdot n_{\text{SiO}_2} + f_{\text{VO}_2} \cdot n_{\text{VO}_2} + f_{\text{air}} \cdot n_{\text{air}} \quad (4.1)$$

where f is the volume fraction of the material and $f_{\text{SiO}_2} + f_{\text{VO}_2} + f_{\text{air}} = 1$. For HCP packed silica sphere MCC, $f_{\text{VO}_2} = 0$, and $f_{\text{SiO}_2} = 0.74$.^[56] As to the SiO₂/VO₂/air ternary system, increasing f_{VO_2} promotes higher N_{eff} , which causes the red-shift of $\lambda_{\max}$, as at room temperature, the VO₂ has a higher refractive index than silica and air.^[13] For example, the visible trough for the 600 nm sample shows a red-shift from 640 nm to 700 nm after VO₂ coating (Figure 4.7i). Similarly, a red-shift can be found for the 700 nm sample. The trough in the visible range disappears for 200 nm sample after coating; which is again attributed to strong absorption of VO₂ itself from 250-300 nm.

Table 4.3 Optical properties of produced films.

Sample (size of MCC)	$T_{lum}/20^{\circ}\text{C}$ (%)	$T_{lum}/90^{\circ}\text{C}$ (%)	ΔT_{lum} (%)	ΔT_{sol} (%)	Contrast at 2500nm (%)	ΔT_{NIR} (%)
Plain	53.1	59.1	6.0	2.8	37.3	-13.6
200 nm	48.5	52.8	-4.3	1.5	24.4	-8.9
400 nm	36.8	44.9	-8.2	2.2	50.4	-13.1
600 nm	41.5	46.9	-5	3.1	54.5	-13.4
700 nm	51.5	57.8	-6.3	0.3	27	-7.8

The experimental results are consistent with simulations with respect to sphere-diameter-dependent diffraction behavior. Figure 4.7i compares the transmittance troughs from simulation (Figure 4.2c), experimentally determined for the produced samples (Figure 4.7g), and MCC templates (Figure 4.7h). Both experiment and simulation found the transmittance trough red-shifts vary nearly linearly with the increase of sphere size of silica sphere MCCs. This linear relationship is reasonably obeying the Bragg diffraction law as discussed above. The same tendency was observed with silica MCC templates, as the photonic structure selectively modulates the diffracted light in the visible range. Transmittance peaks appearing on corresponding troughs also can be identified. Rationally, the transmittance peaks vary linearly with respect to the unit size of applied MCC templates for each case. (Insert of Figure 4.7i) These linear tendencies experimentally and theoretically support the approach that static transmittance color modulation can be indeed achieved with VO_2 films. The slight difference between the simulation and experiment results should be attributed to the non-perfect core/shell SiO_2/VO_2 structures produced in experiment.

4.4 Chapter Summary

In summary, SiO_2/VO_2 2D photonic crystals are proposed for thermochromic smart window applications. Besides the promising dynamic NIR modulation character observed in traditional VO_2 films, these structures display static light tunability in the visible range as predicted by FDTD simulation. By varying the PBG, the transmittance was shown to

continuously tune across most of the visible spectrum. Although experimental sample-behavior was somewhat different from the simulation, the photonic crystals showed distinct color changes from red, green to blue, while maintaining high NIR modulation that demonstrates the effectiveness of PBG engineering. Formation of idealized SiO₂/VO₂ core/shell structures was limited by incomplete precursor infiltration, as well as the high stress during annealing that favors the formation of the VO₂ as individual particles rather than a continuous film. Considering the variety of color requirement for industrial windows, this work could inspire wide-exploration of colorful energy-saving smart window and temperature dependent photonic structures.

This chapter presents the successful modulation of the yellow-brown color of VO₂, providing a way to solving the one of the challenges. It is considered to be more important to improve its thermochromic performance. Next two chapters discuss the ways to promote the performance based on (Chapter 5) the temperature-dependent plasmonic VO₂, and (Chapter 6) the integration of plasmonic VO₂ with reconfigurable structures.

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Chapter 5*

Active Localized Surface Plasmon Resonance in 2D VO₂ Nanostructures for the Smart Window Application

In this chapter, we discuss the active LSPR in 2D pattern VO₂ nanocrystals for smart window application. A universal approach to developing various two-dimensional ordered nanostructures, namely nanoparticle, nanonet and nanodome arrays with controllable periodicity, ranging from 100 nm to 1 μ m, has been developed in centimeter-scale by a nanosphere lithography technique. Hexagonally patterned vanadium dioxide (VO₂) nanoparticle array with average diameter down to sub 100 nm as well as 160 nm of periodicity is fabricated for the first time, exhibiting distinct size-, media-, and temperature-dependent localized surface plasmon resonance (LSPR) switching behaviors, which fits well with the predication of simulations. We specifically explore their decent thermochromic performance in energy saving smart window and develop a proof-of-concept demo which proves the effectiveness of patterned VO₂ film to serve as a smart thermal radiation control.

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5.1 Introduction

Ordered arrays of colloidal nanocrystals (NCs) represent an important class of metamaterials with tunable structures and properties.^[1,2] Two-dimensional (2D) patterned nanostructures, such as 2D ordered nanostructure arrays, surface-patterned nanostructures, and free-standing 2D patterned films, have attracted intensive interests due to the unique pattern-dependent properties.^[3] The fabrication approach based on monolayer colloidal crystal (MCC) templates have been recognized as a facile, inexpensive, efficient, and flexible nanolithography technique for preparing functional 2D patterned nanostructures with high reproducibility.^[4] Previous studies of artificial 2D patterned nanostructures via the templates of hexagonal self-assembly of polystyrene (PS) spheres have been widely used in different fields including sensor,^[5] solar cells,^[6] photocatalysis,^[7] surface-enhanced Raman scattering (SERS),^[8,9] light-emitting diodes (LED),^[10] antireflection layer,^[11] hydrophobia structures,^[12] and so on.^[13,14]

Due to its intriguing near-room-temperature first-order phase transition, a metal-insulator transition (MIT), accompanying with strong electronic, optical, and mechanical changes,^[15,16] vanadium dioxide (VO₂) has been widely used in field-effect devices,^[17,18] energy storage,^[19-21] thermal camouflage,^[22] smart window,^[23,24] four-dimensional imaging,^[25] and so on. However, only a few works on 2D patterned VO₂ were reported, which may be mainly due to limited fabrication methods. Ordered VO₂ nanoparticles have successfully been prepared via a combination of ion beam lithography, pulsed laser deposition followed by thermal oxidation,^[26] but its sophisticated procedure, difficulty in scalability, and high dependence on equipment limit it to fundamental science. VO₂ nanopillar arrays through nanoimprinting and nanonets via controlled directed growth cannot reach sub-100 nm region.^[27,28] Recently, non-metallic nanocrystals with tunable localized surface plasmon resonance (LSPR) attracted great interest as their significance in medicine, sensing, electrocatalysts, microelectronic devices.^[29-31] This particularly important property is increasingly playing critical roles in nanophotonics and nanoelectronics.

In this work, we report 2D patterned VO₂ nanocrystals with different nanostructures, namely nanoparticle, nanonet, and nanodome arrays as well as controlled periodicity. The periodicity of structure achieves down to 200 nm with sub-100 nm of nanoparticle size, while the area of samples can reach up to centimeter-scale. Their size-, media-, and temperature-dependent LSPR tunability in near infra-red (NIR) range are observed for the first time. LSPR red-shifts are observed with the increase of the particle size and the media reflective index, respectively, while the relative LSPR intensity can be dynamically adjusted by varying temperature. Moreover, the hexagonally patterned VO₂ nanoparticle array with the periodicity of 160 nm has been demonstrated with good performance in thermochromic smart window application as well as being a smart thermal radiation control.

5.2 Experimental Methods

5.2.1 Chemicals

Vanadium pentoxide (V₂O₅, 99.6%, Alfa Aesar), oxalic acid (99.99%, Alfa Aesar), hydrogen peroxide (H₂O₂, 30%, Sigma-Aldrich), sodium dodecyl sulfate (SDS, 99%, Sigma-Aldrich), polyethylene glycol (PEG, M_w 600, Sigma-Aldrich), polyvinyl alcohol (PVA, M_w 85000-124000, 99%, Sigma-Aldrich), polyvinylpyrrolidone (PVP, M_w 40000, Sigma-Aldrich), and polystyrene spheres with nominal average diameters of 200, 500, 600, and 800 nm (PS spheres, 10%, Sigma-Aldrich) were used as received.

5.2.2 Preparation of Vanadium Precursors

The preparation methods of precursors were reported previously.^[23,32] Generally, low viscosity vanadium precursor was prepared by mixing 182 mg of V₂O₅ powder with 15 ml of H₂O₂ in 90°C for 1 h, then, 400 mg of oxalic acid was added to reduce the vanadium and turn the solution to blue color. High viscosity precursor was synthesized via mixing 182 mg of V₂O₅ powder with 15 ml of H₂O₂ at room temperature until a homogeneous clear yellow solution formed. The high viscosity precursor was ready for use after aging

for several days. The reaction of V_2O_5 powder with H_2O_2 releases heats violently, which should be done with fully careful.

5.2.3 Assembly of Monolayer Polystyrene Spheres

Close-packed monolayer PS spheres were prepared via an interface method.^[11,23] In brief, 0.2 wt% PS sphere dispersion in a 1: 1 by volume mixture of deionized (DI) water: ethanol was dropped slowly on the water/air interface. Then several drops of SDS were added to push the floating PS spheres to form an iridescent film, followed by being picked up with quartz glass substrates. Subsequently, the close-packed monolayer PS spheres were rendered to hydrophilic, or etched to be non-close-packed by a BSETEQ NT1 Plasma Cleaner/Etch System performed using a mixture gas of argon and oxygen with 1: 5 in pressure, and an RF power of 300 W. The PE duration was 10 s for nanoparticles and nanodomes, while 60 s for the nanonet structures. Details can be referred to the Chapter 3.1

5.2.4 Preparation of 2D Patterned Films

The templates were immersed in certain vanadium oxide precursor (low viscosity precursor for patterned nanoparticles and nanonets, and high viscosity one for nanodome arrays) and dip-coating at a specific withdrawal speed. More specifically, the nanodome arrays were fabricated using PE-10s templates with a dip-coating speed of 14 mm/min in the high viscosity precursor. The nanoparticle arrays were prepared using PE-10s templates with a dip-coating speed of 120 mm/min in the low viscosity precursor. The nanonet arrays were produced using PE-10s templates with a dip-coating speed of 600 mm/min in the low viscosity precursor. After dip-coating and completely drying in room temperature, the samples undergone a high-temperature annealing process at 550°C for 2h under the protection of argon gas with a ramping speed of 1°C/min. During the process, vanadium oxide was crystalized to VO_2 , and PS sphere templates were removed.

