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**NANYANG
TECHNOLOGICAL
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SINGAPORE

**STIMULI-RESPONSIVE POLYMER COMPOSITE FOR
ENERGY SAVING THERMOTROPIC SMART WINDOW**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2018

STIMULI-RESPONSIVE POLYMER COMPOSITE FOR ENERGY SAVING THERMOTROPIC SMART WINDOW

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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

2018

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Authorship Attribution Statement

This thesis contains material from 2 papers published in the following peer-reviewed journals where I was the first author.

Chapter 4 is published as Heng Yeong Lee, Yufeng Cai, Shuguang Bi, Yen Nan Liang, Yujie Song, and Xiao Matthew Hu. A Dual-Responsive Nanocomposite toward Climate-Adaptable Solar Modulation for Energy-Saving Smart Windows. *Applied Materials & Interfaces* **9**, 6054-6063 (2017). DOI: 10.1021/acsami.6b15065.

The contributions of the co-authors are as follows:

- Prof Hu Xiao provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised after discussion with Dr. Cai Yufeng and Dr. Bi Shuguang.
- I designed the experiment and performed all the laboratory work at School of Materials Science and Engineering. I also analyzed the data.
- All microscopy and XRD, including sample preparation, was conducted by me in the Facility for Analysis, Characterization, Testing and Simulation.
- Dr. Liang Yen Nan assisted in the interpretation of TEM images.
- Dr. Song Yujie assisted in the collection and interpretation of dynamic shear mechanical analysis data.

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- Prof Hu Xiao provided the initial project direction and edited the manuscript drafts.
- I wrote the drafts of the manuscript. The manuscript revised after discussion with Dr. Cai Yufeng and Dr. Sadiye Velioglu.
- I designed the experiment and performed all the laboratory work at School of Materials Science and Engineering. I also analyzed the data.
- Prof. Chew Jia Wei and Dr. Sadiye Velioglu conducted molecular dynamics simulation and interpretation of the data.
- Dr. Mu Chenzhong advice on the synthesis of polyurethane.
- FYP students Chang Chen Jian and Chen Yi Ling assisted on the preparation of glass substrates and moulds for synthesis of ionogels.
- Dr. Song Yujie assisted in the collection and interpretation of dynamic shear mechanical analysis data.

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Abstract

In recent years, a family member of thermochromic solar control windows, known as the thermotropic smart windows offer the solutions for energy conservation in buildings and transport vehicles. Thermally responsive hydrogel is considered a promising smart window material because of its broadband switchable optical properties, which is led by the lower critical solution temperature (LCST) mechanism. The temperature driven thermotropic effects make hydrogel a superior candidate of solar modulation smart windows, but the actual application of hydrogels is detracted primarily because of its inability to switch in cold climate and poor cyclic stability. This is because the hydrogels are only thermally responsive and they contain a tremendous amount of aqueous solvent to exhibit LCST. To resolve these challenges, the work covered in this thesis utilizes three approaches, namely PNIPAM/ATO nanocomposite, Agarose hybrid with binary solvent and PU-based ionogel, to achieve climate adaptability and enhanced cyclic stability.

Plasmonic Antimony Tin Oxide nanoparticles (ATO-NP) prepared by solvothermal were encapsulated in the hydrogel matrix, PNIPAM, to form nanocomposites, which realize a dual responsive photothermotropic concept. The plasmonic ATO absorbed exclusively in the near-infrared (NIR) region and photothermal characteristics endowed by the plasmonic particle not only enhance the thermal insulation features of hydrogel hybrid for tropical climates but further enable the hydrogel to perform optical switching in cold weather climates. A modified solar irradiation system aids in materials screening and elucidating the effect of plasmonic heating effect in hydrogel hybrid. Upon one sun solar irradiation, 80 μm photothermotropic hybrid shows an enhanced solar modulation ability and response rate of 3.3 and 2 times, respectively over neat hydrogel. Desirable average luminous transmittance of 62.7% was simultaneously achieved. Nevertheless only 15 cycles of solar irradiation were demonstrated.

A thermotropic hydrogel design with enhance stability was demonstrated by embodying thermal responsive 4-octylphenol polyethoxylate non-ionic surfactants and binary solvents of glycerol/water in agarose. This method provides an industrial scalable way of fabrication

thermotropic hydrogels. The dimensionally stable hydrogels performed solar modulation with tunable transition temperature over a range of 40°C. Glycerol, which consists of hydrophobic and hydrophilic functional groups, lowers the overall polarity of the binary solvent and LCST of the hydrogel. The presence of glycerol decreases the freeze point, lowers the sealing requirement and induces a gentle optical switch with moderate solar modulation characteristic in the thermotropic agarose hydrogel. The underlying reasons for the changes in thermal optical properties of the hydrogel were discussed from the perspective of micelle aggregation/disaggregation microdynamics. This study not only resolves the dimensional instability of thermally responsive hydrogels but also successfully widens the operating temperature range of thermotropic hydrogels with a moderate decrease in thermal optical properties. Nevertheless, this thermotropic hydrogel with enhanced stability still contains an aqueous solvent which can freeze and evaporate. Hence, an intrinsically stable thermotropic material which can perform LCST-based optical switching for solar modulation is highly preferred.

The simulation results from molecular dynamics aid in materials screening for transition temperature tuning of imidazolium-based ionic liquids (ILs) and polypropylene oxide (PPO), and further reveal the underlying behavior of PPO/IL LCST transition. Based on the understanding of various thermally responsive interactions between PPO and IL, a wide LCST tunability range from subzero to more than 150°C was demonstrated with the new thermotropic ionogel. A 3D crosslinked polyurethane network which entraps the ionic liquids endows kinetic stability to the thermotropic ionogel, which guarantees stable and reversible optical switching. The thermotropic ionogel consists of intrinsically stable ionic liquids and polyurethane (PU). The choice of material and nanoconfinement effect of IL endow the mechanically robust ionogel with non-volatility and non-freezing attributes. The presence of multiple attraction forces from IL and a large PU fraction enables dimensional stability in the ionogel for enhanced cyclic stability of 5000 heat-cool cycles. Subsequently, the versatile ionogel was hybridized with plasmonic ATO to achieve climate adaptability and energy conservation of 20°C more than a normal float glass.

Lay Summary

Transparent glasses are hotly pursued as premium construction materials in transport vehicles and architectural buildings for its aesthetic appeal. Due to widespread usage of transparent glasses, 43% of global world primary energy are spent on heating, ventilation and air-conditioning in buildings. Moreover, individual can also experience uncomfortable situations, such as glaring sunlight, skin and thermal discomfort.

Current practice of using multi-layered optical solar films for solar shielding requires costly fabrication process and further results in low visibility and disruption of communication signals. Although solar modulation system driven by external stimuli have been demonstrated, these systems usually involve costly installation, complex device fabrication process and rely on external mechanical or electrical stimuli. Hence, an autonomous system driven by solar heating itself to exhibit broadband solar modulation would be ideal. The closest class of material that could perform in such manner is the thermally responsive hydrogel, a material containing around 90% of water. Unfortunately, their chances of commercialization are largely detracted by their inherent shrinking and aqueous characteristics.

In this thesis, a new class of phase transition material that can respond to temperature change was developed. With the increase in temperature, different degree of reversible solar modulation can be achieved and tailored accordingly to a wide range of operating temperatures. The components in this new material consists of ionic liquids which are intrinsically stable and polyurethane elastomer which is not only cost effective, but further endow the material with mechanical robustness. The distinct advantages of broad transition range tunability, cyclic stability and functional versatility in the material system is unattainable by any existing solar modulation solution. This is the first time where ionic liquids were explored as material for thermotropic smart window and the resulting new material super cyclic stability with critical non-volatile and non-freezing properties can be attributed to the superior intrinsic characteristics of ionic liquids. This new material also allows facile and unparalleled tuning range of transition temperature (tuning *via* multiple

parameters). The mechanism of the underlying thermally responsive interactions in this new class of material was extensively elucidated and applied in smart window application for the very first time.

In a parallel study, plasmonic particles which exclusively absorb in near infrared region was coupled with thermally responsive hydrogel. Experimental results show that both the response speed and solar modulation of the thermotropic composite could be enhanced. Photothermal characteristics endowed by the plasmonic particle not only enhance the thermal insulation features for tropical climates but further enable optical switching in cold weather climates. The mechanism of plasmonic heating coupled with thermally responsive polymer for smart window was reported for the very first time.

Combination of the above novel technologies offers a unique competitive advantage and result in a new class of thermally responsive organic/inorganic hybrid which can be affixed as an interlayer laminate for a fully autonomous smart window to achieve energy conservation. Apart from their application in transport vehicles and architectural buildings, this new material may also find itself in other numerous optical applications, such as over-heating protector for solar panels and other smart devices with memory or sensing functions. It is believed that the novel outcomes from this research thesis will fit neatly into the technological gap concerning green and smart buildings. It will also be propelled by the rapid development and pressing demand of innovative solutions in a highly competitive automotive industry.

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List of Publications

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2. Lee, H. Y.; Cai, Y.; Lim, S. K.; Liang, Y. N.; Song, Y.; Hu, X. M., Thermochromic Agarose Hybrid with Enhanced Stability for Solar Modulation Smart Window, *In Manuscript*.
3. Lee, H. Y.; Cai, Y.; Velioglu, S.; Mu, C.; Chang, C. J.; Chen, Y. L.; Song, Y.; Chew, J. W.; Hu, X. M., Thermochromic Ionogel: A New Class of Stimuli Responsive Materials with Super Cyclic Stability for Solar Modulation. *Chem. Mater.* **2017**, *29* (16), pp 6947–6955

Papers partially mentioned in the thesis:

4. Bi, S.; Zhang, L.; Mu, C.; Lee, H. Y.; Cheah, J. W.; Chua, E. K.; See, K. Y.; Liu, M.; Hu, X., A Comparative Study on Electromagnetic Interference Shielding Behaviors of Chemically Reduced and Thermally Reduced Graphene Aerogels. *J. Colloid Interface Sci.* **2017**, *492*, 112-118.
5. Roy, S.; Kuddannaya, S.; Das, T.; Lee, H. Y.; Lim, J.; Yoon, Y. C.; Kim, J., A Novel Approach for Fabricating Highly Tunable and Fluffy Bioinspired 3d Poly (Vinyl Alcohol) (Pva) Fiber Scaffolds. *Nanoscale* **2017**, *9* (21), 7081-7093.
5. Lee, H. Y.; Velioglu, S.; Cai, Y.; Chew, J. W.; Hu, X. M., A Successful Marriage between Polymer and Ionic Liquid, *In Manuscript*.

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Figure A.2 Rheology plot of PATO, showing all the specimens storage modulus (G') are higher than the loss modulus (G''), indicating they are indeed cross-linked hydrogels. Reprinted with permission from Reference.¹ Copyright 2017, American Chemical Society. 215

Figure A.3 Insufficient and inhomogeneous turbidity could be observed in $180 \mu\text{m}$ thick agarose hydrogel film containing 100% TX-114, above its transition temperature of around 29°C 215

Figure A.4 (a) FTIR spectra monitoring ionogel synthesis reaction after 0, 6 and 24 hours. After 6 hours of curing, the characteristic peak of -NCO group at 2270 cm^{-1} almost vanished, indicating a completion of reaction. (b) FTIR spectra of ionogel and various chemicals for ionogel synthesis. After 24 hours reaction in airtight mould, the solvent MEK still remains in ionogel, to ensure a phase-separation free curing reaction while the transparent ionogel also indicates a homogeneous reaction with the presence of MEK. Reprinted with permission from Reference.² Copyright 2017, American Chemical Society. 217

Figure A.5 (a) Probability distribution of radius of gyration for 30 wt% PPO/IL solution at 90°C over 800 nanoseconds. Both (ai) and (aii) show the iso-surface plots based on volumetric occupancy of $[\text{C}_4\text{mim}][\text{NTf}_2]$ at the average radius of gyration between $7 - 8\text{ \AA}$ and $14 - 15\text{ \AA}$, respectively. The blue and red colour clouds represent the cation and anion, respectively. Reprinted with permission from Reference.² Copyright 2017, American Chemical Society. 217

Figure A.6 UV-Vis-NIR spectra of ionogel/ATO hybrid based on different corresponding saturation temperature obtained from xenon lamp irradiation experiment. These ionogel/ATO hybrid contains 33% $[\text{C}_4\text{dmim}][\text{NTf}_2]$ as binary IL and (a) 0, (b) 0.05, (c) 0.1 and (d) 0.15 wt% ATO plasmonic nanoparticles. 218

Abbreviations

ATR	Attenuated Total Reflectance
BEI	Backscatter Electron Images
BSE	Backscattered Electron
EDS	Energy Dispersive X-ray Spectroscopy
DSC	Differential Scanning Calorimeter
TGA	Thermogravimetric Analysis
FTIR	Fourier Transform Infrared Spectroscopy
HRTEM	High Resolution Transmission Electron Microscopy
PXRD	Powder X-ray Diffraction
SAED	Selected Area Electron Diffraction
SEM	Scanning Electron Microscopy
SE	Secondary Electron
SEI	Secondary Electron Images
TEM	Transmission Electron Microscopy
BF	Bright Field
DF	Dark Field
DP	Diffraction Pattern
XRD	X-ray Diffraction
Z	Atomic Number
LSPR	Localized Surface Plasmon Resonance
Ag	Silver
Au	Gold
LaB ₆	Lanthanum Hexaboride
TCO	Transparent Conducting Oxide
ATO	Antimony Tin Oxide
ATO-NP	Antimony Tin Oxide nanoparticles
GZO	Gallium Zinc Oxide
ITO	Indium Tin Oxide

WO _{3-x}	Reduced Tungsten Oxide
M _x WO _{3-x}	Hexagonal Tungsten Bronze
VO ₂	Vanadium Dioxide
IR	Infrared
NIR	Near-infrared
UV	Ultra-violet
Vis	Visible Light
RI	Refractive Index
PS	Polystyrene
PU	Polyurethane
PNIPAM	Poly (N-isopropylacrylamide)
PPO	Poly (propylene oxide)
PMMA	Poly (methyl methacrylate)
PBnMA	Poly (benzyl methacrylate)
EPE	Poly (ethylene oxide-co-propylene oxide-co-ethylene oxide)
Triton-X	4-octylphenol polyethoxylate
IPN	Interpenetrating Polymer Network
IL	Ionic Liquid
[C ₂ mim][NTf ₂]	1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C ₄ mim][NTf ₂]	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C ₆ mim][NTf ₂]	1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
[C ₄ dmim][NTf ₂]	1-Butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide
LCST	Lower Critical Solution
UCST	Upper Critical Solution Temperature
BP	Boiling Point
DLVO	Derjaguin-Landau-Verwey-Overbeek
2D	Two-dimensional

3D	Three-dimensional
DI	Deionized
Low-E	Low emissivity

Frequently Used Symbols

T_t	Optical Switching Transition Temperature
λ	Wavelength
$T(\lambda)$	Measured Spectral Transmittance
$A(\lambda)$	Measured Spectral Absorbance
$T_{lum/IR/sol}$	Integrated Luminous/IR/Solar Transmittance
$T_{lum/IR/sol(avg)}$	Average Integrated Luminous/IR/Solar Transmittance
ΔT_{lum}	Energy Modulation Ability of Luminous Transmittance
ΔT_{IR}	Energy Modulation Ability of IR Transmittance
ΔT_{sol}	Energy Modulation Ability of Solar Transmittance
BP	Boiling Point
G'	Storage Modulus
G''	Loss Modulus
wt%	Weight Percentage
c.a.	Approximately

Chapter 1

Introduction

Thermotropic smart windows, provide the solutions for energy conservation of buildings or vehicles and thermal optical comfort of inhabitants. Lower critical solution temperature (LCST) derived thermotropism is a promising broadband solar modulation mechanism because of its switchable optical properties, which is led by a tunable range of transition temperatures. The temperature driven thermotropic effects make thermal responsive hydrogel a superior candidate for smart windows, but the practical applications of thermotropic hydrogels are hindered mainly due to its inability to switch in cold climate and its poor cyclic stability. To resolve these issues, the work covered in this thesis utilizes three approaches, namely PNIPAM/ATO nanocomposites, dimensional stable agarose hybrid and a new class of thermal responsive ionogel to achieve dual responsivity and cyclic stability. The hypothesis and motivation for each individual approach in this thesis are discussed in this chapter with their specific objectives and scopes. As a preview of the entire thesis, a brief introduction of each chapter is highlighted. The novelty of overall research is also listed from individual attempt in this thesis.

1.1 Overview

Cooling of buildings consumes a significant amount of energy globally. Because of the imposing threat of global warming, it has been reported that 43% of the world primary energy had been spent on heating, ventilation and air-conditioning for buildings.¹ Smart windows that can dynamically and reversibly modulate its light transmittance, i.e., solar radiation energy input, upon exposure to an external stimulus, was found to be effective in ensuring inhabitant skin comfort and saving more than 50% of energy consumed in buildings.²⁻³

Numerous classes of materials have been attempted which are exemplified by vanadium dioxide,⁴ poly N-isopropylacrylamide (PNIPAM) hydrogels,⁵⁻⁶ tungsten/niobium oxide,⁷ zinc-pyrazolate metal-organic framework⁸ and liquid-crystals.⁹ These smart systems can be categorized into non-autonomous and autonomous switching, as shown in **Table 1.1**.¹⁰⁻¹² Non-autonomous systems like electrochromic and polymer dispersed liquid crystals, usually involve costly installation, complex device fabrication and rely on external stimuli such as electricity to promote solar modulation. Moreover, in the absence of electric field, system such as polymer dispersed liquid crystals appears opaque and are intended for privacy window.¹³ Hence, an autonomous system which utilize solar heat itself as the promoter against solar shielding would be ideal and such example would be thermochromic inorganic vanadium dioxide (VO₂) or thermotropic organic hydrogels. Unfortunately, inorganic VO₂ still faces technical challenges such as insufficient solar modulation, limited transition temperature tuning range and oxidative instability.¹⁴⁻¹⁶

Table 1.1 Showing all the different solar modulation mechanisms with their respective advantages and disadvantages. An ideal mechanism should be economical, easy to implement, autonomous and modulate solar spectrum in a broadband manner.

Solar Modulation Systems	Costly	Complex	Autonomous	Solar Modulation Region		Remarks
				Visible	Near Infrared	
Electrochromic	✓	✓		✓	✓	E.g. Niobium/Tungstate Oxide
Gasochromic	✓	✓		✓	✓	E.g. Tungsten Trioxide
Mechanochromic				✓	✓	E.g. Silica/Polydimethylsiloxane
Thermochromic			✓		✓	E.g. Vanadium dioxide
Thermotropic			✓	✓	✓	E.g. Poly(N-isopropylacrylamide)
Polymer Disperse Liquid Crystal				✓	✓	Exist in opaque/scattering state

It is evident from **Table 1.1**, that thermotropic solar modulation system is incredibly attractive since both visible and NIR transmittance can be modulated autonomously to control the solar luminance intensity as well as thermal comfort for the interior of architectural buildings.

Different kinds of thermotropic smart windows for solar modulation have been explored and they can be classified based on their switching mechanism.¹⁷⁻¹⁸ These mechanism includes phase separation,¹⁹⁻²² aggregation,²³ changes in particle size,²⁴ and phase transition.²⁵⁻²⁷ Among the various thermotropic material candidates, phase separation hydrogels based on lower critical solution temperature (LCST) exhibit superior optical switching performance. More specifically, low switching hysteresis, high solar transmittance of around 82% and high opacity of less than 5% in the clear and scattered state, respectively, have been reported for thermotropic hydrogels.²⁸⁻²⁹ Nevertheless, all thermotropic systems are only thermal responsive and they modulate the solar spectrum mainly in the visible region.¹⁸ Furthermore, thermotropic hydrogel contains a tremendous amount of water and challenges such as restricted operation temperature of 0 – 40°C,³⁰ high demands on sealing efficiency,³¹ and volume reduction (dimensional instability),¹⁷⁻¹⁸ have been reported.

Herein, to resolve the above-mentioned challenges, the works covered in this thesis utilize experimental characterization and computer simulation to implement three distinct approaches, namely PNIPAM/ATO, agarose hybrid and polyurethane based ionogel composites. Hypothesis and motivations for individual approach is discussed in the following sections, and the LCST derived thermotropic performances of different gels will be analyzed and discussed in-depth from Chapter 4 – 6.

1.2 Hypothesis/Problem Statement

1.2.1 Hypothesis #1 – PNIPAM/ATO nanocomposites

Figure 1.1 Depicts the inability of a thermotropic layer [LE+TT] to perform optical switch in cold climate through visual illustration and thermograph. While thermotropic layer equipped with joule heating [LE+heatingTT] shows turbidity with temperature around 32°C. The smart window configuration used in this demonstration consist of LE: low-e, TT: thermotropic, and integrated heating element. Reprinted with permission from Reference.²² Copyright 2008, Elsevier.

For thermotropic hydrogel to function as a fully autonomous smart window in cold climate, optical switching solely based on thermal activation remains a challenge as shown in **Figure 1.1**.

Hence, in Chapter 4 we consider hybridization of thermal responsive PNIPAM with plasmonic transparent conductive oxide (TCO) which absorb exclusively in NIR, as nano heater to endow the composite with both thermal and photo responsiveness. Upon solar irradiation, generated photothermal effect should cause an increase in the temperature which aids in optical switching behavior, enhanced solar modulation ability and response speed. Furthermore, the dual responsive hydrogel hybrid should possess attractive NIR shielding features which is critical for its application in tropical climates.

1.2.2 Hypothesis #2 – Agarose hybrid with enhanced stability

Thermally responsive hydrogels that exhibit reversible volume transition and optical switch properties during LCST transition had been explored for actuators, micro-valves, drugs delivery and other advanced technologies.³²⁻³⁶

Figure 1.2 Illustrate (a) volume reduction characteristics of a PNIPAM hydrogel in response to temperature. The volume of a dry hydrogel at temperature above LCST is about 100 times smaller compared to its swollen state below LCST. Reprinted with permission from Reference.³⁷ Copyright 2013, The Royal Society of Chemistry. While (b) demonstrates the optical switch irreversibility of a PNIPAM film when used as a thermotropic smart window, due to volume reduction. The PNIPAM sample has a dimension of 3 x 2.5 x 0.018 cm.

As shown in **Figure 1.2**, thermal responsive hydrogel that exhibit LCST like phase transition are often accompanied by first order discrete volume transitions which appears to be detrimental for smart window applications. Facile and cost-effective production strategies are often preferred for actual applications. Fabrication of a non-responsive hydrogel scaffold embedded with thermally responsive surfactants for optical switch seems to be an ideal solution. Nonetheless, containment of around 90% aqueous media in hydrogels imposes a stringent requirement on the sealing condition of thermotropic smart windows.^{21, 38-39}

Hereby, in Chapter 5, a dimensional stable physical gel containing thermal responsive surfactants with alcohol/water binary solvent is considered to enhance thermal stability and to simplify the preparation method of thermotropic hydrogels. The effect of glycerol cosolvent on the micelle aggregation-disaggregation micro dynamics should affect the resultant thermotropic properties. Since the polarity of glycerol is lower than that of water, lower LCST should be observed.⁴⁰ Due to the presence of hydrophobic glyceryl and hydrophilic polyhydroxyl functional group in glycerol, an increase of glycerol content should increase bulk solvent hydrophobicity and hydrophilicity at temperature below and above LCST, respectively.²¹ Theoretically, a decrease in solar modulation ability should be observed with an increase in glycerol content. Furthermore, it has been reported that alcohol molecules tend to position themselves at the interface of polyoxyethylene (POE) group and bulk solvent.⁴¹ Hence, a gentler optical transition due to hindrance of the glycerol molecules 'buffer layer' during micelle aggregation-disaggregation transition could be achieved. Similarly, thermal hysteresis might be observed due to thermal lag induced by the 'buffer layer'.

1.2.3 Hypothesis #3 – PU based Thermotropic Ionogel

The cyclic stability of thermotropic hydrogel is of paramount importance for smart window application. Although efforts have been invested on dimensional stable thermotropic hydrogels and binary solvent containing low volatile alcohol,²¹ the hydrogels still undergo formidable drying and freezing, as shown in **Figure 1.3**. Moreover, these hydrogels are intrinsically weak in mechanical properties which poses restriction in its process-ability and handling.

Figure 1.3 Depicts the (a) freezing point DSC thermogram and (b) mass loss evaporation profile at 60°C for PNIPAM microgel colloids prepared with different ratio of water/glycerol solvent. The wt% indicated in the graphs represent the amount of glycerol present in the solvent mixture and the PNIPAM microgel contains c.a. 95% of solvent. Reprinted with permission from Reference.²¹ Copyright 2014, American Chemical Society.

Hence, the presence of volatile solvents should be eliminated in the designing of thermotropic smart window. Meanwhile, the underlying mechanism of LCST between ionic liquid (IL) and polymer have been investigated extensively and employed in applications such as nanoactuators and smart electrolytes.⁴²⁻⁴³ Compared to PNIPAM hydrogels, the LCST transition of IL and polymer is of lower enthalpy change which result in biphasic separation layer of IL-rich and polymer-rich phase.⁴⁴ The lower enthalpy transition could be a consequence of residual attractive forces such as dipolar force and dispersion forces which would help to constrain the phase separation between IL and polymer.

Ideally, a 3D polymeric network should enable reversibility for LCST derived optical switch from polymer/IL.⁴⁵ Theoretically, cations of IL should still be capable of forming solvation shell around functional groups of polymethacrylate or poly ether, upon formation of ionogel. Hence, an ionogel with polyurethane functional groups would exhibit LCST in the presence of IL.