5.2.5 Enclosing VO₂ Nanoparticles in Dielectric Media

The 2D patterned VO₂ films were dip-coated in dielectric medium (PEG, PVA, or PVP) solutions, followed by drying in an oven at 100 °C for 1.5 h to remove DI water. The dried films were ready for measurement.

5.2.6 Optical Spectrum Simulation

The transmission spectra and surface electric field distribution of VO₂ array were simulated with three dimensional (3D) finite-different-time-domain (FDTD) method. The cylinder arrays were established with corresponding diameters to the experiment results and a fixed height of 60 nm on x-y plane. The incident light is set along the z-axis. Perfectly matched layer (PML) was applied to serve as the absorbing boundaries and the structure was set as a periodic disk array with the measured size. The refractive index of air and quartz substrate are 1 and 1.46 respectively. The refractive index $n(\lambda, \tau)$ and extinction coefficient $k(\lambda, \tau)$ of the VO₂ under low and high temperature is adopted from the previous report.^[33]

5.2.7 Characterization

The morphology and surface topology were characterized using field-emission scanning electron microscope (SEM, JEOL JSM-6340F) at an accelerating voltage of 5 kV, and atomic force microscopy (AFM, Bruker, DI-3100) at room temperature. The crystal phases were identified by thin film glancing angle X-ray diffraction (XRD, Shimadzu XRD-6000) with Cu K- α X-rays. The transmittance spectra were measured from 250 to 2500 nm by UV-vis-NIR spectrophotometry (Cary 5000, Agilent Ltd) as a function of temperature, which was controlled by a heating and cooling stage (Linkam PE120). Calculation methods for Integrated luminous transmittance (T_{lum} , 380 - 780 nm) and solar energy modulation (ΔT_{sol} , 250-2500 nm).^[34,35] ΔT_{NIR} at 2000 nm is the transmittance contrast between the high and low temperature at a wavelength of 2000 nm.

5.3 Results

5.3.1 Proposed Preparation Mechanism

Monolayer hexagonal-close-packed (HCP) VO_2 nanoparticle, nanodome, and nanonet arrays are prepared by varying the viscosity of vanadium precursor and plasma etching (PE) duration as well as controlling the separation distance between adjacent PS spheres in MCC template (Figure 5.1). Low separation distance results in the infiltrated precursor forming as islands in interspace among PS spheres under low precursor viscosity condition; in contrast, covering MCCs as contiguous domes under high precursor viscosity circumstance. Meanwhile, high separation distance in MCCs allows a large quantity of the low viscosity precursor to infiltrate and adhere to the substrate, which develops into the nanonet structure to cover the lower part of the spheres. The final morphology of VO_2 films is highly dependent on the patterning of infiltrated vanadium precursor in related to PS spheres before annealing and can be largely preserved after the removal of the PS spheres and the VO_2 crystallization.

Figure 5.1 Effect of synthesis conditions on the morphology evolution. Route 1: nanoparticle arrays are prepared via short PE duration and low viscosity precursor; Route 2: nanodome arrays

are produced, using high viscosity precursor that can stick on the tops of PS spheres; Route 3, nanonet arrays are fabricated by controlling the interval space between adjacent spheres via prolonging PE duration.

5.3.2 Produced Monolayer Colloidal Crystals of Polystyrene Nanospheres

The template with PS spheres diameter down to 160 nm can be assembled in the hexagonally close-packed way (Figure 5.2a). The height of the template is measured to be 160 nm which is consistent with the diameter of the PS sphere, suggesting it is monolayer assembled (Figure 5.2b). The inter-distance between two adjacent PS spheres is controlled

Figure 5.2 a, b) AFM measurements of high-quality 160-nm PS sphere MCC template. Inset of (b) is the AFM analysis along the MCC edge denoting as the red line. c) SEM images of 640-nm PS sphere MCC template after PE treatment of 300 s, and its original morphology as the inset. d) The linear relationship of PS sphere diameter and PE duration.

via Ar/O₂ PE. For example, the size of PS spheres with a diameter of 640 nm (inset of Figure 5.2c) is diminished after Ar/O₂ PE treatment for 300 s (Figure 5.2c), while the sphere morphology maintains, which demonstrates the etching process happens isotropically. The HCP structure remains and adheres well on quartz substrate after the treatment. The diameter of spheres decreases linearly with etching duration with a speed of 1.55 ± 0.06 nm/s (Figure 5.2d). These characters combining with the high reproducibility demonstrate that the PE method is a facile way to precisely control the size of the PS sphere in MCC templates.

5.3.3 Produced 2D Patterned VO₂ Nanoparticle, Nanonet, and Nanodome Arrays

As shown in Scheme 1, the high-quality 2D VO₂ nanoparticle (Figure 5.3a-c), nanonet (Figure 5.3d-f), and nanodome arrays (Figure 5.3g-i) are prepared with variable periodicities, which are 160, 490, and 830 nm showing from left to right columns in Figure 2. The HCP structure and periodicity of final VO₂ crystals are well maintained from the PS spheres MCC template for all morphologies. Except for the monoclinic VO₂, no other phase is detectable after annealing (Figure 5.4a).

The VO₂ nanoparticle shows quasi-sphere shape (Figure 5.3a-c), which is thermodynamically stable since such shape lowers the surface energy under high annealing temperature. The periodicities of hexagonal arrays, across 160 to 830 nm, are the same as used nanosphere masks (denoting as the yellow hexagons in Figures 5.3a-c). Average diameters of VO₂ particles are measured to be as 67, 125, and 287 nm, respectively (Figure 5.4b-d), increasing with the size of PS nanospheres (Figure 5.4e). The interspace among PS spheres performs as templates to generate size-controlled island particles. This MCC templated-assisted growth is believed to be broadly suitable for nanoparticles with various compositions, because of its low requirement for the precursor properties, while is more time-saving, cost-efficient, and facile than other methods, such as dip-pen nanolithography and ion beam lithography.^[26,36]

Ordered VO₂ nanonet arrays with various periodicities are prepared by increasing the inter-spheres distance (Figure 5.3e-f). Short duration, such as 50 s, gives “egg carton” nanonet

structure, where VO_2 crystals on nodes are higher than on lines (Figure 5.4f,g), as the MCC offers more space for precursor accumulation in the intersections formed among three adjacent PS spheres during the dip-coating process.

Figure 5.3 SEM images of patterned VO_2 films. a-c) nanoparticle, d-f) nanonet, and g-i) nanodome arrays prepared using 160-, 490-, and 830-nm PS spheres from left to right, respectively. (a-f) are the top-views, while (g-i) are the tilted-views. The inset of (h) is high magnification tilted-view image of 490-nm periodic nanodome arrays on edge. Periodicities of the nanoparticle arrays are illustrated as yellow hexagons and measured to be 160, 490, and 830 nm for (a-c), respectively.

When using the vanadium precursor with high viscosity, uniform VO_2 nanodomains are produced with HCP monolayer, (Figure 5.3h) with the morphology preserved from the structure before annealing (Figure 5.4h). In the VO_2 nanodome arrays, each dome is

constructed by numbers of nanoparticles with clear boundaries (inset of Figure 5.3h). The bubbles form below the domes because the crystallized vanadium precursor develops enough mechanical strength before the removal of PS spheres during heating up. Different from the previous report,^[37] it is demonstrated the deformation of MCC templates is caused by melting of PS spheres, starting from 120 °C (Figure 5.4i), rather than by being dissolved by vanadium precursor. The nanodome structures are widely investigated in photovoltaic (PV) devices,^[38] chemical and biological sensors,^[39] plasmonic sensing relays on surface-enhanced Raman scattering (SERS) or surface plasmon polaritons (SPP) modes,^[40,41] and so on, which cover materials from semiconductor, metallic to composite.

The periodicity of the patterned films is adjusted from 160 to 830 nm by tuning the PS sphere size of MCC templates. Morphologies are consistent for the nanoparticle (Figure 5.3a-c) and nanonet arrays (Figure 5.3d-f) with the change of periodicity. For the nanodome arrays, the distinct dome structure maintains well in 490- and 830-nm (Figure 5.3h, i) periodicity samples, but becomes obscure when 160-nm PS spheres are used (Figure 5.3g). This is because 160-nm PS templates provide limited interspace among spheres, which prevents the high viscosity precursor from penetrating into the lower part of spheres. This demonstrates periodicity is another critical parameter to affect the morphology of final products via adjusting volume ratio of the PS sphere to the infiltrated vanadium precursor. Maintaining nanostructure with periodicity less than 200 nm is always challenging,^[11,23] the current method achieves the VO₂ nanoparticle, nanonet, and nanodome arrays with periodicity as low as 160 nm and can be easily applied to other systems.

Figure 5.4 a) XRD analysis of VO₂ nanonet, nanoparticle, and nanodome arrays under room temperature. Characteristic peaks of monoclinic VO₂, (011), (200), and (220), are observed (JCPDS card no. 72-0514, space group: p21/c). All samples are demonstrated with monoclinic VO₂. b-e) Size distributions of the VO₂ nanoparticles fabrication via (b) 160, (c) 490, and (d) 830 nm PS sphere templates. e) the increasing relation of PS spheres diameters in templates with the size of prepared VO₂ nanoparticles. f,g) SEM images of the sample prepared using 490-nm MCC with PE duration of (f) 40 and (g) 80 s. h) Tilted SEM image of the nanodome sample on edge before annealing. i) SEM image of the 490 nm MCC annealed under 120°C for 1 h.