It is worthwhile to note that a large change in enthalpy during phase transition always involve a large-scale phase separation accompanied with liquid expulsion.⁴⁶ For example, thermally responsive IPN hydrogel usually takes advantage of the small enthalpy change during heating transition to engender microscopic phase change, inducing minute volume reduction, leading to controlled drug delivery at temperature above LCST.⁴⁷ According to Flory-Huggins theory,⁴⁸ the second derivatives of Helmholtz mixing free energy per lattice site, $\frac{\partial^2 \Delta F_{mix}}{\partial \phi^2}$ could be minimized with a larger polymer fraction and theoretically, lesser free energy for liquid expulsion could result in a zero-volume change ionogel.

ILs are non-volatile and assume a high thermal stability of around 300°C, with a melting point at around -15°C.⁴⁹ However, it is possible to significantly depress the melting point of ILs when they are immobilized in nano-spaces.⁵⁰ Based on Gibbs-Thomson Equation,⁵¹ the shift in melting point of IL with respect to bulk IL, increases with its confinement by decreasing the pore size. Hence, the fabrication of an ionogel could induce nano-scale confinement of IL to achieve largely depressed sub-zero melting point.

1.3 Objective and Scope

The objective of this thesis is to adopt various LCST-based organic/inorganic hybrid gels in the applications of thermotropic smart windows with simultaneous climate adaptability and cyclic-stability. To achieve the objective, the following strategies are implemented within the scope of this thesis.

- a) Introducing a simple and effective approach to achieve climate adaptable thermotropic composite with solvothermal synthesized plasmonic ATO dispersed in a thermally responsive PNIPAM hydrogel.
- b) Applying glycerol/water binary solvent in Agarose hydrogel with octylphenol ethoxylates based surfactant to achieve thermotropic composite with dimensional stability and enhanced thermal stability, thereby striking a balance between stability and solar modulation ability.

- c) Design and implement a new class of cyclic stable thermotropic ionogel consisting of intrinsically stable imidazolium ionic liquids and crosslinked polyurethane. Use of molecular dynamics simulation for materials selection and tuning of transition temperature. Nano composites of ATO/PU ionogel to obtain cyclic stable thermotropic material with climate adaptable features.

1.4 Dissertation Overview

This thesis addresses the intrinsic problems of thermotropic hydrogels based on contemporary literature review and develops three thermotropic systems to achieve climate adaptability and cyclic stability through means of experimental methods and computer simulations.

Chapter 1 discuss the research motivation, objectives and outcomes.

Chapter 2 reviews the literature concerning the fundamentals of smart windows, thermotropic polymers, contemporary solutions for climate adaptable and cyclic-stable hydrogels, plasmonic TCO and interactions between polymer and ionic liquids.

Chapter 3 elaborates the rationale for materials selection and the underlying principles for materials synthesis and characterization techniques.

Chapter 4 introduces an original idea of climate adaptable thermotropic material based on plasmonic heating of transparent conducting oxides. The new mechanism of such photothermotropic smart window with enhanced solar modulation and response speed is discussed.

Chapter 5 elaborates the synthesis and characterization of Agarose hybrid composite with non-ionic surfactant and binary solvent to achieve enhance stability. The underlying mechanism of glycerol effect on Agarose thermotropic properties was discussed.

Chapter 6 introduces an original idea of thermotropic ionogel based on molecular dynamic simulation and implements a novel energy saving material by developing a polyurethane based ionogel with versatility, wide transition temperature tunability and super cyclic stability.

Chapter 7 demonstrates how hypothesis in this thesis is proven with experimental results, and how research objectives are met. The prospects for future development of thermotropic smart window are discussed.

1.5 Findings and Outcomes/Originality

Several novel outcomes from this research includes:

- a) Establishing a solar irradiation approach to (i) more realistically characterize smart window thermal optical behavior and further (ii) elucidate plasmonic nanoparticles photothermal effect on thermotropic smart window properties.
- b) New optical switching mechanism of thermotropic smart window driven by plasmonic heating. The solar modulation ability and response rate were enhanced simultaneously.
- c) Micro dynamic insight of glycerol co-solvent effect on LCST derived thermotropic properties from amphiphilic non-ionic surfactants. The thermal optical properties of interest include decreased transition temperature, gradual optical switching, negligible thermal hysteresis and moderate solar modulation ability.
- d) A new class of superior thermotropic materials based on polyurethane ionogels. Underlying mechanism for ionogel transition temperature tunability and cyclic stability were investigated and discussed. Upon solar irradiation, this solar modulation material further demonstrates a promising energy saving performance in terms of temperature reduction.

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Chapter 2

Literature Review

Solar control windows are of great importance for energy conservation in buildings and vehicles. Thermotropic hydrogels have been extensively investigated as promising candidates for thermotropic smart windows, since they possess reversible broadband solar modulation properties with tunable transition temperatures. Because they are only thermally responsive and contain a large amount of aqueous solvent, these thermotropic hydrogels suffer from the inability to perform optical switch in cold climate and has poor cyclic stability, respectively. To resolve these challenges, different material systems, nanostructures and system integration approach were considered in the preliminary investigation to achieve improvement in climate adaptability and cyclic stability. Meanwhile, several questions are raised from existing literatures and identified issues were addressed in the context of this Ph.D. study to enable further development of thermotropic smart windows.

2.1 Background of Solar Control Window

Transparent glasses are extensively used as premium construction materials in transport vehicles and architectures. These glazing allows sunlight to illuminate the interior space while offering thermal insulation to a certain extent. Both optical and thermal comfort can be realized through selective transmittance of solar spectrum wavelength (λ). More specifically, certain degree of visible light in the range of 400 – 700 nm is permitted to pass through the glasses, enabling daylighting and comfortable visibility. On the contrary, both ultra-violet (UV) and near-infrared (NIR) in the wavelength region of $\lambda < 400$ nm and $\lambda > 700$ nm, respectively, do not contribute to visibility and the latter further amount to around 49% of solar heating on Earth.¹ Therefore, control of energy influx from the solar spectrum is important.

Conventional low emissivity (low-e) coating of silver tends to result in relatively low visible light transmittance and easy oxidation.²⁻³ Although multilayer optical films that aim to stabilize the temperature of a highly glazed room have been implemented, yet many of them are unresponsive to surrounding ambient temperature changes or require extra and continuous energy inputs for dynamic control. Hence, there is an opportunity to provide passive and dynamic control of solar heat gain, with a substantial reduction of heat and dimming of glaring sunlight. The typical requirements of an ideal smart window include appropriate response speed, high visible transmittance before switching, high solar modulation while maintaining visibility upon optical switching, reversible and reproducible solar modulation performance, and fully autonomous modulation in both the visible and NIR regions.⁴

For energy conservation, immense efforts had been channeled into the development of chromogenic materials with different modes of activation, such as photochromic,⁵⁻⁶ gasochromic,⁷⁻⁸ piezochromic,⁹ mechanochromic,¹⁰ electrochromic,¹¹⁻¹² and thermochromic¹³⁻¹⁸ smart window. Among them, a self-contained and autonomous systems triggered by temperature or solar irradiation would be more advantageous for smart window applications owing to its simplicity and ease of implementation. Paradoxically for

thermochromic materials, the very solar heating itself is being utilized to activate the heat shielding function. The already developed autonomous thermochromic materials, such as inorganic vanadium dioxide semiconductor oxides and organic dyes, have shown great promise though they tend to have low modulation contrast and limited modulating wavelength range.¹⁹⁻²² In addition, the optical switch temperature tuning of these thermochromic materials is achievable but usually not straightforward or effective. On the other hand, thermotropic polymers which is a member of the thermochromic family, assume high optical contrast and ability to modulate broadband wavelength in the entire solar spectrum to control the solar luminance intensity as well as thermal comfort of the interior architecture.

2.2 Thermotropic Smart Windows: Optical Properties of Interest

For quantification of visible light that appeal to the human vision, integrated luminous transmittance (T_{lum}) is adopted and defined based on the photopically averaged transmittance as shown in **Equation 2.1**. According to the photopic luminous efficiency of the human eyes in **Figure 2.1**, evaluation of T_{lum} is based on wavelength range from 380 to 780 nm. It is important to know that 99.2% of terrestrial solar energy lies within the wavelength region of 250 to 2500 nm as illustrated by the green curve of **Figure 2.1**. Hence, averaged transmittance in the NIR region and the entire solar spectrum could be evaluated by calculation of integrated infrared (IR) transmittance (T_{IR}) and integrated solar transmittance (T_{sol}) in the λ range of 780 to 2500 nm and 250 to 2500 nm, respectively. Furthermore, another set of important optical parameters for thermotropic smart windows are the energy modulation abilities ($\Delta T_{lum/IR/sol}$) in different regions of the solar spectrum. As shown in **Equation 2.2**, they indicate the differences in the energy transmitted when the thermotropic material are subjected to two different temperature.

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

$$\Delta T_{lum/IR/sol} = T_{lum/IR/sol (low)} - T_{lum/IR/sol (high)} \quad (2.2)$$

$$T_{lum/IR/sol(avg)} = \frac{T_{lum/IR/sol(low)} + T_{lum/IR/sol(high)}}{2} \quad (2.3)$$

Where $T(\lambda)$ represent the measured spectral transmittance, Φ_{lum} is the standard luminous efficiency function of photonic vision,²³ for wavelength in the range of 380 – 780 nm as illustrated in **Figure 2.1** orange curve, and $\Phi_{IR/sol}$ is the IR/solar irradiance spectrum distribution for air mass (AM) 1.5 illustrated by the green curve in **Figure 2.1**.²⁴ An overall yearly average for mid-latitudes including diffuse light from the ground and sky on a south facing surface tilted 37° from horizontal can also be represented by Φ_{sol} .

While, $T_{lum/IR/sol(avg)}$ in **Equation 2.3** represent the average integrated $T(\lambda)$ in the corresponding wavelength range obtained at both low and high temperatures. $T_{lum(avg)}$ is often used to quantify the appropriate visibility before and after solar modulation. The typical key evaluation parameters of thermotropic smart windows are namely T_{lum} , T_{IR} , $T_{lum(avg)}$ and ΔT_{sol} .

Figure 2.1 Spectrum of interest used in Equation 2.1 – 2.3 for the calculation of integral transmittance. The orange curve peaking at 550 nm represents the photopic luminous efficiency of human eyes,²³ while the green spectrum represent that of AM 1.5 solar irradiance spectrum.²⁴

2.3 Thermotropic Polymers

Thermotropic polymers typically consist of at least two components with different refractive indices (RI). The different components are homogenized at molecular level below the switching temperature and they appear transparent. Phase separation or phase transition occur at transition temperature result in components of different RI, generating scattering domains that are comparable to the scale of solar irradiations wavelength. Light scattering occurs at the interface of components with different RI and subsequently solar modulation is achieved when the incident solar radiation is back scattered or reflected.

2.3.1 Classification of Thermotropic Polymers

Numerous forms of materials such as block copolymers, nanoparticles, paraffin wax and polymer gels have been explored for their thermotropic effect and they can be classified based on different switching mechanism namely, aggregation,²⁵⁻²⁶ change of particle size,²⁷ phase transition²⁸⁻²⁹ and phase separation,^{4, 30} respectively.

Thermally induced aggregation of micelles was reported for amphiphilic triblock copolymer.³¹ For example, at critical micelle concentration, poly (ethylene oxide-co-propylene oxide-co-ethylene oxide) triblock terpolymer (EPE) first form micelles followed by packing of micelles into aggregation of micelle clusters at temperature above its lower critical solution temperature (LCST), leading to light scattering. The LCST could be tuned with a variety of salts and surfactants.²⁶

The change in size of nanoparticle *via* volume reduction could also leads to thermotropic effect. An example was demonstrated with Polystyrene core and PNIPAM shell, whereby difference in refractive index (RI) between the shrunken nanoparticle and its surrounding, result in light scattering.²⁷ More specifically, the thermotropic solution changes from intense blue at 25°C to pale blue at 31°C when the particle size reduces from 1000 to 430 nm at temperature above PNIPAM LCST. The visible transmittance at 630 nm was reported to decrease from 58% at 20°C to 10% at 42°C.

An example of optical switching by phase transition mechanism would be the casting resins with fixed domain. Typically, domain materials such as long chain alkanes and fatty acid esters that exhibit reversible solid to liquid phase transition are embedded into casting resins and sandwiched between laminated glasses. An commercial product would be the T-Opal® with optical switching temperature range from 10 to 50°C.³² In further development, the thermotropic domain additives were also introduced as core shell particles into extruded polyolefin films.²⁹

Phase separation induced thermotropic effect could be achieved by both polymer blends and polymer gels.^{16, 33} For thermotropic polymer blends, usually a thermoplastic component is embedded in a crosslinked matrix similar to that of semi-IPN structure. Reversible functionality and mechanical stability is provided by the crosslinked matrix polymer. The crosslink network also controls the maximal size of the thermoplastic component domains for maximum back scattering efficiency and its optical switch temperature. For example, a copolymer of poly (styrene-*co*-2-hydroxyethyl methacrylate) blended with poly (propylene oxide) thermally crosslinked with a trifunctional isocyanate was reported in a patented study.³⁴ A change in transmittance from 92 to 30% was reported to be observed at 20 and 90°C, respectively for a 400 μm film.

Thermotropic polymer gels usually assume large optical contrast, economical and light stability. These polymer gels could either be natural or synthetic polymers filled with varying amounts of aqueous solution (hydrogel) or organic solvent (organogel) to exhibit LCST behavior. Their optical switching temperature could be tuned by altering the microstructure to adjust the hydrophobicity and hydrophilicity balance of the polymer chain or by additions of salts or solvents into the swelling agent.

Among the various reported systems, thermotropic system with fixed domains (TSFD) and polymer gel appears to be very attractive for their reliability and solar modulation performance, respectively. TSFD working on the basis of phase transition appears to be a more reliable system and have been the focus of many patented studies.³⁵⁻³⁷ Through exploitation of phase change materials such as waxy polymer³⁷ and n-alkanes³⁵ as

thermotropic additives, dimensional and thermal stability issues faced by the hydrogels could be easily avoided. However, poor optical properties such as low solar transmittance (<70%) in the clear state due to refractive index (RI) mismatch, moderate switching ranges of about 25% and high switching hysteresis have been reported for TSFD system.^{29, 38-39} Olaf et al. presented an improved version of TSFD by changing the thermotropic component into an n-alkane@PMMA core shell structure with the addition of n-docosanol as nucleating agent in the n-alkane mixture.²⁹ Although these modification resulted in a better backscattering efficiency and low switching hysteresis, yet tedious emulsion polymerization is required to achieve controlled and narrow particle size distribution such that the scattering domain could optimally lies in the preferred range of 200 – 400 nm.⁴⁰ Secondly numerous processing optimization,⁴¹⁻⁴² and screening of materials,^{28, 43-44} studies had to be conduct to realize the matching of RI between the core, shell and matrix. Furthermore, the switching range for such systems reported thus far, are still much lower (c.a. 50%) as compared to that of polymer gels (c.a. 70%), as shown in **Table 2.1**.

Table 2.1 Performance comparison among various thermotropic polymer based systems. The notation, n.a. indicates that data is not available. Reprinted with permission from Reference.⁴⁵ Copyright 2009, Elsevier.

Properties	Thermotropic hydrogels	Thermotropic polymer blends	Thermotropic systems with fixed domains
Switching temperature	5–60 °C	30–130 °C	25–100 °C
Highest solar transmittance in clear state	82%	> 85%	84%
Maximum switching range and collector stagnation temperature according to switching range (determined for an all polymeric flat-plate collector with twin-wall sheet glazing and black absorber)	77% 75 °C	52% 90 °C	25% 125 °C
Reversibility	High	High	High
Reproducibility	High	n.a.	High
Homogeneous stability	High	n.a.	High
Hysteresis	Low	High	Low
Haze in clear state	Low	Low	High
Turbidity in opaque state	Uniform	Uniform	Uniform
Switching process	Steep	Gradual	Steep
Diameter of scattering domain	400–2500 nm	480 nm	> 800 nm
Ageing and long-term stability	UV protection required; susceptible to dessication	Susceptible to humidity	Delamination
Ecologic aspects	Innocuously	Innocuously	Innocuously
Availability in large area	Yes	Yes	Yes
Costs	Expensive if synthetic materials used	No data available	Low
State of the art	Commercially available <i>Affinity Intelligent Window™</i>	No products available	With thermoplastic matrix: commercially available product developed by Buehler and Hewel at EMS Chemie AG (CH) With crosslinked matrix: no products available

2.3.2 Thermotropic Polymer Gels

Development of thermally responsive hydrogels for thermotropic smart window application have been reported as early as 1950.⁴⁶ The thermotropic hydrogels can be classified into physically and chemically cross link, depending on the type of cross linker used during polymerization process.

Thermotropic crosslink hydrogel based on polyalkoxides derivatives and salts as physical cross-linker have been reported.⁴⁷⁻⁴⁹ The switching temperature of these physical cross link hydrogels could be tuned from 25 to 80°C by variation of propyleneoxide and ethyleneoxide monomeric units as well as types of salts.

Seeboth et al. investigated the role of LiCl cross linker on the gelation behavior of hydrogel by means of rheological measurement,⁴⁹ while the salt induced physical crosslinking mechanism shown in **Figure 2.2(a)** and its influence on optical switch temperature shown in **Figure 2.2(b)**,⁴⁷ was elucidated by Fischer et al. in a separate study. It is worthwhile to note that these physically crosslinked hydrogels can exhibit high optical contrast of around 90% and they maintain a constant volume during optical switching.

Figure 2.2 (a) Proposed model depicting the role of salt ‘S’ as physical cross linker in polyalkoxy based hydrogels. While (b) shows that these dual functional salts could also be used for tuning of hydrogel phase separation temperature. Reprinted with permission from Reference.⁴⁷ Copyright 1999, John Wiley & Sons.

Both synthetic and biopolymers have been explored as chemical crosslinked thermotropic hydrogels. While synthetic polymers include several polymer class such as polyvinyl, polyamide, polyethers etc., biopolymers are based on cellulose derivatives.⁴⁵ Due to its biodegradability and commercial availability at low costs, biopolymers are attractive for smart window applications.

Haruo Watanabe reported on the hydroxypropylcellulose (HPC) biopolymer (**Figure 2.3**) based “Affinity Intelligent Window” (AIW), which could function well over a period of two years out in the field.⁵⁰ The transition temperature was reported to be tunable from 25 to 60°C by varying the content of sodium chloride and polymer. However, due to drastic increase in viscosity which leads to irreversible flocculation of cellulose derivative during sol-gel optical switch transition, an amphiphilic surfactant (polyoxypropylen-2-ether-2-hydroxymethyl-1,3-propanediol) must be included. This non-ionic amphiphile function as a spacer that prevents the complete phase separation of HPC.⁵⁰⁻⁵¹

J. Schneider et al. reported on an alternative method to prevent irreversible HPC flocculation such that addition of surfactant could be eliminated if part of the constituent is a polysaccharide.⁵¹

Figure 2.3 Showing the phase transition concept model of thermotropic HPC biopolymer with reversible sol-gel transition due to the presence of amphiphilic molecules. Reprinted with permission from Reference.⁵⁰ Copyright 1998, Elsevier.

The addition of hydroxyethyl cellulose (HEC) to HPC solution with ratio of (1 : 4.6) not only lowers the optical switching temperature, but also help to cushion the drastic viscosity change of pure HPC solution at its transition temperature (43°C). Hence, HEC could be used as a viscosity stabilizer due to its large structural similarity with HPC to prevent irreversible flocculation issue.

For synthetic thermotropic hydrogels, an example of polyether based polymer would be poly methyl vinyl ether (PMVE). Charoudi developed Cloud Gel™, a PMVE hydrogel crosslinked with methylene-bis-acrylamide (BIS).⁵² Similarly, switching temperature of Cloud Gel™ could be tuned between 10 and 70°C by varying its composition.⁵³ A 1 mm thick thermotropic layer exhibit large visible light modulation from 92 to 6% when the temperature was raised from 25 to 50°C. While for polyamide based polymers, PNIPAM have been extensively investigated in the recent years and it appears to be an attractive candidate for thermotropic smart window, as shown in **Figure 2.4**.¹⁶⁻¹⁷ PNIPAM transition temperature of 32°C could be easily tuned and it does not show sign of irreversible flocculation and structural instability, unlike that of HPC biopolymer. In addition, structural stability as well as optical properties of PNIPAM based hydrogel can be preserved even after 1 year in the field.³⁰

Figure 2.4 (a) Schematic illustrate the LCST operating mechanism of PNIPAM as the interlayer in-between two glass panels for a thermotropic smart window and (b) shows how the variation of hydrogel film thickness affects the solar modulation performance between 20 and 40°C. Reprinted with permission from Reference.¹⁶ Copyright 2014, The Royal Society of Chemistry.

2.4 Contemporary Solutions for Climate Adaptable Thermotropic Hydrogels

The requirements of thermotropic hydrogel smart window are multi-fold including thermal optical comfort control,¹⁶⁻¹⁷ cyclic stability,^{30, 54} and optical switching behavior.^{15, 30, 55-57} The thermotropic smart window switching problem had been reported back in 2003, where optical switching could not take place in cold climates even in the presence of high intensity solar luminance.¹³ This is because the thermotropic material in that report is only thermal responsive. Subsequently, several solutions such as reducing transition temperature of the gel,³⁰ switching by electrical means,¹³⁻¹⁵ and addition of solar absorber material⁵⁷ had been proposed and investigated.

2.4.1 Lowering LCST of PNIPAM based Smart Window

The transition temperature of thermotropic polymer gel could be lowered to facilitate the optical switching behavior in cold climate. Wang et al. prepared PNIPAM microgel by suspension polymerization in water/alcohol binary solvent and N,N'-methylene-bis-acrylamide (BIS) as cross linker.³⁰ Binary solvent consisting of glycol/water and glycerol/water were chosen to investigate their ability in lowering of PNIPAM LCST and restraining of solvent evaporation rate. Their role on thermal optical response of PNIPAM smart window were investigated.

The addition of a lower polarity solvent can result in lowering of both hydrophilic interaction before phase separation and hydrophobic interaction upon phase separation. It can be seen from **Figure 2.5** and **Figure 2.6**, that both solar modulation ability and response rate of the PNIPAM microgel decreased with increasing glycerol content, respectively.

Figure 2.5 Thermal optical properties of PNIPAM microgel with 0 to 35 wt% of glycerol (of total solvent), depicted by (a) UV-Vis-NIR transmittance spectra, (b) integral solar transmittance at temperatures below (15°C) and above (50°C) its LCST, (c) solar modulation ability and (d) reversibility of solar modulation performance. Reprinted with permission from Reference.³⁰ Copyright 2014, American Chemical Society.

The optical properties are largely influenced by the swelling and deswelling behavior of PNIPAM, hence smaller degree of optical properties deterioration was observed for glycerol as compared to glycol. Higher solubility of swollen microgels and lower solubility of de-swollen microgels result in better solar modulation ability. With increasing glycerol content from 0 to 35 wt%, integral transmittance managed to remain above 80% at 15°C without significant changes, while integral transmittance increased from 8 to 21% at 50°C, as evidence from **Figure 2.5(a)** and **Figure 2.5(b)**. Since the polarity of glycerol is still lower than water, the reduced hydrophobic interaction during phase separation thus result in reduced opacity and solar modulation ability.

The responsive rate of the microgel colloids was investigated as shown in **Figure 2.6**. The specimens at 15°C was transferred to a water bath at 50°C, and both transmittance at 1100 nm and specimen temperature were measured as a function of time. The time span for the change in transmittance between neighboring points larger than 2% during the transparent to opaque transition was defined as the duration time. With increasing glycerol content from 0 to 30 wt%, the duration time increased from 50 to 150 secs as shown by the right shifting of peak derivative in **Figure 2.6(d)**. The reason behind the deterioration in response rate can be attributed to the kinetics of deswelling process. The hydrogel deswelling process can be broken down into two parts namely, breaking of hydrogen bonds between solvent and polymers during dehydration, followed by formation of new hydrogen bonds between polymers during shrinking.

Figure 2.6 Heating and cooling double Y axis (transmittance and temperature) time graph for PNIPAM microgel with glycerol content of (a) 0, (b) 10, (c) 20, and (d) 30 wt%. Insets show the derivative of transmittance time (dTr/dt) plots. Reprinted with permission from Reference.³⁰ Copyright 2014, American Chemical Society.

Figure 2.7 Molecular structure illustrating the hydrophobic isopropyl and hydrophilic amide groups of (left) PNIPAM. While the hydrophobic and hydrophilic component of glycerol is indicated as the glyceryl and polyhydroxyl group, respectively.

As shown in **Figure 2.7**, the hydrophobic isopropyl groups of PNIPAM and the main chains will first undergo dehydration followed by diffusion and flocculation. Hydrogen bonding between the hydrophilic groups of PNIPAM and solvent will be broken. New hydrogen bonds between the hydrophilic groups of the polymer chain will then form for structural stability. Towards the end of the dehydration, interactions between the glyceryl groups of glycerol and the isopropyl groups of PNIPAM could hinder the subsequent hydrophobic interaction, resulting in slower response rate.

The LCST of PNIPAM microgel reduced from 32.2 to 20°C when glycerol content was increased from 0 to 35 wt%. The increase in glycerol content result in both the weakening of hydrogen bonds between PNIPAM and solvent below the transition temperature as well as the hydrophobic interaction of PNIPAM chain aggregation above transition temperature. Therefore, a gradual restrained swelling and deswelling transition of the microgels were observed and lower energy is needed during the hydration and dehydration of the polymer networks. In addition, DSC thermogram in **Figure 2.8** shows reduced freezing point from -18.1 to -32°C when glycerol content increases from 0 to 35 wt% in binary solvent, respectively. Hence, PNIPAM in glycerol/water binary solvent system demonstrates that LCST, freezing point and evaporation rate of hydrogel could be reduced at the expense of decreased solar modulation ability and response rate.