5.3.4 PE-Duration-Dependent Structure Evolution.

The samples with 160-nm periodicity are presented to illustrate the effect of PE duration. By prolonging PE duration (from 10, 30, 45, to 60 s), the patterned nanostructure changes from isolated small VO₂ particles (Figure 5.5a) to large particles (Figure 5.5b), then to partially linked particles (Figure 5.5c). Finally, nanonet structure forms after PE treatment for 60 s and sufficient precursor infiltration (Figure 5.5d). This evolution is experimentally verified as shown in SEM images (Figure 5.5e-h). The PE technique can maintain the periodicity, while changing the interspace between neighboring spheres. Besides precursor

viscosity and periodicity of the template as explained above, the PE technique is also demonstrated to be an efficient method for patterned morphology control, introducing more flexibility for the template-based nanostructure fabrication.

Figure 5.5 Illustrations of VO₂ film morphological evolution, which mainly includes four sequential stages: a) the small nanoparticles, b) the large nanoparticles, c) the partially linked nanoparticles, and d) the nanonet array. VO₂ nanocrystals are indicated by blue color, while the green slats below them stand for the quartz substrates. The morphological evolution is verified experimentally by e-h) the corresponding SEM images. Patterned VO₂ nanocrystals are observed with the change from (e) the small particles to (f) the big nanoparticles, then (g) develop to the partially linked nanoparticles. Finally, (h) the nanonet array forms.

5.3.5 Tunable Localized Surface Plasmon Resonance (LSPR) in Patterned VO₂ Nanoparticles

LSPR phenomenon is typically observed in nanostructured noble metals,^[29] and heavily-doped semiconductors,^[42] but none of them are temperature-dependent. The transmittance spectra measured in air of three samples with a particles size of 67, 125, and 287 nm (Figure 5.3a-c), are normalized and presented in Figure 5.6a. The LSPR in NIR range can be observed at 95 °C instead of at 20 °C due to the metal phase formation above the critical temperature as well as the controllable size of the particles down to sub-100 nm region. At

a temperature of 95 °C, a red-shift of LSPR from 1120 to 1210 nm (Figure 5.6a) is observed with increasing diameter of VO₂ nanoparticles (Figure 5.6b). This size-dependent LSPR red-shift is further confirmed by simulation. The simulated transmission as shown in the dashed line in Figure 5.6a matches the experimental results very well. Both the resonance wavelength of simulation and experiment are extracted and compared in Figure 5.6b, the minor deviation from the experiment may be due to the ideal and uniform size and shape used in the simulation is slightly different with the real size distribution and shape variations. Figure 5.6c-e displays the electric field distribution of the nanoparticle with the size of 67, 125, and 287 nm at their resonance wavelength, respectively. The highly confined electromagnetic field at two ends of nanoparticle indicates the electric moment is in resonance with external light at the resonance wavelength. In addition, the electric-field distribution suggests that the coupling between two adjacent particles is negligible and the optical response comes from the individual particles.

In addition, by changing the dielectric medium that encapsulates the VO₂ nanoparticles, the LSPR exhibits adjustability with 67-nm VO₂ nanoparticle array (Figure 5.6f). The LSPR is measured with a distinct difference of VO₂ nanoparticles in air (1120 nm as shown in Figure 5.6a) and in polymer matrixes, which is 1220 nm in polyethylene glycol (PEG), 1270 nm in polyvinyl alcohol (PVA), and 1350 nm in polyvinylpyrrolidone (PVP) (inset of Figure 5.6f). A red-shift of LSPR peaks can be observed with a higher reflective index of overcoat (Figure 5.6g), this effect is consistent with the observation in heavily doped semiconductor system and is extensively applied to the chemical as well as biological sensors.^[43] The dipole moment inside the nanoparticle can be expressed as:

$$\mathbf{p} = 4\pi\epsilon_0\epsilon_m a^3 \frac{\epsilon(\lambda) - \epsilon_m}{\epsilon(\lambda) + 2\epsilon_m} \mathbf{E}_0 \quad (5.1)$$

where $\epsilon(\lambda)$ and ϵ_m is the permittivity of metal and surrounding dielectric respectively. At the resonant condition, the permittivity of the VO₂, $\epsilon(\lambda) = -2\epsilon_m$, so that the resonance wavelength will change once the surrounding dielectric changed.

Interestingly, LSPR intensity in VO₂ nanoparticles can be dynamically tuned by temperature. The corresponding spectra are recorded in Figure 5.6h showing that LSPR

appears at high temperature, and gradually quenches at a low temperature of 20°C. The enhanced LSPR intensity with higher temperature is due to the emergence of intermediate states during the metal-insulator gradual transition and the structural phase transition.^[44] These intermediate states display the temperature-dependence of the metallic fraction with enhanced carrier density by increasing temperature, bringing about the gradual enhancement of the relative LSPR intensity. Moreover, the relative LSPR intensity can be reversibly tuned during cooling and heating processes (Figure 5.6i). In addition, it is interesting that a gradual red-shift of the resonance peak is observed when the temperature is above 75°C during heating and the blue-shift to its original position when the sample is under 70 °C during cooling down process (Figure 5.6j). Both the intensity and peak position are hysteretic in the heating-cooling circle, which is consistent with the hysteresis nature of the VO₂ phase transition. The dynamically and reversibly tunable LSPR characters in VO₂ system make it great potential in programmable devices.

For the first time, the VO₂ nanoparticle arrays exhibit size-, media-, and temperature-dependent LSPR in NIR range, which is of great significant in various applications. We specifically discuss the LSPR effects on the thermochromic properties as LSPR is favorable in enhancing the solar modulation. Because of the LSPR intensity increases at a higher temperature which results in higher absorption and lower transmittance, and moreover the LSPR peak position tunes to the region with higher solar energy density in the solar spectrum range.^[45]

Figure 5.6 a) Calculated (dashed lines) and measured (solid lines) transmittance spectra of nanoparticle arrays with diameters of 67, 125, and 287 nm, respectively. All spectra are normalized for LSPR peak position comparison. Inset of (a) is the magnified spectra for the measured peaks,

which indicated by the corresponding triangles. b) Experimental and simulated correlations of the LSPR peak positions (nm) and particle diameters. c-e) In-plane (x-y) electric-fields at VO₂-air interfaces of the VO₂ nanoparticle arrays with diameters of (c) 67, (d) 125, and (e) 287 nm at resonances of 1075, 1085, 1230 nm, respectively. f) Transmittance spectra of 67-nm VO₂ arrays in PEG, PVA, and PVP. Inset of (f) is the magnified spectra for the LSPR peaks pointed out by the triangles. g) Effect of the medium reflective index to LSPR peak position. h) Temperature-dependent LSPR tunability of the 67-nm VO₂ nanoparticle array in the temperature range from 20 to 100 °C. Extinction (A) is calculated via $A = -\log_{10}(\text{transmittance})$. i,j) are the hysteresis loops of the relative LSPR intensity and the LSPR peak position. The relative LSPR intensity relies on the normalized integrated area under curves.

5.3.6 Patterned VO₂ Nanoparticles for Smart Windows

Thermochromic smart window is considered as a promising way to reduce the architectural energy consumption by blocking the NIR transmittance at high temperature.^[46] 2D patterned VO₂ nanocrystal array is a promising candidate for thermochromic modulation due to its LSPR on rutile phase at high temperature,^[47] self-generated antireflection behavior,^[48] and porosity-induced visible transmittance enhancement.^[49]

The optimized thermochromic performance is observed on the sample with the structure shown in Figure 5.5c. Samples were prepared on quartz glasses with centimeter-scale shown as the inserted photograph in Figure 5.7a. The performance is further promoted by simply overlaying the foils for 1, 2, and 3 layers (Figure 5.7a). All spectra display conspicuous dips at high temperature in NIR transmittance (Figure 5.7b), which are consistent with the nature of thermal-induced monoclinic to the rutile phase transition of VO₂. When increasing the number of layers, transmittance crossing visible to NIR decreases, while the thermal-induced NIR contrast increases.

Figure 5.7 (a) Illustration of the way to overlay VO_2 nanoparticle array foils, inserted photograph on left is the 1 layer sample. 2D nanostructured VO_2 nanocrystals are prepared with 1.2 mm in length. The inserted table of (a) is calculated thermochromic performance based on (b) the transmittance spectra at 20°C and 95°C . (c) Durability test for the double-layered sample. (d,e) The thermochromic performance comparisons of the double-layered sample in this work with (d) reported periodic VO_2 nanostructures, and (e) the best through other methods. Data in (d) and (e) include honeycomb,^[50] 2D phononic crystals,^[23] periodic nanonets,^[51] truss network,^[28] biomimetic

moth-eyed structure,^[48] anti-reflective multilayer,^[52] controlled porosity,^[53] VO₂ nanoparticles/transparent media composite,^[54] and doping.^[55]

The optimized thermochromic properties is observed on double-layered sample, which exhibits an average high T_{lum} of 46%, accompanied with a transmittance contrast at 2000 nm ($\Delta T_{NIR} = 44\%$) and a ΔT_{sol} up to 13.2% (inserted table of Figure 5.7a), and no transmittance change observed at 2500 nm after 100 cycles, which indicates the high stability of the thermochromic performance (Figure 5.7c). This performance largely surpasses those reported on periodic VO₂ nanostructures in NIR modulation ability (Figure 5.7d), and is comparable to the best thermochromic performance reported among anti-reflective multilayer,^[52] controlled porosity,^[53] biomimetic moth-eyed structure,^[48] VO₂ nanoparticles/transparent media composite,^[54] and doping (Figure 5.7e).^[55] In addition, this inexpensive and facile method is easily incorporated with other technologies, such as doping and composite, to further enhance the thermochromic performance. The result demonstrates the great potential of the periodic VO₂ nanoparticle array in smart window application.

5.4 Chapter Summary

In this paper, periodic two-dimensional VO₂ nanonet, nanodome, and nanoparticle arrays are reported with controllable periodicity as well as well-defined morphologies in centimeter-scale via nanosphere lithography. For the first time patterned VO₂ nanodome, and nanoparticle arrays with an average diameter of sub 100 nm are produced. More importantly, such nano patterning gives rise to LSPR exhibiting distinct temperature-response switching behavior as well as size- and media-dependent characteristic position tunability. In addition, the pattern arrays are demonstrated with high NIR modulation for thermochromic smart window application and are further demonstrated to be a smart thermal radiation control. The inexpensive, and universal fabrication process, combined with the intriguing phase change characteristic of VO₂ nanocrystals may inspire various development in processable and functional devices.

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Chapter 6*

Adaptive, Broadband, and High-Efficient Optical Modulation by Pairing Kirigami-Inspired Reconfigurable Metamaterials with Active Localized Surface Plasmon Resonances

In this chapter, we demonstrate a new method for optical modulation by pairing reconfigurable metamaterials with the active LSPR. Here, a kirigami-inspired elastomer containing plasmonic VO₂, exhibiting adaptive, broadband, and high-efficient optical modulation is developed. The geometrical transition and the active LSPR are complementary to each other by dominating in ultraviolet-visible and near-infrared regions, respectively. We also demonstrate the thermal- and aggregation-dependent LSPR, as well as a novel active LSPR control, relying on stretch-induced local dielectric changes, while it is quenched on kirigami metamaterials due to their unique strain distributions. Furthermore, an energy-saving smart window adopting such materials is demonstrated, which exhibits an unprecedented ΔT_{sol} of 37.7%, surpassing the best reported VO₂ thermochromic.

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6.1 Introduction

Kirigami originating from the ancient art of paper cutting has been transitioning to the toolbox of modern materials design.^[1-3] The cut patterns endow materials with unusual mechanical properties such as the 2D-to-3D transformation,^[4-5] the predictive deformation,^[2,6] and the extensibility enhancement with negligible impact on conductance of a material,^[7-8] promoting the quick development in stretchable electronics,^[1,7] sensors,^[9] wearable devices,^[8,10] as well as energy conversion and storage applications.^[8,11] Kirigami-inspired metamaterials can programmatically switch their physical properties by changing the configurations. Recently, these materials have been exploited on optical devices for dynamic light tracking and manipulation.^[11-14] Current studies only apply the non-responsive composition to the kirigami structures serving as the scaffolds to integrate with complex optical devices or interact with the incident light by simple reflection or diffraction.^[11-14] Integration with stimuli-responsive additives promises the multiple stimuli-responsive functionalities toward a broadband optical modulation.

Active plasmonics is another important technology for light manipulation, attracting extensive research attentions in the past decade.^[15-16] Localized surface plasmon resonance (LSPR) occurs when the electromagnetic wave induces a collective oscillation of charge carriers on the surface of a confined subwavelength structure, accompanying with enhanced absorption and scattering resonances. It was widely applied to extensive research areas, including biomedical diagnostics,^[17] catalysis,^[18-19] smart window,^[20] and high-resolution resolution display.^[21] Actively tuning LSPR can be achieved by dynamically controlling dielectrics, distances, or carriers,^[15] which mainly relies on sophisticated devices,^[22] such as the battery-type electrochemical device for the in-situ oxidation-reduction reaction,^[23-24] which significantly limits their potential to combine with other technologies.

Here we develop a kirigami-inspired elastomer containing phase-change vanadium dioxide (VO₂) nanoparticles (NPs) and it exhibits adaptive, broad-band, and high-efficient optical modulation. The geometrical transition and the temperature-dependent LSPR present dominated controls in VU-visible and NIR ranges respectively. Besides the thermal- and

aggregation-induced LSPR tunability, we also demonstrate a novel LSPR control, basing on stretch-induced local dielectric changes. This stretch-induced LSPR is observed on planar films, while is quenched on kirigami structures due to their unique strain distributions. In addition, the metamaterial exhibits an ultrahigh solar energy modulation ($\Delta T_{\text{sol}}=37.7\%$) while adopting to energy-saving smart window applications, which surpasses the best results of VO₂-based thermochromic.

6.2 Experimental Methods

6.2.1 Preparation of Composite Films

Composite films are prepared by curing the pre-mixed NPs with the precursor and curing agent of PDMS gel (SYLGARD 184, Dow Corning). In detail, vanadium dioxide nanoparticles (VO₂ NPs, Jincheng, China), and the precursor and curing agent of PDMS gel are mixed with 54 ml hexane (Aik Moh, Singapore) in a glass bottle. The quantities of the precursor and the curing agent are fixed to 2.0 and 0.2 (weight ratio of 10:1). The VO₂ NPs are weighted to be 15, 30, 45 mg as nominal 0.75wt%, 1.5wt%, and 2.25 wt% for samples with different VO₂ concentration. The mixture was blended by a magnetic stirrer, followed by an ultrasonic and/or a standing process to reduce the concentration of aggregated VO₂ NPs. All sample is stirred overnight, while durations for ultrasonic and standing processes are varied for samples and detail on the next paragraph. After that, 18 ml supernatant of the suspension was transferred to a glass petri dish with a diameter of 5.6 cm. The hexane is removed by overnight evaporation at room temperature in a fume hood. After the hexane removal, the stiff mixture is curing in an oven under 100 °C for 30 mins then 150 °C for 10 mins. The produced VO₂-PDMS film is easily peeled off from the petri dish by a tweezer. A cutter is used directly to fabricate Kirigami patterns on produced films.

6.2.2 Demonstration of the House with Smart Window

The kirigami composite film is integrated with thermal-shrinkable tapes (FIX- 105-25-0) to fulfill the thermal-induced configuration transition. The thermal-responsive system is installed inside the house model with the composite film is aligned with the window model. The house model is made of wood to sustain following high-temperature tests. Temperature tests were conducted in an oven. After a 2-mins test at a certain temperature, the demo was taken out for photographing. Films are stretched before tests at low temperature ($\sim 20^{\circ}\text{C}$).

6.2.3 Characterization

The crystal phase was identified in a two-theta mode (a fixed incident angle of 1.0°) at room temperature by a thin-film glancing angle X-ray diffraction (XRD, Shimadzu XRD-6000) with Cu $K\alpha$ X-ray. Crystal morphology was characterized using a transmission electron microscopy (TEM, JOEL JEM2010) at an accelerating voltage of 200 kV. The transmittance spectra were measured from 250 to 2500 nm by a UV-vis-NIR spectrophotometry (Cary 5000, Agilent Ltd.), equipped with an accessory containing a customized heating and cooling stage and a digital controller (Linkam PE120). Films were pre-stretched and fixed to the sample holder for strain-induced spectrum measurement. Tensile tests were conducted using Mechanical Tester MTS Model C4.

6.2.4 Optical Spectrum Simulation

A three-dimensional finite-different-time-domain (3D FDTD) method was used to calculate the extinction spectra and surface electric field distribution of VO_2 NPs in the PDMS matrix. The perfectly matched layer was applied to serve as the absorbing boundaries. The diameter of the VO_2 NPs is fixed to 80 nm according to the experimental measurements. For distance-dependent LSPR shift, extinction spectra are calculated based on two NPs with varied gaps of 20, 40, 100, 150, and 200 nm. As to the stretch-induced LSPR shift, an individual VO_2 NP surround by PDMS is calculated as original state. The

spectra of stretched VO₂-PDMS film is calculated based on an individual VO₂ NP surrounded by an ellipse air void elongating along the x -axis from 107 (33% strain), 133 (67% strain), and 160 (100% strain) nm. The refractive indices of air and PDMS are 1 and 1.4, respectively.

6.2.5 Mechanical Simulation

Commercial Finite Element software (ABAQUS) is used to simulate the tensile testing process of both local VO₂/PDMS unit and global kirigami structure. We modeled a small 2D modeled unit with plane stress elements (CPS4R) of a PDMS layer including VO₂ particle under tension controlled by displacement. The PDMS layer and VO₂ particle are modeled respectively as a hyperelastic neo-Hookean material ($E = 2$ MPa and $\nu = 0.45$) and a linear elastic material ($E = 50$ GPa). The mechanical response of kirigami structure is simulated as a 3D solid model under uniaxial tensile stretching considering nonlinear effects of large displacements. A locally refined mesh is applied to the uncut edge to ensure the accuracy.

6.2.6 Building Energy Simulation

The window model and the building model were coupled and imported into Energyplus for simulation calculation. The inner surface convection algorithm uses the TRAP method, and the outer surface convection algorithm uses a simple combination method. In addition, the heat transfer equation is used as the heat balance equation, and the simulation time step is set to 10 min. The performance of thermochromic windows is analyzed by comparing the heating and cooling energy consumption of Houston and Minneapolis with the baseline windows. For the convenience of comparison, take electricity consumption as the uniform unit and the converting factor for gas to electricity is 0.342.

The two-story residential model of Houston and Minneapolis were established in the Energyplus according to the IECC 2003. The internal load's settings refer to the DOE's residential building simulation model (RPBM, 2012). As for cooling

and heating, Heat pump for Houston; gas furnace and air conditioning for heating and cooling Minneapolis.

6.3 Results and discussion

6.3.1 Concept of Synergistic Effect

Active modulation of optical transmittance can be achieved by either the structural transition or the active LSPR of VO₂ NPs under external stimuli. The modulation induced by one method alone is restricted in a certain spectrum range. These two methods are complementary to each other to enhance the transmittance modulation in a broad range of the spectrum. The train-induced transition to compact state remarkably reduces UV-visible transmittance but providing limited NIR control due to the relatively high transparency of VO₂-elastomer composite in NIR region (Figure 6.1a).

Figure 6.1 Schematic of transmittance modulation methods based on a) reconfigurable metamaterials for UV-visible modulation, b) active LSPR for NIR modulation, and c) the integration of active LSPR and reconfigurable metamaterials for UV-visible-NIR modulation.