Figure 2.8 (a) DSC thermograms depicting the (b) freezing points and absolute enthalpy change (ΔH) calculated for PNIPAM microgel with different glycerol content (of total solvent). Reprinted with permission from Reference.³⁰ Copyright 2014, American Chemical Society.

2.4.2 Optical Switching by Joule-Heating

Gyenes et al. reported a comparison study of PNIPAM (T_t : 35.2°C) and PVA/PMVE (T_t : 35.1°C) for electrically adjustable window, that are able to moderate the amount of sunlight transmittance.¹³ The prototype window comprises of a thermotropic polymer gel layer with printed circuit board sandwich by conductive ITO glasses. A minimum switching time of 97 seconds was obtained with optimized electrical signal. Genes et al. studies not only demonstrate that PNIPAM is more suitable for electrically adjustable window due to its unique phase separation mechanism, but the necessity for joule heating to induce optical switch was also highlighted. Unfortunately, the setup for electrical induce switching compromises the window optical properties. The transparency of the conductive substrate is only around 50% due to the dense layers of ITO. Besides, the response rate of the optical switching would be limited by both the thermal capacity and heat conductivity of the conductive substrate. Furthermore, the operating electrical signals must be thoroughly optimized to avoid electrolysis and gas generation of water in the hydrogels.

Takashi Inoue et al. reported that solar dimming control could not be achieved with thermotropic hydrogel (T_t : 30°C) during cold climate and introduce the approach of joule heating and solar absorption with electrochromic layer to induce optical switching of hydrogel. The proposed approach was investigated by means of experimental and

simulation.¹⁵ Thermotropic hydrogel was coupled together with both low-emissivity (low-E) coating and heating layer, as seen from **Figure 2.9(a)**. Due to low exterior air temperature of 10°C in the winter, the thermotropic hydrogel with only low-E configuration could not perform optical switching despite intense solar radiation of around 600 W m⁻² at 15:00. As shown in **Figure 2.9(c)**, electric power of 480 W m⁻² were applied for joule heating from 14:05 to 14:11 and complete optical switching could be achieved only after 6 minutes whereby surface temperature of the window rose by 10°C. It was found that around 20 kWh m⁻² would be required for joule heating configured glass to achieve 100% effectiveness.

Figure 2.9 Showing the (a) configuration of window glazing equipped with Low-E coating, thermotropic hydrogel and heating layer. While (b) illustrate the simulated energy requirement for joule heating of hydrogel layer during winter to achieve optical switch. The actual (c) temperature and time profile during application of joule heating for thermotropic hydrogel to perform optical switch. Reprinted with permission from Reference.¹⁵ Copyright 2008, Elsevier.

Figure 2.10 Illustrate the (a) setup for multi-glass glazing with different configuration of Low-E, thermotropic hydrogel and electrochromic layer. While (b) depicts the actual temperature and time profile during application of the multi-glass glazing with different configurations in winter. Reprinted with permission from Reference.¹⁵ Copyright 2008, Elsevier.

When compared to a glazing model operated solely by joule heating, it shows that only 16% of heating energy required for optical switch is derived from solar energy. Subsequently, incidence of direct solar irradiation exceeding 25 W m^{-2} for more than 1 m into the room was defined as threshold for active solar shading and the extent to which glass configuration with joule heating could satisfy a typical office requirement in Tokyo, was investigated by means of simulation.

The second approach was to induce optical switch in hydrogel through solar absorptivity with electrochromic layer in the tinted state. The tinted electrochromic layer concurrently helps to reduce direct solar irradiation until thermotropic hydrogel is clouded. The effect of coupling electrochromic layer to thermotropic hydrogel was investigated with multi-glass configuration shown in **Figure 2.10(a)**. It was found the only the hydrogel in

[LE+ECTT] and [LE+TTEC] configuration could perform optical switch. The electrochromic layer which are located right next to the thermotropic layer would first be tinted to absorb solar irradiation which facilitate the optical switch of hydrogel. Subsequently, the electrochromic layer was controlled to be clear 30 mins later after optical switch of hydrogel is complete. The actual temperature and time profile during operation of electrochromic and thermotropic layer could be seen from **Figure 2.11(b)**. Their study also reveal that the best glazing configuration varies with regional characteristics of weather, use of internals rooms and orientation of the windows.

2.4.3 Photothermal enabled Optical Switching

Kim et al. reported a dual responsive photothermotropic smart window comprising of graphene oxide (GO) and PNIPAM for autonomous optical switching recently.⁵⁷ The GO dispersed in PNIPAM matrix by *insitu* polymerization function as a solar absorber to facilitate optical switching of PNIPAM/GO (PGO) hybrid in cold climate. Interestingly, a near 0% transmittance from 400 – 900 nm was observed for PGO at 40°C as evidence from **Figure 2.11(a)**. While in **Figure 2.11(b)**, around 1°C of thermal hysteresis was observed for both PNIPAM and PGO with no difference in LCST.

Figure 2.11 Depicting the transmittance spectra for neat PNIPAM and PNIPAM/GO hybrid as a function of (a) wavelength with different temperature of 25 and 40 °C, and (b) temperature which shows their heating and cooling profile. These spectra were generated from a UV-Vis-NIR spectrophotometer modified with a bath circulator for temperature control. Reprinted with permission from Reference.⁵⁷ Copyright 2015, Springer Nature.

Figure 2.12 (a) Temperature increment of distilled water and 0.5 mg mL⁻¹ aqueous GO dispersion upon sunlight irradiation. (b) Temperature increment of 0.5 mg mL⁻¹ aqueous GO after different intensity of blue light irradiation. Reprinted with permission from Reference.⁵⁷ Copyright 2015, Springer Nature.

It was further demonstrated in this study that, GO absorb in the visible region when blue light of different intensity was used to test for its photothermal properties, with 0.5 mg mL⁻¹ aqueous GO as shown in **Figure 2.12**. More specifically, temperature of GO dispersion increases linearly by 0.7, 1.3, 2.2 and 3.2°C when irradiated by 4.5, 14.9, 24.8 and 45.0 mW cm⁻² of blue light, respectively.

An outdoor switching test was performed under sunlight at 30°C with a 140 µm thick photothermotropic hydrogel layer, containing 0.5 mg mL⁻¹ aqueous GO in the pre-gel solution. The PGO composite temperature rose to 38°C and shows an opaque appearance while no significant temperature increment was observed for the pure hydrogel. It is worthwhile to note that although PGO could respond to both sunlight and temperature, GO is also known to exhibit low optical absorption in the NIR region.⁵⁸⁻⁵⁹ Hence, efficient thermal comfort with NIR shielding could not be achieved for tropical climate.⁶⁰⁻⁶¹ Beside, other important optical properties such as the response speed and solar modulation ability was not elucidated in this study.

2.5 Nano Plasmonic: Localized Surface Plasmon Resonance

Although carbon rich materials such as carbon nanotubes and reduced graphene oxide shows good solar absorbing and thermal conversion properties, nanocrystals which are of better optical transparency and exhibit localized surface plasmon resonance (LSPR) can be exploited for their plasmonic heating feature.

2.5.1 Fundamental of Nano Plasmonic

The coherent oscillation of free carrier cloud in a metallic nanoparticle result in LSPR phenomenon, illustrated in **Figure 2.13(a)**. Incident electromagnetic wave drives the free carriers to oscillate according to the frequency of electromagnetic wave. The displacement of free carriers from the core of nanoparticle result in net charges at its surface with restoring force provided by nanoparticle positive nuclei. The behavior of free carriers in bulk metal can be described by a harmonic oscillator model. While in nano scale, the small volume confines the free carrier's oscillation and localize surface plasmon to the nanoparticle. The LSPR phenomenon leads to pronounced absorption when resonance condition shown in **Equation 2.4** is fulfilled.⁶²⁻⁶³

Figure 2.13 Schematic illustrating (a) plasmon resonance of metal nanoparticle and the relative electron cloud charges displacement from its core in an oscillating electric field. While (b) depicts LSPR tuning of degenerately doped semiconductor nanocrystals with increase in carrier concentration. Reprinted with permission from Reference.⁶² Copyright 2017, Elsevier.

$$\omega_{LSPR} = \sqrt{\frac{\omega_p^2}{1 + 2\varepsilon_m} - \gamma^2} \quad (2.4)$$

where ε_m refers to the surrounding medium dielectric constant and γ is relevant to damping of free carrier. The relation described in **Equation 2.4** is valid for spherical nanoparticle which is small enough, such that electromagnetic interaction between various parts of nanostructure is nearly immediate and excitations are limited to dipolar modes. The changes in carrier density will affect resonance frequency of the plasma oscillation. Hence, an increase in carrier density of nanostructures induce a blue shift of the LSPR as seen from **Figure 2.15(b)**. Beside free carrier density, medium surrounding the nanoparticle also influence the LSPR. A medium with high dielectric constant causes weak coulombic restoring force of electron cloud, which result in a decrease of LSPR.⁶² As shown in **Figure 2.14**, this explains why the LSPR for bulk metals like gold and silver with carrier densities of around 10^{23} cm^{-3} , is in the visible region while LSPR for degenerately doped semiconductor with carrier densities of around 10^{21} cm^{-3} , is in the IR region.⁶⁴ More importantly, degenerately doped semiconductor offers better tunability of LSPR compared to metals, and small changes in carrier density can induce a large effect on its LSPR profile.

Figure 2.14 Shows the dependence of free carrier concentration on the LSPR frequency of different materials. For nanoparticle of 2 to 12 nm, the amount of dopant atoms required to obtain free carrier density between 10^{17} to 10^{23} cm^{-3} is calculated and shown in top panel. Note that LSPR mode in nanoparticle might not be supported if its carrier density is less than 10^{19} cm^{-3} . Reprinted with permission from Reference.⁶⁴ Copyright 2011, Springer Nature.

The collective oscillations of free carriers encounter scattering with electrons, phonons, lattice defects and impurities. When the effective path length of electrons is larger than the size of nanoparticle, surface scattering effect will be significant and it results in broadening of LSPR line width. The various contributions from scattering can be described by the damping constant γ , as shown in **Equation 2.5**. Therefore, the line width of plasmon resonance is indirectly related to damping of the free carrier's oscillations.

$$\gamma = \gamma_{e-e} + \gamma_{e-phonon} + \gamma_{e-defect} + \gamma_{e-surface} \quad (2.5)$$

The ratio of LSPR peak value to full width at half maximum (FWHM) of the resonance peak can be used to define a quality factor of the LSPR profile. This quality factor provides information on the plasmonic response and damping properties. Briefly, higher quality factor is due to stronger plasmonic response while broader resonance line width implies larger damping. The LSPR absorption spectra also provides information on different resonances due to nanostructures that are differently shaped. For example, both transverse and longitudinal LSPR is present in nanorods due to excitation along the diameter and length of the rod, respectively. Compared to the transverse mode, the longitudinal LSPR shows higher intensity and red shifted to higher wavelength.⁶³

Interestingly, the scattering effect of electrons and phonons result in damping which causes heat to be generated. This process occurs in the scale of few hundred femtoseconds and the heat generated diffuses away from the nanoparticle to increase temperature of the surrounding environment. This plasmonic heating effect is enhanced by the presence of free carriers and reaches a maximum at peak of LSPR. More importantly, this mechanism enables the nanostructure to serve as a nano heater using photo energy from different region of the solar spectrum.

For visible light induced plasmonic heating, very creative photo responsive actuator based on two-way shape memory poly (ethylene co vinyl acetate) (EVA) with gold nanoparticles was demonstrated.⁶⁵ The mechanical actuation of EVA originates from the reversible melting and recrystallization of polymer crystallites which could be activated remotely by

a 532 nm light, facilitated by the AuNPs. Furthermore, the photothermal to mechanical energy conversion was explored for photothermal motor application where a new propulsion mechanism based on hot vapor jet ejection at liquid and air interface was demonstrated.⁶⁶

In NIR induced plasmonic heating, bio related applications such as contrast agent for bioimaging and photothermal ablation typically requires the plasmonic absorption to be within the therapeutic window, due to interference of blood and water at lower wavelength of less than 650 nm and higher wavelength of more than 1350 nm, respectively.⁶⁷ Beside biological applications, interesting legible patterns on polymer surfaces fabricated with NIR laser patterning (1064 nm), facilitated by polycarbonate coated with nano antimony tin oxide, core shell structure was reported.⁶⁸ NIR irradiation of immobilized $\text{Cs}_{0.33}\text{WO}_3$ inside a polydimethylsiloxane based microreactor, result in antibacterial activity of over 99.9%, during the continuous operation of up to 30 days.⁶⁹ Furthermore, solar vapor generation could be achieved with lossy plasmonic resonance (broad line width) of titanium nitride nanoparticle. The titanium nitride nanoparticle was also reported to exhibit better sunlight absorption efficiency compared to gold and carbon black nanoparticles.⁷⁰

2.5.2 NIR Active Plasmonic

Degenerately doped semiconductor nanocrystals had been of great interest to the plasmonic community in the recent years, due to their tunable localized surface plasmon resonances (LSPR) in the near infrared (NIR). Typically, there are two classes of these semiconductors, namely the impurity doped semiconductors (e.g. metal oxides) and vacancy doped semiconductors (e.g. copper chalcogenides). As shown in **Figure 2.15**, the LSPR of these plasmonic nanocrystals have different line width and lies in different infrared region.

Figure 2.15 Shows the (a) LSPR profile at different wavelength region for different metal and metal oxide nanocrystals in solutions and films. Reprinted with permission from Reference.⁷¹ Copyright 2014, American Chemical Society. While the list in (b) specifies the LSPR wavelength region for different degenerately doped semiconductors. Reprinted with permission from Reference.⁷² Copyright 2014, The Royal Society of Chemistry.

The high level of carrier densities around 10^{21} cm^{-3} in these plasmonic nanocrystal result in degeneracy of doping levels and significant plasmonic absorption in NIR. The strategy to tune the Fermi level can be achieved by heterovalent doping which changes the electron or hole concentration to achieve a sufficiently high density of delocalized carriers to facilitate LSPR. Compared to metals, changes in carrier density of these degenerate semiconductors can be easily controlled by their doping concentration which allows facile tuning of LSPR from near-infrared to mid-infrared region.

For vacancy doped semiconductor like copper chalcogenides, it is the copper vacancies that determines the free carrier concentration, while for impurity doped semiconductor like metal oxides, the added impurity atoms provide free carriers to the system. The chemical modification of copper vacancy density in copper chalcogenides will result in structural change of its crystal lattice while the free carrier density in doped metal oxide can be controlled *via* doping concentration or by selection of dopant and host atoms. It is worth mentioning that introduction of capacitive charge carriers to conduction band of metal oxide is possible even during post synthetic treatments by means of electrochemical or photodoping.

The distinct advantages of NIR plasmonic for applications includes, enhanced absorption in infrared region, observable LSPR peak shift with small variation in doping density, and flexibility of reversible LSPR mode tuning in post-synthesized nanocrystals. These unique features allows the exploration of NIR plasmonic for bioimaging, photothermal therapy, bio sensor based on LSPR tracking and on-off NIR shielding for electrochromic smart window.^{63, 72}

2.5.2.1 Classification of Doped Semi-conductor

The different classes of degenerate semiconductors can be better categorized as shown in **Figure 2.16**, which depicts their different doping strategies and corresponding LSPR regions.

Self-doping mechanism are realized in copper chalcogenides since the Cu deficiency in Cu_{2-x}S nanocrystal leads to valence band holes. The LSPR profile of copper chalcogenides changes with hole densities in the valence band, which can be reversibly controlled by exposure to an oxidation or reduction environment. While sufficient electron density in conduction band can be achieved by both self-doping for oxygen vacancies (e.g. MoO_{3-x} and WO_{3-x}) and interstitial doping mechanism (e.g. Cs^+ in CsWO_3).

Figure 2.16 Shows the examples and categories of degenerately doped semiconductor based on different doping strategies, namely self-doping (vacancies) and extrinsic doping. Reprinted with permission from Reference.⁶³ Copyright 2017, John Wiley & Sons.

For extrinsically doped metal oxides, they are typically transparent conducting oxides (TCO) which assume a high density of free carriers in their conduction band because of substitutional doping. The LSPR of plasmonic TCO is dominated by n-type doping which mainly originate from cation dopant. It was found that the versatility of doping and tunability of plasmonic band can be further modified. Cation-anion co-doping was reported for F and In co-doped CdO where both substituted cation and anion dopants provides free electrons for cooperative tuning of LSPR over a wide spectrum range.⁶³

2.5.2.2 LSPR Theory in Plasmonic TCO

The LSPR peaks profile of plasmonic TCO is primarily affected by its electron concentration.⁷² The Drude's model equations could be used to explain the underlying mechanism of NIR plasmonic absorption in TCO.⁷³ Drude's model states that the absorption coefficient, α , is direct proportional to charge carrier density N , which is related to the free electron according to **Equation 2.6**. Where e refers to electron charge, m_e is an electron effective mass, ϵ_0 is permittivity of vacuum, τ is free electrons relaxation time, n is undoped semiconductor refractive indices, c is speed of light and ω refers to the frequency of light. While the IR absorption wavelength is in direct proportional relationship to electron plasma frequency, ω_p , as shown in **Equation 2.7** where ω_{sp} refers to the surface plasma absorption frequency and ϵ_m is the surrounding medium dielectric constant.

$$\alpha = \frac{Ne^2}{m_e \epsilon_0 n c \tau \omega^2} \quad (2.6)$$

$$\omega_{sp^2} = \frac{\omega_p^2}{1 + \epsilon_m} \quad (2.7)$$

$$\omega_p = \sqrt{\frac{Ne^2}{m_e \epsilon_\infty \epsilon_0}} \quad (2.8)$$

$$R = 1 - \frac{2}{\omega_p \epsilon_\infty \frac{1}{2} \tau} \quad (2.9)$$

The notation ω_p refers to the plasma frequency of the electron, which shows a square root dependence with free electron concentration according to **Equation 2.8**, where ϵ_∞ refers to optical dielectric constant. The above equations highlight the significance of free electrons in the n-type semiconductor for NIR absorption. More importantly, **Equation 2.6**, shows that the absorption wavelength can be tuned by controlling the free electron concentration in the metal oxide semiconductor. Therefore, an increase in free electron with dopant concentration can result in both enhanced NIR absorption as well as blue shifting of the absorption maxima. The relaxation time, τ of electron is the main contribution factor towards the NIR shielding mechanism as seen from **Equation 2.9**, where R can be expressed as infrared reflection. More specifically, shorter free electron relaxation time result in larger NIR absorption and lower NIR reflection.

2.6 Contemporary Solutions for Dimensional Stable Thermotropic Hydrogels

The typical strategies to achieve dimensional stable thermotropic hydrogels, with negligible or zero volume change includes formation of interpenetrating networks,⁷⁴⁻⁷⁷ multi-site binding with 2D nanosheets,⁷⁸⁻⁸⁰ and inactive polymer scaffold.²⁵⁻²⁶

2.6.1 Interpenetrating Network (IPN) Thermotropic Hydrogels

Interpenetrating polymer network (IPN) formation occurs when polymer chains of two components are not chemically bonded but physically interwoven. They can be classified as semi-IPN, where only one of the component is crosslinked to form three-dimensional network or full-IPN, when both components are crosslinked. IPN technology are often practiced in drug delivery to achieve controlled drug release profile. Generally, micro domains of thermal responsive polymer increase with crosslink density of interlaced polymer, resulting in weaker volume phase transition and less thermal sensitive drug

release.^{75, 81-82} Similarly, dimensional stable semi-IPN hydrogel which assume PNIPAM optical switch while preserving all other inherent properties of crosslinked chitosan hydrogel such as gelation rate, swelling behavior and electrical induced contraction have been reported too.⁷⁴ The formation of IPN have also been reported to result in mechanical strength enhancement of hydrogels.^{77, 83}

2.6.1.1 Full IPN

Zadrazil et al. reported a full IPN where NIPAM monomer were loaded into calcium alginate hydrogel and polymerized above its LCST.⁷⁶ As shown in **Figure 2.17**, both quasi-static and dynamic thermal optical behavior of the IPN were investigated *via* grey scale level index. They attribute the dimensional stability of the IPN to polymerization and crosslinking of NIPAM above its LCST which result in the collapsed state of PNIPAM being its natural state within the composite hydrogel. While the hydrated chains of PNIPAM can expand into the aqueous phase within the IPN below its LCST. Hence, no structural stress will be induced on the interpenetrating alginate hydrogel network.

Figure 2.17 Shows the spot (left) taken from full IPN calcium alginate/PNIPAM hydrogel for grey scale level index measurement while the graph (right) depicts a typical LCST optical response of a thermotropic hydrogel. The NIPAM concentration in this hydrogel was 0.31 mol L⁻¹ while the heating rate for grey scale measurement was 3°C min⁻¹. Reprinted with permission from Reference.⁷⁶ Copyright 2010, Elsevier.

Although complete repeatability was observed during dynamic thermal cycling, the full IPN synthesis procedure is tedious. Firstly, calcium alginate hydrogel is synthesized by syringe extrusion, followed by soaking of hydrogel in NIPAM monomer solution. The NIPAM monomers are then polymerize and cross linked within alginate at 60°C, followed by removal of the oil phase and other unreacted precursors.

The mechanisms for dimensional stability in full-IPN are discussed in the perspective of phase transition energetics by Carmen et al. for controlled drug release application.⁷⁵ The changes in swelling degree with temperature and high-sensitive DSC was used to investigate the thermal transitions of a chitosan/PNIPAM hydrogel. The presence of chitosan network minimizes the collapsing degree of PNIPAM in IPN compared to pure PNIPAM. It was found that an increase in post cross-link density of chitosan causes a decrease in thermal transition enthalpy and widening of heat capacity endotherm. These observations are attributed to the microdomains of PNIPAM network in the IPN, where certain regions of the domains could not participate in the thermal transitions. Hence, IPN with higher chitosan crosslink density results in a lower thermal sensitive drug release profile since the PNIPAM microdomains are smaller and the volume phase transition are less abrupt. Similarly, the synthesis procedure involving the conversion of a semi-IPN to full-IPN for this full-IPN hydrogel is tedious.

2.6.1.2 Semi-IPN

Very interesting semi-IPN that assume characteristics of both polymer chain were demonstrated by Wang et al. where chitosan/PNIPAM hydrogel were investigated for its gelation rate, swelling behaviors in water/ethanol mixtures, electrical induced contraction and thermal responses.⁷⁴ With 25 wt% PNIPAM content in semi-IPN, thermal responsive optical switch property was achieved while preserving all other inherent properties of chitosan. Beside the combination of individual polymer characteristics, enhancement in mechanical properties could be achieved simultaneously.

Figure 2.18 Schematic illustrating the extended ($T < \text{LCST}$) to collapsed ($T > \text{LCST}$) state of PNIPAM chain with the increase in temperature. Structural support of collapsed PNIPAM chains is provided by the swollen PAAm network in water. Reprinted with permission from Reference.⁷⁷ Copyright 2001, American Chemical Society.

Muniz et al. reported a semi-IPN hydrogel consisting of crosslinked polyacrylamide (PAAm) and PNIPAM.⁷⁷ The swelling ratio and compression elastic modulus of hydrogels were investigated as a function of temperatures. PNIPAM were first synthesized by redox polymerization and added to PAAm pre-gel solution. Polymerization of PAAm then took place after exposure to gamma irradiation.

The reason for the semi-IPN dimensional stability above LCST could be attributed to two factors. Firstly, the collapsed PNIPAM chains are mechanically supported by PAAm network, shown in **Figure 2.18**. Secondly, the entanglement of PNIPAM chains inside the semi-IPN could contribute to the decrease in swelling ratio due to higher polymer volume fraction. It was found that the semi-IPN hydrogels possess superior mechanical properties as compared to PAAm hydrogel and this improvement is attributed to the increase in polymer fraction at temperature below and above LCST. More importantly, shrinking of the hydrogel is significantly suppressed while optical switch is reversible and rapid within a few minutes. Nevertheless, the synthesis procedure of semi-IPN and full-IPN is similar, where tedious multi-steps procedures are required.

2.6.2 Multi-site Binding with 2D Nanosheets

Figure 2.19 Depicts the proposed photoinduced hydrogelation process. Firstly, carbon nitride facilitates (left) photocatalytic generation of hydroxyl radical from water, followed by (right) *in situ* polymerization of vinyl monomers and physical cross link of NIPAM chains by carbon nitride with noncovalent interactions. Reprinted with permission from Reference.⁷⁸ Copyright 2017, The Royal Society of Chemistry.

The role of 2D graphitic carbon nitride and titania nanosheets as dual functional photocatalytic initiators and cross linkers were explored in thermal responsive hydrogel and a microphase separation which result in insignificant volume phase transition were reported.⁷⁸⁻⁸⁰

As shown in **Figure 2.19**, upon photo irradiation, electron hole pairs generated from the nanosheets form hydroxyl radicals in aqueous medium to initiate *insitu* polymerization of monomers. Subsequent multi-site binding of polymer chains to 2D nanosheets were achieved through physical crosslinking of polymer chains *via* noncovalent interactions. The dimensional transformation of the hydrogel composite above its LCST is weak due to nanosheet scaffolding and microphase separation mechanism, where water movement is localized. Furthermore, optical switching of hydrogel is fast due to local structural rearrangements in a smaller length scale during phase transition. As shown in **Figure 2.20(a)** inset, the absence of tyndall scattering suggest well dispersed carbon nitride nanosheets as physical cross linker in the hydrogel to provide mechanical integrity. Furthermore, when these nanosheets are aligned co-facially in the hydrogel, a variety of novel and intriguing properties could be realized.⁷⁹⁻⁸⁰

Figure 2.20 (a) TEM showing carbon nitride lateral dimension in micron meter scale. Optical transparency of carbon nitride in (b) NIPAM pre-gel solution and (c) composite hydrogel, before and after visible light irradiation, respectively. (d) The proposed polymerization pathway induced by photoirradiation. Reprinted with permission from Reference.⁷⁸ Copyright 2017, The Royal Society of Chemistry.