On the contrary, the switch-on of LSPR under elevated temperature induces strong transmittance decrease in NIR spectrum range while offers negligible effect in UV-visible regions (Figure 6.1b). The integration of the active LSPR of VO₂ NPs with the reconfigurable structures is able to independently control the light transmittance in UV-visible and NIR range, leading to a broad-band transmittance modulation (Figure 6.1c).

6.3.2 Produced Composite Films

The NPs are demonstrated as monoclinic VO₂ and no other phase observed as showing in the X-ray diffraction (XRD) pattern (Figure 6.2a). They are characterized as the quasi-sphere morphology by transmission electron microscopy (TEM) (Figure 6.2b) with a narrow size distribution and an average diameter of ~80 nm (Figure 6.2c).

Figure 6.2 a) XRD pattern of the VO₂ NPs with identified planes based on the PDF card No. JCPDS# 82-661. b) A TEM image of quasi-sphere VO₂ NPs. c) The size distribution diagram. d) SEAD pattern with identified four rings corresponding to the (022), (210), (200), and (011) planes

of monoclinic VO_2 . e) The HRTEM image of a VO_2 NP on edge and the corresponding fast Fourier transition (FTT) image as the inset. The interplane spacing of 0.24 nm and (200) plane are indicated.

Figure 6.3 a) Illustration of the produced composite film consisted of well-dispersed VO_2 NPs in PDMS matrix. b) Transmittance spectra of the planar PDMS film at 20 (The black line) and 95 (The red line) °C, respectively. c) Photographs of the roll-up process of the yellow-brown composite film from figures on 1 to 6. b) Photographs of the VO_2 -PDMS composite film under a stretch of 0%, 20%, 40%, 60%, 80%, and 100% from left to right. The film is observed being elongated in a uniaxial direction and no distinct fracture is observed during the process, demonstrating the VO_2 -PDMS film is stretchable.

In the selected area electron diffraction (SAED) pattern, four identified bright rings are identified to be the (022), (210), (200), and (011) planes of monoclinic VO_2 (Figure 6.2d).

An interplanar spacing of 0.24 nm is observed by high-resolution TEM (HRTEM), corresponding to the (200) plane of monoclinic VO₂ (Figure 6.2e and the inset).

These NPs are dispersed in Poly(dimethylsiloxane) (PDMS) matrixes (Figure 6.3a) with a very low concentration (nominal 0.75%-2.25%) to maintain the mechanical property of elastomer as well as offer sufficient optical property of VO₂. PDMS is applied due to its high transparence in the UV-vis-NIR spectrum (Figure 6.3b). The composite film displays a yellow-brown appearance and is easily rolled up by a tweezer, demonstrating its flexibility (Figure 6.3c). It is also stretchable, benefitting from the elastomer PDMS matrix (Figure 6.3d).

6.3.3 Tunable Localized Surface Plasmon Resonance (LSPR) in Composite Films

On the composite film, a temperature-dependent LSPR on/off a character is demonstrated. The LSPR is totally quenched at room temperature while its intensity is gradually increasing when elevating the temperature (Figure 6.4a). This attributes to the thermal-induced crystal phase transition of VO₂. Upon increasing temperature, the crystal phase changes from insulating monoclinic to metallic rutile states, accompanying with drastic carrier density enhancement.

Figure 6.4 a) Temperature-dependent extinction spectra of VO₂-PDMS composite under an increasing temperature from 20 to 100 °C. b) The hysteresis loop of extinction intensity at 1260 nm (0.98 eV) during a heating and cooling process. c) Transmittance spectra of the composite films with different VO₂ concentrations at 20 and 95 °C, respectively.

In addition, an LSPR red-shift is observed when increasing temperature (Figure 6.4a), which is consistent with the previous report on 2D-patterned VO₂ NPs on quartz substrates.^[25] The gradual emergence of LSPR in 70-90 °C is corresponding to the hysteresis loop under increasing temperature (Figure 6.4b). These intermediate states during the transition display a gradient of a metallic fraction,^[25] resulting in a gradual LSPR change. The critical temperature of VO₂ (~65 °C) maintained in PDMS matrix. The LSPR on/off ratio is dependent on the quantity of VO₂ NPs and the transmittance contrast in NIR range increases with increasing VO₂ concentration from nominal 0.75% to 2.25% (Figure

6.4c). To our knowledge, actively tuning on/off the LSPR is rarely observed on other plasmonic materials. Reported methods for active control of LSPR usually result in peak shifts, accompanying with peak width changes.^[15] The active LSPR based on phase transition makes VO₂ a distinct category among plasmonic materials. In addition, the thermal-induced LSPR control is facile and easily be integrated with other technologies. The LSPR position in the produced film is dependent on the ways to disperse VO₂ NPs during film preparation (unless specifying, the LSPR of VO₂ is measured on 95°C). The fabrication process includes stir, ultrasonic, and standing. The LSPR position is observed to be blue-shift from ~1380 to ~1250 nm when introducing the ultrasonic process or prolonging the standing duration (Figure 6.5a,b). The blue-shift can be explained by the decrease in NPs aggregation, which decreases gaps among NPs. Plasmonic coupling arises when rutile VO₂ NPs come close to each other in nanoscale, inducing the LSPR position shift to a longer wavelength. To further understand the plasmonic coupling effects of VO₂, the extinction spectra of two VO₂ NPs (spheres of 80 nm in diameter) are calculated under a varied gap from 20 to 200 nm. It was observed the extinction peak shifts from ~1390 to ~1250 nm at the gap of 20 and 200 nm, respectively (Figure 6.5c,d), resulting in an increasing intensity of the electric field in the gap (Figure 6.6e). This simulation result supports the aggregation effect in the experiment, of which both are observed the blue-shift (Figure 6.5b). In the experiment, the ultrasonic procedure facilitates the separation of aggregated NPs to individuals, while the standing process can precipitate aggregated NPs and reduce their amount in final films. Controlling the dispersion condition is considered as a static method for tunable LSPR because the condition is dependent on fabrication processes and is fixed on a produced film. The static tunable LSPR position is important, for example, in bio-sensing, imaging, and therapy as well as in solar energy-related applications.

Figure 6.5 a) Transmittance spectra of the samples under different dispersion conditions. The spectra are normalized for the convenience of LSPR position comparison. b) Experimental LSPR positions on the sample #1-4 corresponding to Figure 2d and calculated results on two VO₂ NPs with a gap varied from 20 to 200 nm. Inset is the illustration of the gap (d). c) Simulated configuration transition of a VO₂ NP in PDMS matrix under an increasing strain, illustrated by four simulated stress contours under the strains of 0%, 33%, 67%, and 100%. d) Illustration of the gap (d) between two VO₂ NPs. e) Calculated extinction spectra of two VO₂ NPs in PDMS matrix with a gap of 20, 40, 100, 150, and 200 nm, respectively. c) Electric fields (x - y) of two VO₂ NPs in PDMS with a gap of 20, 100, and 200 nm. The extinction peak positions are observed with a blue-shift under increase of the gap (d).

It is worth to mention an LSPR shift is also observed when a film is stretched (Figure 6.6a,b). The LSPR position of the unstretched film is ~ 1260 nm and shifts to shorter wavelength ~ 1230 nm under a strain of 33%, while increasing the strain to 67% or 100% does not induce further position change (Figure 6.6a,b). This stretch-induced LSPR shift is quite interesting. Previous studies of elastomerically active plasmonics commonly rely on dynamically tuning the gap in nanoscale between two patterned plasmonic nanostructures on an elastomer surface.^[15,26-27] However, the case here is totally different. The well-dispersed VO₂ NPs with a very low concentration (much lower than 1%) in the elastomer exhibit long distances (microscales) among each other. Tuning gaps in such distances do not contribute to the coupling effect,^[28-29] eliminating the possibility of gap-dependent LSPR position as in previous reports.

To investigate the stretch-induced LSPR, we further simulate the in-plane configuration of a VO₂ NP (diameter of 80 nm) in PDMS matrix under different stains (Figure 6.6c). It was demonstrated a phase separation of PDMS and VO₂ NP locally in high-stress regions under increasing stress. This attributes to the weak adhesion force between hydrophobic PDMS and hydrophilic VO₂.^[30] Similar phase separation has also been observed on SiO₂ microspheres (hydrophilic) in a stretched PDMS matrix (hydrophobic).^[31] The void forms and elongates along the axial direction under increasing strain (Figure 6.6c), leading to the dielectric change on the surface of VO₂ PNs. The change from PDMS (reflective index of 1.4) to the air (reflective index of 1) lead the blue-shift of LSPR peak position. We further calculated the extinction spectra of a VO₂ NP in the stretched PDMS matrix. A blue-shift of LSPR is also observed from strains of 0% to 33% then maintain unchanged under further strains, which is aligned with the experimental result (Figure 6.6d). The deviation from the experiment may be due to the idea individual NP in the simulation cannot perfectly present the collective NPs in the experiment, including the imperfect surface property of NPs, anisotropic morphologies of NPs rather than perfect spheres, or non-sufficient local strains. To our knowledge, such method for actively tuning the plasmonics has not been reported in literature. The method exhibits at least several advantages, including facile, robust, and inexpensive, then other methods for dynamically tuning the plasmonics. Reported methods either require sophisticated devices or complicated and expensive fabrications process for

materials, such as an electrochemical system for dynamic redox reactions,^[23-24] or the electron-beam lithography for metasurface fabrications.^[27] However, the method here simply relies on the void-induced dielectric change under stretch, showing facile operation and preparation processes. The method may be further improved and applied to diverse plasmonic materials.^[22]

Figure 6.6 a) Normalized transmittance spectra of the composite film under strains of 0%, 33%, 67%, and 100%. b) Experimental and simulated LSPR positions under the strains. c) Simulated configuration transition of a VO₂ NP in PDMS matrix under an increasing strain, illustrated by four simulated stress contours under the strains of 0%, 33%, 67%, and 100%. d) Calculated extinction spectra of the stretched VO₂-PDMS film based on the model illustrated in (c).

6.3.4 Composite Films with Kirigami-Inspired Reconfigurable Configurations

The composite films are easy-processable. They are tailored by a cutter into various shapes including the complex curve designs of “lion”, “butterfly”, and “flowers” (Figure 6.7a). The darkness variation amount samples are due to the different VO₂ concentration. They are further developed to kirigami patterns. Figure 6.7b shows a design with alternant parallel lines cuts. The initially patterned composites gradually decouple from each other under in-plane axial stress, transforming to compact configuration as cuts open up (Figure 6.7b). A 2D-to-3D transformation is also achievable by a kirigami design with perpendicular crossed lines cuts (Figure 6.7c). This planar design is transformed programmable to a 3D architecture under out-plane stress through a similar process as cuts open up (Figure 6.7c). Specific geometric designs of these two kirigami patterns are indicated in the supporting information (Figure 6.7d,e). The easy processing character is attributed to the well-maintained mechanical property of PDMS matrix as the very low concentration of incorporated VO₂ NPs.

Figure 6.7 a) Photography of the curved designs prepared by tailoring the VO₂-PDMS films, including “lion”, “butterfly”, and “flowers”. b,c) Kirigami designs and their configurational

transitions under stretch. b) Illustration of the design with alternant parallel lines cuts and the photography of its configurations under an in-plane axial strain from 0% to 100%. c) Illustration of the design with perpendicular crossed lines cuts and the photographs of its 2D-to-3D configurations transitions under out-plane stress. c) Illustration of the kirigami design with alternant parallel lines cuts. The geometry is identified as the red arrows in a magnified unit cell. d) Illustration of the kirigami design with perpendicular crossed lines cuts. The geometry is identified as the red arrows in a magnified unit cell as the image on right.

To better understand the effects of kirigami patterns and VO₂ incorporation on produced films, we examine the mechanical properties of the films based on the pure PDMS, the VO₂-PDMS composite, and the kirigami-patterned VO₂-PDMS composite. The kirigami design in Figure 6.7b is applied in the following the discussion. Similar stress-strain properties are observed on PDMS and VO₂-PDMS samples (Figure 6.8a,b) and on samples with VO₂ concentration from normal 0.75‰ to 2.25% (Figure 6.8c,d), demonstrating the incorporation in such low concentrations induces little effect to mechanical properties of PDMS. The VO₂-PDMS composite films with nominal VO₂ concentration of 0.75‰, 1.50‰, and 2.25‰ present similar stress-strain curves as well as similar mechanical properties. There is not a distinct trend regarding mechanical properties under increasing VO₂ concentrations. This because of the low concentration of VO₂ NPs in the PDMS matrix. The normal concentration is used according to the quantity of VO₂ NPs amount the PDMS in the initial solution. The exact quantity of VO₂ NPs amount PDMS in produced samples should be significantly lower than this nominal value due to the remove of precipitated NPs during the long-duration standing process in film preparation. However, the introduction of kirigami patterns promote the strain from 100% to 260% and drastically reduce stress (Figure 6.8b). Comparing with the other two, the kirigami-patterned VO₂-PDMS film displays significantly lower your modules and toughness (Figure 6.8b). The stretchability enhancement is strongly related with the cutting design, especially the cut length (l) (Figure 6.7d).^[7]

Figure 6.8 a) Measured uniaxial stress-strain curves of the planar PDMS, the planar VO₂-PDMS composite, and the kirigami VO₂-PDMS films with the design in Figure 6.7b. b) Mechanical property analysis of stress, strain, Young's modulus, and toughness. c) d) Measured uniaxial stress-strain curves of the planar VO₂-PDMS composite films with nominal VO₂ concentration of 0.75‰, 1.50‰, and 2.25‰, respectively. e) Mechanical property analysis of stress, strain, Young's modulus, and toughness.

More importantly, such low stress is due to the configuration transition, resulting in very low local strains along the materials. We further applied a finite element method (FEM) simulation to investigate the local strain distribution. Under a strain of 100%, it is observed a very low local strain (less than 5%) is distributed along the majority of belt structures and it is less than 10% even at cut tip area (Figure 6.9a and the inset), which is the most stress

concentrated area.^[13] The low local strain under stretch leads to the significant low stress as well as enhanced stretchability.

It is well to remind the local strain is demonstrated to affect the LSPR position. Comparing to the film without the kirigami pattern, the drastic lower local strains definitely prevent the formation of air voids around the VO₂ NPs. Thus, the introduction of kirigami pattern can maintain the LSPR position unchanged during the film stretch and play a role to preserve the LSPR of VO₂.

The stretch-induced reconfigurable structures also bring about dynamic transmittance control. It is demonstrated the transmittance of normal incidence gradually increases by stretching the kirigami VO₂-PDMS film in an in-plane axial direction (Figure 6.9a). This can be attributed to the decrease of the effective areas under increase strains from 0% to 100%. We further examine the modulation effectiveness in different wavelength for stretch-induced structural transition and thermal-induced active-LSPR methods, respectively (Figure 6.9b). The analysis is based on the transmittance spectra in Figure 6.4c and 6.9b by calculating the normalized transmittance contrast in different wavelengths under the respective stimuli. It is observed the structural transition and the thermal-induced active-LSPR present dominated controls in UV-visible and NIR ranges, respectively (Figure 6.9c). In the UV-visible region, the VO₂-PDMS film shows a high absorbance that is sensitive to the effective area change. In NIR region, the film with relatively high transparency display the less sensitivity to the effective are change, while is very sensitive to the temperature-dependent LSPR. These two are complementary to each other toward a broad-band tenability covering 250-2500 nm spectrum range.

Figure 6.9 a) SEM simulated strain distributions of the kirigami VO₂-PDMS film and the magnified strain contour on a cut tip area as the inset. b) Transmittance spectra of kirigami-patterned VO₂-PDMS film under strains of 0%, 33%, 67%, and 100%. c) Normalized transmittance contrasts in the wavelength range from 250-2500 nm. The black histogram indicates the contrast of kirigami-patterned composite film under 0% and 100%. The red histogram represents the contrast of composite film under the temperature of 20 and 95 °C.

6.3.5 Reconfigurable Composite Films in the Smart Window Application

The kirigami VO₂-PDMS film (nominal 2.25%) is further applied to smart window application. Among various types of smart windows,^[32] the thermochromic-based one promises a passive way to reduce the building energy consumption by dynamically modulating the in door solar energy in response to environmental temperature (Figure

6.10a). Fully thermal response is achieved on a produced sample by, for example, integrating with thermal-shrinkable tapes made of polyolefin. The adaptive thermal-responsive system is applied in a house demo to demonstrate the potential for the thermochromic smart window (Figure 6.10b). It was observed the film changes from a noncompact (strain of 100%) to a compact (strain of 0%) state through a gradual close up of kirigami cuts under increasing temperature, accompanying with a less clear image of the indoor clamp (Figure 6.10c). To examine the performance when applying to energy-saving smart windows, we further measure the transmittance spectra of the film in the thermal-responsive system at 20 and 95 °C temperatures. The film at 95 °C (States 1 in Figure 6.10d) is demonstrated a significant lower transmittance in UV-vis-NIR regions comparing with it at 20 °C (State 3 in Figure 6.10d). This is because the film exhibits a compact structure with an “on” state of LSPR, while it displays a noncompact structure with an “off” state of LSPR. The film is stable during the switch between these two states and no obvious contrast decrease is observed on 1260 nm after 100 times switch between these two states (Figure 6.10e). This good stability is attributed to the good cyclicity of VO₂ NPs and kirigami structures, respectively.^[8,25]

Respective contributions of the active LSPR and the kirigami structure are identified by comparing to the transmittance spectrum of the 100% stretched film at 20 °C (State 2 in Figure 6.10d). The ΔT_{sol} , average visible transmittance (T_{lum}), and the transmittance contrast at 1260 nm ($\Delta T_{1260 \text{ nm}}$) are calculated based on these spectra and shows in Figure 6.10f. It is demonstrated sole active LSPR and kirigami structure effects contribute to ΔT_{sol} of 9.7% and 28.0%, respectively. These two effects are complementary to each other toward a ΔT_{sol} up to 37.7%. Besides the high ΔT_{sol} , the integration of these two are demonstrated several other advantages: 1) the introduction of kirigami structure significantly promote the T_{lum} of films from 17.6% on the plasmonic sample to 35.2% on the plasmonic kirigami sample (Figure 6.10f); 2) the introduction of active LSPR largely enhance the NIR controllability, such as the contrast at 1260 nm from 16.1% on the kirigami sample to 49.3% on the plasmonic kirigami sample (Figure 6.10f); 3) all of the three parameters are enhanced simultaneously that is no distinct sacrifice to one of them.

To our knowledge, the method has not been reported yet by integrating reconfigurable metamaterials with active LSPR of VO₂, though the VO₂ is the most studied materials for thermochroic smart windows.^[32] The produced reconfigurable metamaterial with active LSPR displays ~490% greater ΔT_{sol} and ~100% higher T_{lum} than the reference of a planar

Figure 6.10 a) Illustration of an energy-saving smart window that adaptively reduces the indoor solar energy irradiation under elevated temperature. b) The photograph of the house model for the smart window demo. c) The configuration transition of the smart window model under increasing temperature. The fully thermal responsive system is applied, which fabricated based on kirigami-patterned VO₂-PDMS film. d) Transmittance spectra of the film at (state 3) 20 °C with noncompact configuration (strain of 100%), (state 2) 20 °C with compact configuration, and (state 1) 95 °C with compact configuration. e) Cycling test of the film switching between state 1 and 3. The transmittance at 1260 nm are recorded. f) Calculated ΔT_{sol} , T_{lum} , and $\Delta T_{1260 \text{ nm}}$ of the film in state 1-3 and the reference film based on planar VO₂ and PDMS, respectively. g) Comparison of this work

with the best-reported experiment and simulation works regarding the T_{lum} and ΔT_{sol} .^[25, 28, 33-46] The trend lines of experiment and simulation results are indicated as the blue and orange lines, respectively. Reported methods are classified and denoted using difference colors on the right of (g)

thermochromic VO₂ film (Figure 6.10f). The achieved ΔT_{sol} of 37.7% is decent and surpasses the results in reported works among VO₂-based thermochromism. Comparing to reported works, the method here provides a significantly greater ΔT_{sol} than other approaches targeting performance enhancement as summarized in Figure 6.10g.^[25, 28, 33-42] The experimental results even break the theoretical limitations simulated based on these methods (Figure 6.10g).^[28, 34, 43-46] Shortages remain such as the visible reconfigurable transition and additional space required when applying in practice. These may be solved by reducing the dimension of kirigami cuts and the delicate design of windows.