Although weak hydrogel dimensional transformation results in minor macroscopic deswelling, several other practical limitations exist for such strategy. This includes requirement of a photo irradiation source, visible light for carbon nitride and UV for titania nanosheets, during the synthesis process. The photo-irradiation for complete gelation typically requires at least 40 minutes even with 0.04 wt% of carbon nitride nanosheets, since further addition of nanosheets appear to be unstable. Hence, there is a compromise between good transparency and short irradiation duration. Furthermore, presence of micron scale 2D nanosheet causes both pre-gel and hydrogel to exhibit low optical transparency, seen from **Figure 2.20(b)** and **Figure 2.20(c)**.

2.6.3 Inactive Polymer Scaffold

The use of thermal responsive amphiphilic molecules embodied by an inactive transparent polymer scaffold is an attractive method for preparation of dimensionally stable thermotropic hydrogel.

Figure 2.21 (a) Schematic illustrating the reversible thermal optical characteristics of the thermal responsive hydrogel. The increase in temperature above EPE transition temperature causes the EPE molecules to aggregate and form clusters. The SEM images shows similar pore size of polyacrylamide hydrogel with (b) 5 w/v% and (c) 10 w/v% acrylamide content. Reprinted with permission from Reference.²⁶ Copyright 2016, Hindawi.

Thermal responsive amphiphilic surfactants can be dispersed uniformly in water and these molecules detach from water and aggregate to form clusters at temperature above its LCST. Feng et al. demonstrated this strategy by confining triblock poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (EPE) molecules in the pores of polyacrylamide (PAM) framework *via* radical polymerization.²⁶ While a facile and scalable fabrication was demonstrated with agarose physical gel containing similar non-ionic surfactants.²⁵

The working mechanism for EPE molecules in the PAM hydrogel are illustrated in **Figure 2.21(a)**. The confine EPE molecule self-assemble to form micelles in aqueous solvent through dehydration of PPO segment, above the critical micellization temperature. The core of micelle consists of hydrophobic PPO segments, with hydrophilic PEO chains surrounding it. When surrounding temperature is above its LCST, the hydrophilic PEO chains entangle, resulting in micelles aggregation to form clusters which precipitate out of the mixture due to insolubility. As shown in **Figure 2.21(b)** and **Figure 2.21(c)**, no changes in the thermal responsive behavior of EPE molecules was observed in PAM hydrogel with different acrylamide content, since the pore size of hydrogel are much bigger than EPE

molecules. The transmittance of PAM/EPE hydrogel can reach almost zero when temperature is above 30°C and a complete phase separation process could be achieved in 1 minute using a 12 V DC power source or in 4 minutes using a 9 V battery.

Alternatively, a one pot synthesis with facile and scalable process is possible with physical gels such as gellan gum or agarose. The resulting thermotropic hydrogel is not only dimensional stable and tunable, but is also innocuous, cost effective and completely biodegradable. The aggregation phenomenon of an agarose hydrogel containing EPE or 4-octylphenol polyethoxylate (Triton™ X) was investigated by Li et al. with fluorescence microscopy.²⁵ Rhodamine B was doped into hydrogel to investigate the formation of micelles clusters. Based on fluorescence microscopy, the micelle aggregation mechanism described by Li et al. as shown in **Figure 2.22**, corroborated with what Feng et al. had reported. Although dimensional stability of thermotropic hydrogel can be achieved by the facile preparation method of physical gel, evaporation and freezing of the contained aqueous solvent remains inevitable. Moreover, satisfactory viscosity of smart window would not be possible if the thermotropic hydrogel shows an abrupt optical switch, as shown in **Figure 2.22(d)** where 8°C change result in complete opacity.

Figure 2.22 Schematic illustrating the (a) facile preparation procedure of thermoresponsive agarose and (b) micelle aggregation of surfactant, marked with rhodamine B within hydrogel at temperature above LCST. While the hydrogel shows (c) no sign of micelle colloid at temperature below LCST. The graph in (d) depicts the lowering of hydrogel transition temperature with sodium sulfate and their respectively thermal sensitivity profile. Reprinted with permission from Reference.²⁵ Copyright 2011, IOP Publishing.

2.7 Polymers in Ionic Liquid

Ionic liquids (ILs) are environmental benign room temperature molten salts with attractive properties including non-volatility, non-flammability, high ionic conductivity and electrochemical stability. They have been used as solvents for polymerization and dissolution of sparingly soluble polymers like wool, silk and cellulose. In addition, they can also be a medium for dispersion of carbon nanotubes or preservation of biopolymers such as DNA and proteins.⁸⁴⁻⁸⁵

The combination of ILs with solid state polymers enable the fabrication of functional soft matters where ILs can be design for specific task. By far, applications such as solid-state electrolytes,⁸⁶⁻⁸⁷ membranes,⁸⁸ and organic thin film transistors,⁸⁹ have been demonstrated with these IL containing functional soft matters. Due to IL intrinsic thermal stability and wide liquidus temperature range, soft matters containing ILs can be applied in open environment for prolong usage without concerns of solvent evaporation and operating temperature range. When exposed to external stimuli (heat), the underlying mechanism of how polymer solubility changes in medium containing only ions, is intriguing from the perspective of fundamental polymer science.

2.7.1 Stimuli-Responsive Polymers in Ionic Liquids

The Gibbs free energy of mixing shown in **Equation 2.10** could be used to determine the temperature dependent solubility between polymer and solvent.⁸⁴ Where ΔH_{mix} and ΔS_{mix} refers to the enthalpy and entropy of mixing, respectively, while T is absolute temperature.

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (2.10)$$

When the value of ΔG_{mix} is negative, the solvent and polymer spontaneously mix to produce a homogeneous solution. On the contrary, when values of ΔG_{mix} is positive, the polymer solution becomes turbid due to phase separation of polymer and solvent. For LCST transition to occur, both ΔH_{mix} and ΔS_{mix} should be negative with a larger

contribution from the entropy term, so that ΔG_{mix} could transit from negative to positive with the increase in temperature. The LCST phase separation behaviors of various polymers in IL have been reported with the focus on its thermodynamic transition. An example would be poly (benzyl methacrylate) (PBnMA), which exhibit similar phase separation behaviors to PNIPAM in aqueous solution. The formation of hydration shell around the hydrophobic isopropyl group of PNIPAM is a structure forming solvation activity that decreases the entropy of solution, when temperature is below LCST. While for the LCST transition of PBnMA in $[\text{C}_n\text{mim}][\text{NTf}_2]$, liquid clathrate structure formation was investigated by means of both high energy X-ray diffraction and molecular dynamics simulation.⁹⁰

More specifically, as shown in **Figure 2.23(a)**, $[\text{C}_2\text{mim}]$ cation was found distributed in an orderly manner above and below the benzyl group of BnMA, while **Figure 2.23(b)** shows $[\text{NTf}_2]$ anion located around the equatorial position of BnMA. This distribution implies weak interactions between $[\text{NTf}_2]$ and BnMA. The liquid clathrate structure typically forms between ILs and aromatic compounds due to cation- π interactions, as shown in **Figure 2.23(c)**.⁹¹

Figure 2.23 Schematic illustrating the distribution manner of (a) $[\text{C}_2\text{mim}]$ cation and (b) $[\text{NTf}_2]$ anion around the benzyl group of BnMA. Reprinted with permission from Reference.⁹⁰ Copyright 2013, The Japan Society for Analytical Chemistry. While (c) shows the liquid clathrate structure formation between $[\text{C}_2\text{mim}][\text{NTf}_2]$ and benzene. The IL ions are surrounding the tube-like structure of benzene. Reprinted with permission from Reference.⁹¹ Copyright 2006, The Royal Society of Chemistry.

Similar to hydrophobic hydration shells in PNIPAM aqueous solution, the microscopic solvation of benzyl group in BnMA decreases the mixing entropy to facilitate LCST behavior. The LCST transition of PNIPAM in aqueous solution is accompanied by low temperature swollen and high temperature shrunken phase. Interestingly, this characteristic was also observed in a crosslinked PBnMA network infused with $[C_2mim][NTf_2]$.⁹²

As depicted in **Figure 2.24(a)**, the phase transition (volume reduction) of PBnMA/[C₂mim][NTf₂] ion gels is discrete and reversible, with a large hysteresis loop that is typical of a first-order transition. Since the ion gel is not only thermally responsive but also non-volatile and moisture-insensitive, its development could result in environmentally stable smart gels. The phase behaviors of polymer in ILs account for their transition temperature, which could be engineered by modification of polymer and/or IL molecular structures, as shown by the many examples demonstrated in **Figure 2.24(b)**. Nevertheless, the LCST of polymer in IL is also strongly dependent on the polymer concentration and its molecular weight.

Figure 2.24 Graphical illustration of (a) PBnMA/[C₂mim][NTf₂] ion gels with LCST induced volumetric change. Reprinted with permission from Reference.⁹² Copyright 2007, American Chemical Society. While (b) shows the different types of polymethacrylates and ionic liquids, investigated for their phase separation temperature. Reprinted with permission from Reference.⁸⁴ Copyright 2014, Springer Nature. The transition temperatures indicated in the chart is applicable only to specified polymer molecular weight and concentration that had been investigated.

2.7.1.1 LCST of Polymethacrylates and Ionic Liquids

The important factors for the phase separation temperature of PBnMA homo polymer (3 wt%) in IL, had been investigated systematically by modification of both polymer and ILs chemical structure (**Figure 2.25**) and several observations were made.⁹³ Firstly, the phase separation temperature increases with increase in alkyl chain length at imidazolium cation. Secondly, the phase separation temperature does not vary significantly with methyl substitution at the C2 position of the imidazolium cation, where the C2 position is known to provide strong hydrogen bonding. Lastly, the phase separation temperature strongly depends on both cation and anion structure of the ILs.

Based on the first two general observation, Van der Waals interactions seems more dominant and applicable in tuning of methacrylate polymers/IL phase separation temperature, as compared to hydrogen bonding. In other reports, IL anion was found to affect the transition temperature, although the anion does not appear to contribute to the decrease in mixing entropy by forming structure solvation.⁸⁷ This indicate possibility of exothermic enthalpic contributions, which was postulated to be the result of solvation between IL anion and ester group in methacrylate polymers.⁸⁴⁻⁸⁵

Figure 2.25 Depicts the structural modifications of (left) PBnMA derivatives and (right) ILs that were investigated. The arrows on (left) indicates the specific position where chemical modification was made to PBnMA. Reprinted with permission from Reference.⁹³ Copyright 2009, American Chemical Society.

Structural modifications which affects the entropy contribution can significantly altered the phase separation temperature of methacrylate polymers in ILs. For example, a methylene spacer inserted between aromatic group and methacrylate backbone of PBnMA result in PPhEtMA, a polymer with LCST of 63°C lower than PBnMA. This study also implies that tuning of LCST is more effective with steric hindrance mechanism as compared to tailoring the electron density of benzyl group through aromatic substitution.⁸⁴

The random copolymerization of different monomers for PNIPAM in aqueous solution, will result in changes of phase separation temperature, and similar behavior was realized for polymers in IL. However, the magnitude of temperature change for polymer and IL system is much larger than thermally responsive polymer in aqueous media. In comparison to their individual homo polymer counterpart, a random copolymer (P(MMA₁₀-r-BnMA)), which consist of BnMA and solvatophilic methyl methacrylate (MMA) in [C₂mim][NTf₂], shows a difference in phase separation temperature as large as 30°C.⁹² Whereas, only 5°C difference in LCST was observed for random copolymer of NIPAM and hydrophilic N,N-dimethylacrylamide (DMAAm), P(DMAAm₁₀-r-NIPAAm) in aqueous solution.⁹⁴ The exact underlying reason for such observation is still currently under investigation, but a comparative study of PBnMA in IL and PNIPAM in water, conducted with high sensitive differential scanning calorimetry have revealed that the smaller changes in ΔH_{mix} and ΔS_{mix} for PBnMA in [C₂mim][NTf₂] might contribute to its larger changes in phase separation temperature, based on the Gibbs free equation.

2.7.1.2 LCST of Polyethers and Ionic Liquids

The other class of polymer that had been reported for its LCST behavior in IL are the polyethers, with a different set of underlying thermodynamics mechanism. Similarly, the effect of poly ether and IL structural modification on its phase separation temperature had been investigated with different polyethers and different ILs, as shown in **Figure 2.26**.⁹⁵ Firstly, for ILs of same anions shown in **Figure 2.26(a)**, PEGE were found to be soluble in imidazolium or pyridinium based ILs, but not in ammonium or phosphonium based ILs. This was attributed to the aromatic based cation which increases solubility due to its highly

‘active’ proton donors. The ranking of IL’s anion influence on phase separation temperature was also found to be almost consistent with the order in Lewis basicities of anion. Secondly, an increase in alkyl chain length of imidazolium cation and polarity of polyethers resulted in higher LCST, as depicted in **Figure 2.26(b)**.⁸⁴ The extent of microphase segregation also increases with cation alkyl chain length, which reduces the entropy of IL. The observation of LCST change induced by the systematic variation in polyethers polarity implies that hydrogen bonding is more dominant than Van der Waals interaction.