6.3.6 Building Energy Conservation Property

The electric conservation ability the smart window is evaluated by applying to architectures in Houston (US), Hong Kong (China), and Madrid (Spain). The building (Figure 6.11a) with the smart window demonstrates 7.54, 6.05, and 2.41 GJ lower energy consumption per year than it with base glasses in Houston, Hong Kong, and Madrid, respectively (Figure 6.11b). Comparing to low emissivity (low E) glasses, this material also displays better energy conservation being applied in Houston and Madrid (Figure 6.11b). To further assess its performance in a year, we calculated monthly energy consumption for heating and cooling of the room in Houston (Figure 6.11c). It is demonstrated the room with such smart windows shows less energy consumption than it with base glasses from February to December (Figure 6.11c). Moreover, we calculate the energy conservation by plotting the energy consumption difference between the smart window and base glasses as the black line in Figure 6.11c. The smart window displays peak energy conservation during the summer (The pink area in Figure 6.11c), which demonstrates the smart window can significantly reduce the energy for cooling in summer. We further demonstrated the

integration of reconfiguration and active LSPR displays significant enhancement in energy conservation than the individual one, attributing to the benefits of the reconfiguration and active LSPR in cold seasons and hot seasons, respectively (Figure 6.11d,e). This calculation demonstrated the great potential of the produced material for smart windows toward adaptive energy-saving over years.

Figure 6.11 a) Schematic of the building model. Size of the building model is 10.56 m × 10.56 m × 2.6 m × 2 stories. Two windows (1.2 m × 1.5 m) are evenly arranged for each orientation of each floor to average out the effects of orientation. The window to wall ratio of the model is 13%. Insert form presents the air condition information applied for simulation. b,c) Simulation results of building heating and cooling energy. b) Calculated energy consumptions per year for the material

applied in Houston (US), Hong Kong (China), and Madrid (Spain), respectively, comparing to the base and low E glasses. c) Comparison of the monthly energy consumption of the material and base glasses applied in Houston. d,e) Simulation results of building heating and cooling energy of films based on kirigami-LSPR, LSPR, and kirigami, respectively. d) Calculated energy consumptions per year for the materials applied in these three cities. e) Monthly energy conservation of the materials in Houston. The energy conservation of the materials is calculated based on the reduction of the energy consumption of the materials to the bare glasses.

6.4 Chapter Summary

In conclusion, we demonstrate a facile method to facile and high-efficient optical modulation by pairing the reconfigurable metamaterials with the active LSPR technology. A kirigami-inspired reconfigurable metamaterial is developed using stimuli-responsive composite consisting elastomer and well-dispersed VO₂ NPs, exhibiting adaptive, broadband and high-contrast optical modulation. The reconfigurable structure transition display dominated controls in UV-vis spectrum range, while the thermal-induced switchable LSPR of VO₂ offers remarkable tunability in NIR range. The thermal- and aggregation-induced LSPR changes of VO₂ NPs are demonstrated. Moreover, we demonstrate an active LSPR control basing on stretch-induced local dielectric changes, which to our knowledge, have not been reported yet. This active LSPR is observed on planar film, while is quenched on kirigami structure due to its unique spatial and strain distributions. When applying this material in thermochromic-based smart windows, it exhibits an ultrahigh $\Delta T_{\text{sol}} = 37.7\%$, surpassing the best reported results based on VO₂ thermochromic. This method is inexpensive, facile, and robust, may inspiring developments in optical switching, stimuli-responsive materials, and intelligent devices.

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Chapter 7*

Conclusion and Future Work

In this chapter, we conclude the results of the three projects, the responsive photonic, the active LSPR, and the kirigami-inspired structures in smart window applications. Conclusions are discussed for each project respectively with specific concerns on the novelty of concepts and the results. Since these projects have an aim for performance promotions, leading to the discussions on the achieved performance compared to previous results. Then, we conclude the thesis by highlight the significance, main findings, and hopefully the contributions to the field. Finally, we share our opinions in the challenges and future development in the field from the aspects of VO₂-based smart windows, emerging thermochromic materials, and potential integrated technologies toward multifunctionality. It is wished that the projects in the thesis may hopefully contribute to the development of energy-efficient smart windows from lab to practical architectures.

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7.1 Conclusion

7.1.1 Discussion of 2D SiO₂-VO₂ Photonic Crystals for Smart Windows

There is a long-standing desire to develop products with beautiful appearance and powerful functionality. In this project, the leading thermochromic material of VO₂, is for the first time, integrated with 2D photonic structures, widely used for generating PBGs in a variety of materials, to change its undesirable yellow-brown color, while maintaining the NIR modulation for energy saving smart window deployment (Figure 7.1).^[1] Here presents a SiO₂/VO₂ core/shell 2D photonic crystal, which is demonstrated by three-dimensional 3D FDTD simulation to tune the transmittance across the visible spectrum, while modulating the NIR transmission in reacted with temperature. Structural color changes and a good ΔT_{sol} of 11.0% and a high T_{lum} of 49.6% are achieved simultaneously. Experiments found that the color change of VO₂ films is accompanied by NIR modulation. This work presents a novel way to manipulate VO₂ photonic structures to modulate light transmission as a function of wavelength at different temperatures.

Figure 7.1 Illustration of the design of the SiO₂/VO₂ core/shell 2D photonic crystals and the simulated transmittance spectra with statically visible and dynamically infrared modulated for smart window deployment.

Meanwhile, the method that achieves statically visible and dynamically infrared modulation on one material enriches the library of optics regulation to meet the versatile functionality and various demands in applications. As such, this project should be of interest to a broad readership, including those interested in improving the thermochromic properties of energy efficient smart windows and investigating the microstructure-optical property relationship of VO₂ at different temperatures.

7.1.2 Discussion of 2D VO₂-Based Nanostructures with Active Plasmons for Smart Windows

In this project, two-dimensional patterned VO₂ nanocrystals are reported with controllable periodicity as well as tunable morphologies, from nanonet, nanodome, to nanoparticle arrays in centimeter-scale.^[2] For the first time hexagonally patterned VO₂ nanoparticle array with the average diameter down to 60 nm and the periodicity of 160 nm has been fabricated in centimeter scales. This highly reproducible and facile fabrication method combining with intriguing near-room-temperature phase transformation of VO₂ opens a new avenue to study the temperature-dependent physical response as well as smart devices. It is of great interest that such structure gives rise to tunable localized surface plasmon resonance (LSPR) at different temperatures (Figure 7.2a,b). The LSPR red-shift is observed with the increase of the particle size and the media reflective index, respectively and the experimental results fit well with the simulation (Figure 7.2c). We particularly examined its thermochromic performance and a competitive solar regulation efficiency ($\Delta T_{\text{sol}} = 13.2\%$) and a transmittance contrast at 2000 nm ($\Delta T_{\text{NIR}} = 44\%$) can be achieved, which is the best compared with the previously reported periodic VO₂ nanostructures. These patterned VO₂ films have been further demonstrated as an efficient smart thermal radiation control by a proof of concept demo. As such, this paper should be of great interest to a broad readership, including, but not limited to those interested in advanced nanostructure fabrication, LSPR phenomena as well as smart optic, thermal, and electronic regulation devices design.

Figure 7.2 a) Illustration of preparation of 2D VO₂ nanoparticle arrays through the colloidal lithography method. b) Temperature-dependent extinction spectra, indicating the switch-on behavior of active LSPR. c) The LSPR position changes in related to the VO₂ NPs diameter and the medium reflective index. Insert are the SEM images of prepared VO₂ NPs with corresponding particle diameter.

7.1.3 Discussion of Pairing Plasmonic VO₂ with Kirigami Metamaterials for Smart Windows

Adaptive solar modulation with a high on/off ratio holds long-standing scientific interests. In this project, we demonstrate a new method by pairing the actively localized surface plasmon resonance (LSPR) with kirigami-inspired metamaterials.^[3] We successfully developed plasmonic vanadium dioxide (VO₂) nanoparticles (NPs) in a kirigami-inspired elastomer, exhibiting adaptive, broadband, and high-efficient optical modulation (Figure 7.3a). We investigate a novel active LSPR control *via* stretch-induced local dielectric changes in nanoscale which is mitigated on kirigami metamaterials due to their unique strain distributions. We also demonstrated the geometrical transition and the active LSPR of VO₂ NPs function synergistically by manipulating ultraviolet-visible and near-infrared regions, respectively.

We further apply the material into smart window application, resulting in a new mechanical-thermal smart window (Figure 7.3b) with an unprecedented ΔT_{sol} of 37.7%, surpassing the best reported VO₂ thermochromic. Moreover, such a smart window exhibits

a superior performance than the low E glasses in Houston (US), Hong Kong (China), and Madrid (Spain).

Figure 7.3 a) The schematic of the synthetic effect of the reconfigurable transition of kirigami-inspired structures and the active LSPR of VO₂ NPs, targeting the adaptive, broadband, and high-efficient solar modulation. b) The schematic smart window with functional layer based on such materials, which block the solar energy in hot days while permitting the solar energy in hot days.

7.1.4 Summary

In conclusion, the projects in the thesis aim to improve the VO₂-based thermochromic smart window, which can mainly be concluded as to improve the intrinsic yellow-brown color of VO₂-based smart windows and to promote the thermochromic performance, the combination of T_{lum} and ΔT_{sol} .

The background is introduced, covering the building energy consumption, the energy-saving thermochromic smart windows, and the advances of VO₂-based thermochromic smart windows. The advantages and disadvantages of VO₂-based thermochromic smart windows are summarized, compared to other reported thermochromic materials.

Methods are applied by engineering the photonics and plasmonics in patterned VO₂ nanostructures as well as introducing the adaptive reconfiguration structures. In the first

project (Chapter 4), the introduction of photonic crystals structures is able to modify the yellow-brown color of VO₂ film. This concept is demonstrated on SiO₂/VO₂ core/shell 2D photonic crystals, which results in a tunable transmittance across the visible spectrum while maintaining good ΔT_{sol} of 11.0% and high T_{lum} of 49.6%. In the second project (Chapter 5), controlling the LSPR in the NIR region is demonstrated to promote the ΔT_{sol} by tuning the absorbance peak to the region with dense solar energy. This concept is demonstrated on 2D patterned VO₂-based nanocrystals. More specifically, the nanoparticle arrays exhibit tunable LSPR at different temperatures and the LSPR red-shift is observed with the increase of the particle size and the media reflective index. A competitive $\Delta T_{\text{sol}} = 13.2\%$ and a transmittance contrast at 2000 nm ($\Delta T_{\text{NIR}} = 44\%$) can be achieved. In the last project (Chapter 6), the introduction of kirigami-inspired reconfigurable structures is demonstrated to be an effective way to promote performance. This method is facile and can pair with the LSPR of VO₂. This concept is demonstrated on a kirigami-inspired elastomer containing plasmonic vanadium dioxide (VO₂), in which the geometrical transition and the active LSPR function synergistically by manipulating ultraviolet-visible and near-infrared regions, respectively. We further demonstrate a new mechanical-thermal energy-saving smart window adopting such materials exhibits an unprecedented solar energy modulation ($\Delta T_{\text{sol}} = 37.7\%$). Fully thermal responsiveness is also achieved in such a system.

To our knowledge, these findings are original and reported for the first time by us in our related publications. To the published date of these works, recorded performance is achieved: (1) the ΔT_{sol} of 13.2% in the 2D patterned VO₂ nanoparticles, surpassing the best result in reported periodic VO₂ nanostructures and (2) the ΔT_{sol} of 37.7% and T_{lum} of 35.2% in the method by integrating the active LSPR with kirigami-reconfiguration structures, outperforming the best reports based on multilayer, porosity, composite, grid, and biomimetic structure.

Though these progress made, the problems remain and there still much work needed to fulfill the practical application of the VO₂-based thermochromic smart windows in architectures. Considering the energy-efficient smart windows hold much promise for contributing to a future, it is hoped that these projects can contribute to the development to

some extend and may inspire further works targeting the performance promotion smart windows, which includes but not limited to that of the VO₂-based thermochromism.

7.2 Future Work

7.2.1 Improvements on VO₂-Based Thermochromic Smart Windows

The application of VO₂ thermochromic smart windows is promising and just beginning. However, some problems still needed to be addressed to further widen their applications. Here the future work is suggested as follow, aiming to solve the existing problems, including the color, the limited ΔT_{sol} , the balance between ΔT_{sol} and T_{lum} , the emissivity, the stability, and the toxicity. ^[4,5] Also, it is anticipated to build practical demo to assess the energy-saving ability of the technology in real buildings.

7.2.1.1 Improving the Yellow-Brown Color

The first shortcoming is color. Due to its strong absorption, VO₂ typically demonstrates a brownish-yellow color. The color has limited effects on the visible transmittance, and color preference is closely related to cultural background. Generally, a colorless coating or coloration with light gray/blue is most favorable (at least in China). In some areas of Southeastern Asia or Arabia, a golden color is more favorable. In this case, the brownish-yellow color of VO₂ would be acceptable. However, certain modifications are still required to tune the color. Although some simulations have suggested that doping may be an effective strategy for modifying the color by shifting the adsorption edges, experimental results have shown that only limited changes can be achieved. Complexion with dyes or pigments, either organic or inorganic, can modulate the original color of VO₂ at the expense of the visible transmittance of VO₂ films, which is unquestionably not a good resolution. To address this concern, creative ideas are needed.

7.2.1.2 Promoting Solar Modulation Ability (ΔT_{sol})

Blocking infrared light in warm weather is a fundamental requirement for energy-saving applications of thermochromic materials. The solar modulation ability refers to the energy difference in the solar spectrum across the thermochromic phase transition. The former represents the ability to block heat, and the latter represents how well the material can respond to temperature changes in terms of its infrared transmittance. These two parameters are still low in state-of-the-art designs, *i.e.*, less than 30% and 70% for the former and the latter, respectively. For comparison, commercial low-emission glass with the application of 3 Ag layers as the blocking material can reach an infrared transmittance of 90%. To expand the applications of VO₂ films, this value should be largely increased from 70% to 90%. However, this is a big challenge.

7.2.1.3 Balancing the Visible Transmittance (ΔT_{sol}) and the Solar Modulation Ability (T_{lum})

Based on recent studies, the simultaneous enhancement of luminous transmittance and solar modulation ability is rather difficult. From the analysis of the film thickness, thinner films are favorable for increasing the luminous transmittance but unfavorable for the solar modulation ability. Doping is undoubtedly an effective strategy to decrease the τ_c , but the solar modulation ability is typically decreased as well. For the practical applications, a balance between the visible transmittance and solar modulation ability is required. For this purpose, one should understand the causes responsible for the degradation of optical properties. Clearly, further investigation is required, possibly through the combination of simulations and experiments.

7.2.1.4 Emissivity Is an Important Parameter for Architectural Energy Economization

From the transmittance spectrum, one can understand how much and in which wavelength span solar light is transmitted. It is commonly considered that lower transmittance implies better thermal insulator properties. This understanding is correct to some degree. On the other hand, solar heat usually results from the near-infrared region of the solar spectrum, whereas blackbody emissivity occurs in the mid- to far-infrared regions. The former contributes to heat gains from the outdoor environment, while the latter is the reason for heat loss in an indoor environment. A coating should have suitable transmittance to control heat gain as well as low emissivity to suppress heat loss, which is very important for areas with low temperatures. VO₂ films, especially those porous films synthesized by the solution-based process, usually demonstrate emissivities as large as 0.83, which is much larger than that of double-layered silver-based low-emission glass with the emissivity of 0.3-0.4. This implies that VO₂ glass in the winter may have limited energy-saving ability due to heat flowing outwards. Using a double-layered film composed of VO₂ and a layer of notable metals or transparent conductive oxides can decrease the emissivity, but increasing the reflectivity resulted in a large decrease in the solar modulation ability of VO₂. To resolve this problem, some new structures and/or material systems should be developed and integrated with VO₂.

7.2.1.5 Making the Smart Window More Stable

As a transition metal, vanadium is a multi-valence element, which exhibits +3, +4, +5 and mixed valences. VO₂(M) can be oxidized to vanadium oxides or their hydroxides, especially in the presence of moisture. This instability results in serious durability problems in practical applications. One solution involves the formation of VO₂ in an inert oxide shell, which is used to separate VO₂ from oxygen. This method has been certified to be useful to some degree, but the process to prepare a core-shell structure is not easy to control. Furthermore, this treatment step leads to the aggregation of well-dispersed nanoparticles,

making them difficult to use. Increasing the crystallinity of VO₂ is also effective, but this method cannot completely address the problem.

7.2.1.6 Toxicity Assessment Is Essential

The fate of nanoparticles in a variety of environmental and manufacturing settings has attracted immense attention and is a major obstacle for practical applications, especially in applications that have close contact with people and pets. Although some VO₂ products are commercially available (such as VO₂ foils in China), thorough research into the toxicological impact and possible hazards of VO₂ materials, especially in nanoparticle form, to human health and the environment is still in its infancy and is an urgent task to achieve large-scale applications of VO₂. Addressing this issue seems more meaningful when considering that some vanadium oxides known today, for example, V(V) and V(III), are toxic, although the toxicity of these oxides is closely related to their quantity. Therefore, collaboration studies should be done on the mechanisms at the cellular level, entry routes into the body and possible impacts on public health. In addition, the ways life cycle assessment (LCA) studies should be applied to analyze the fate of VO₂ nanoparticles.

7.2.2 Emerging Materials Beyond VO₂

Challenges and opportunities remain in the future development of the smart architectural window, with the aim of achieving high energy-saving efficiency. On the materials side, it is worthwhile to explore novel thermoresponsive materials as well as to further optimize the properties of current materials. Considering the expansive range of thermoresponsive materials, the exploration of new materials and improvement of the current emerging system is still in its early stages. Firstly a suitable temperature-responsive material should display switchability in the temperature range of ~30 to ~40 °C, accompanied by a drastic and reversible change in optical properties in the NIR range. Modulation in the visible range is dependent on the specific application circumstances since it can enhance solar energy modulation ability but the concomitant appearance variation and reduced T_{lum} may

or may not be desirable. Secondly, for the four emerging thermoresponsive reviewed, further research could be explored such as the structure modification to enhance thermochromic properties, which has been much more extensively investigated in VO₂ system. Thirdly, the hybridization between different categories of thermoresponsive materials have been proved successful to further enhance the performance, hence more efforts can be devoted to this direction.

7.2.3 Towards Multifunctionality

As for the multifunctionality by integrations of technologies, one direction for further exploration is the combination of active control techniques with thermoresponsive smart windows, which have hitherto been primarily considered as passive devices, controlled by temperature solely. For example, the electro-thermal approach adds extra control to cost-effective temperature-responsive smart windows, competing with other commercially available pricey electrochromic devices. However, in contrast with the one-time switch in electrochromic devices, electro-thermal smart window need constant heating to remain switched which is more energy consuming. How to cut down the energy consumption is a key to promote the electro-thermal windows. Moreover, it is vital by integration thermochromic performance should not be compromised. Additionally, integrated techniques should address the toxicity and durability issue of the thermochromic layer considering the daily human contact with windows and decades service life of architecture windows. And there are likely to be further, unexplored techniques that could be integrated with thermoresponsive to produce more efficient, sustainable, and multifunctional energy-efficient smart windows for buildings as well as other applications. Advances in ease of manufacture and cost-effectiveness for both thermoresponsive and integrated techniques are also necessary to bring these technologies from the laboratory to daily life.

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