Figure 2.26 Shows the influence of (a) the types of IL’s cation on LCST of poly ether, while (b) shows the influence of poly ether and IL’s imidazolium cation structural modification on the LCST. The polymer concentration in ionic liquid was 10 wt% for both graphs and the polymer investigated in (a) is poly (ethyl glycidyl ether) (PEGE). Reprinted with permission from Reference.⁹⁵ Copyright 2011, Springer Nature.

Hence, methyl group substitution on IL imidazolium cation can cause a decrease in LCST of polyethers. This was not observed for the case of poly methacrylates in ILs. From these observations, it appears that hydrogen bonds between cation protons and oxygen atoms of ether groups is the driving force for LCST behavior. It was also postulated that the hydrogen bonding interactions between cation protons and ether oxygen atoms is responsible for both negative ΔH_{mix} and ΔS_{mix} to induce LCST behaviour.⁸⁴⁻⁸⁵

2.7.2 Functional Design with Stimuli-Responsive Polymers

The phase behaviors of thermally responsive polymers in ILs have led to new developments of functional materials. For instance, the volume phase transition of PBnMA ion gel with imidazolium ILs can be applied to a variety of stimuli responsive smart systems that had been proposed but could not be realized in hydrogel systems for all practical reasons. These smart systems include actuators, optical and switching devices and many others.

2.7.2.1 Thermally Responsive Nanogel Shuttle

A thermally responsive ‘round-trip’ nanogel that shuttles between water and hydrophobic ILs was first reported by Lodge et al. where micelles of PB-b-PEG block copolymer was found to shuttle reversibly between interface of water and hydrophobic $[\text{C}_2\text{mim}][\text{NTf}_2]$, with the influence of heat.⁹⁶ They investigate the shuttle behavior with nuclear magnetic resonance studies and ascribed the micelle shuttle phenomenon to the change in relative affinity of corona PEG chains towards water and ILs. It is also known that PEG exhibits significant solubility change (LCST) in water, and not IL. Therefore, their findings strongly suggest that the PEG shell is a universal material design that permit round trip shuttle behavior between water and IL, with the influence of temperature.

Figure 2.27 Conceptual illustration of nanogel shuttle based on reversible thermally driven mechanism. The PNIPAM core exhibits low temperature swollen and high temperature shrunken phase transition in the water phase (LCST) while showing the opposite behavior (UCST) in the IL phase. The PEO shell enable the nanogel to shuttle between water and IL phase due to its LCST behavior. Reprinted with permission from Reference.⁹⁷ Copyright 2013, American Chemical Society.

Inspired by the round-trip shuttle PEG shell design, Ueki et al. demonstrated a potential load-transfer-release nanogel shuttle between water and hydrophobic IL, based on similar thermally responsive mechanism as shown in **Figure 2.27**.⁹⁷ The nanogel comprises of crosslinked PNIPAM core with PEG shell. The LCST behavior of PNIPAM in water and upper critical solution temperature (UCST) behavior of PNIPAM in IL, might eventually allow the nanogel to perform loading and unloading of substrates in the water or IL phase.

2.7.2.2 Surface Modification with Thermally Responsive Polymers

In addition to load transfer in different medium based on thermal responsive behavior of polymer in IL, their application at interfaces can result in novel approach for existing technologies. Guo et al. demonstrated a thermally responsive ion gate by modifying a nano porous surface with PBNMA polymer brush, illustrated in **Figure 2.28(a)**. With the influence of heat, these polymer brush function as intelligent molecular nanoactuators to block organic charge carriers. This new design of smart gating not only exhibit functionalities akin to biological ion channels but can also function over a wide temperature range.⁹⁸

While very interesting optical properties derived from thermally responsive interactions between polymer and IL have also been demonstrated with the interface of SiO₂ nanoparticles. Ueno et al. investigated the rheological and optical properties of SiO₂ in [C₂mim][NTf₂], where silica nanoparticles are grafted with PBnMA *via* surface-initiated atom transfer radical polymerization.⁹⁹

As shown in **Figure 2.28(b)**, when the SiO₂ content is above 14.2 wt%, the formation of short range ordered glassy colloidal array result in a non-brilliant and angle-independent structural color. The viscoelastic response of PBnMA-g-SiO₂ solution was investigated as a function of temperature and both the storage and loss modulus first decreases up to the phase separation of 95°C and subsequently increase at higher temperatures. The V-shaped rheological profile can be ascribed to the thermal responsive behavior of PBnMA-g-SiO₂. Below the LCST, steric hindrance effect of PBnMA result in a repulsive interaction among the modified particles. It is known that the repulsive particles tend to form colloidal glass at high particle concentration, showing gel like characteristics. Therefore, grafted PBnMA collapse at temperature above LCST, leading to the formation of ion gel with percolation of PBnMA-g-SiO₂ into particulate networks.

Hence, this novel ion gel was proposed to find itself as applications in functional fluids, color displays and electrochemical devices.^{84, 99} The most attractive attributes of ILs are its thermal stability, wide liquidus temperature range and ability to impart reversible thermal responsive interactions in specific polymer systems. Hence, the application of ILs as solvent for functional soft matters not only induce additional thermal responsive smart features but also largely extend the duration and operating temperature range of the soft matter.

Figure 2.28 (a) Schematic illustration of PBnMA polymer brushes grafted onto anodic aluminium oxide (AAO) substrate and operated in $[C_2mim][NTf_2]$ medium to provide the nanopores as smart gating for organic ion transportation. Reprinted with permission from Reference.⁹⁸ Copyright 2012, John Wiley and Sons. (b) Photograph illustrate the structured colored colloidal array with different content of PBnMA-g-SiO₂, with (bi) showing the in-situ TEM images of 25 wt% PBnMA-g-SiO₂ in $[C_2mim][NTf_2]$ before and after heating at 100°C. Reprinted with permission from Reference.⁹⁹ Copyright 2010, American Chemical Society.

2.8 Questions Raised from Climate Adaptable Thermotropic Hydrogels

The inability to perform optical switch in cold climate is because the thermotropic polymer is only thermally responsive. Hence, various strategies including lowering of LCST, electrical induce switching and photothermal enabled switching had been explored. The idea of lowering LCST by tuning of transition temperature is to increase the overall hydrophobicity of the system. While joule heating by electrical means allow optical switching to be perform in both passive and active manner. Whereas optical switch by photothermal means will enable the thermotropic polymer to be both photo and thermally responsive.

Wang et al. demonstrated a PNIPAM microgel with the addition of binary solvent containing glycerol and water.³⁰ The cosolvent reduces the hydrophilic interactions between polymer and water to reduces the system LCST. However, reducing the transition temperature is always unfortunately compromised by both the solar modulation ability and the response speed. Gyenes et al. and Takashi et al. investigated the possibility of electrical

induced optical switching.¹³⁻¹⁵ The incorporation of conductive ITO electrodes enables the thermotropic materials to realize switching at lower temperature by joule-heating, at the expense of low visible transmittance (45 – 55%) and constant energy consumption. Moreover, the hydrogel contains a tremendous amount of aqueous solvent and electrolysis of water might occur due to its small electrochemical window.

Similarly, although extra thermal energy from the photothermal effect of graphene oxide (GO) in PNIPAM hydrogel has been proved by Kim et al. to implement switching at lower temperatures,⁵⁷ GO inherently high absorption in visible and low absorption in NIR region largely detract the application of the composite hydrogel as thermotropic smart window.⁵⁸⁻⁵⁹ Moreover, GO's inherent brownish appearance would be aesthetically undesirable for window application. Therefore, thermotropic polymer that primarily modulates in visible region coupled with a transparent photothermal material that exclusively absorbs in UV and NIR region seems to be the ideal solution for a climate adaptable passive smart window.

2.9 Questions Raised from Dimensional Stable Thermotropic Hydrogels

The solar modulation ability which is responsible for thermotropic hydrogels energy saving feature is directly derived from its LCST mechanism. The origin of thermal responsive hydrogel (e.g. PNIPAM) dimensional instability can be ascribed to its relatively large enthalpy change during LCST transition.⁷⁵ Hence several strategies including IPN formation, multi-site polymer chain binding with 2D nanosheets and inactive polymer scaffolding had been explored. Unfortunately, the synthesise of full IPNs are often tedious, consisting of multiple procedures and micro phase volume transitions remain unavoidable.^{75, 77} While preparation of semi-IPN appears to be easier than full-IPN, the interlace linear polymer of semi-IPN could dislodge from the crosslinked polymer during post-synthesis treatment.⁷⁵ Kim et al. and Liu et al. demonstrated multi-site physical cross linking of PNIPAM with titania nano sheet and graphitic carbon nitride, respectively.^{78, 80} Although significant reduction in macroscopic deswelling was achieved, the resulting composite exhibit poor optical transparency with only 30 – 40% visible transmittance.

An example of thermotropic hydrogel with inactive scaffolding was demonstrated with agarose and thermal responsive poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) molecules, by Li et al.²⁵ Although the synthesis procedure is facile and scalable, yet the hydrogel contains a tremendous amount of aqueous solvent. Therefore, partial substitution of aqueous solvent in thermotropic hydrogels with inactive scaffolding, appears to be an attractive and practical solution. Nevertheless, modified hydrogel that exhibit lower volatility and evaporation characteristics, still encounter formidable drying and freezing.³⁰ Hence, cyclic stability which is critical for actual application remains unachievable. Moreover, thermotropic hydrogels which are mechanically weak, not only poses a challenge to their physical handling, but also limit its application to an interlayer material. Therefore, this warrant a need for a cyclic stable LCST-based thermotropic system which is non-volatile and dimensionally stable.

2.10 PhD in the Context of Literature

Firstly, a scalable approach for preparation of dual responsive photothermotropic PNIPAM/ATO nanocomposite is considered with the solvothermal synthesized ATO-NP homogeneously dispersed in a thermally responsive PNIPAM hydrogel. Variables including thickness of composite film, doping and particle content of ATO is investigated to strike a subtle balance between optical and thermal comfort.

Secondly, the effect of glycerol on the thermal optical properties of dimensional stable thermotropic hydrogel was investigated. Agarose hybrid containing glycerol/water binary solvent physically allows a wider range of operating temperature, while retaining high T_{lum} , satisfactory ΔT_{sol} and gentle optical switch characteristics. The transition temperature tunability with poly oxyethylene based surfactant mixtures circumvents the complex materials structure modification and paves the way for practical applications of thermotropic hydrogel smart window.

Furthermore, this Ph.D. study initiate a new class of thermotropic material with the assistance of molecular dynamics simulation, whereby screening of IL candidates and

design guideline of transition temperature tuning were established. The contribution factors for the cyclic stable thermotropic ionogel with zero-volume change was postulated and discussed in the view point of thermodynamic. Lastly, the thermotropic polyurethane (PU)/ILs ionogel concept can be experimentally realized with an unprecedented wide range of tuning temperature, which is primarily based on altering the hydrogen bond and Van der Waals interactions between ethers group in PU and the cation of IL. The ionogel/ATO nanocomposite modulates the influx of solar spectrum in a broadband manner while ATO-NP provides the NIR attenuation properties, to enable superior energy conservation feature. The type of IL, ratio of binary ILs as well as ATO-NP content are taken into optimization for achieving both high T_{lum} and ΔT_{sol} , with remarkable cyclic stability simultaneously.

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Chapter 3

Experimental Methodology

This chapter focuses on the underlying rationale and principle for the selections of material candidates, synthesis methodology and characterization techniques for plasmonic antimony tin oxide (ATO) nanoparticles, thermotropic gels and their composite. The working principles of characterization tools, such as UV-Vis-NIR, XRD, DSC, TGA, and others are illustrated and discussed in detail. In addition, the theory of plasmonic heating was demonstrated with an improvised characterization technique to more appropriately address the influence of photothermal effect on thermotropic smart windows.

3.1 Materials Selection

3.1.1 Plasmonic Transparent Conducting Oxide – Antimony Tin Oxide

A thermotropic polymer, e.g. PNIPAM that primarily modulates solar spectrum in the visible region coupled with a transparent photothermal material that exclusively absorbs in the UV and NIR regions seems to be the ideal solution for an adaptable passive smart window.

Nanoparticles that exhibit localized surface plasmon resonance (LSPR) have been and are being investigated as a form of nano heater in various applications.¹⁻⁵ Three different classes of nanomaterials where their LSPR does not interfere in the visible region typically includes, rare-earth hexaboride, noble metal nanoparticles and doped semiconductors. Stringent processing criteria, such as high temperature of around 1500°C and vacuum are required for the synthesis of rare-earth hexaboride materials like lanthanum hexaboride (LaB₆).⁶ While noble metal nanoparticles such as Au or Ag with high aspect ratio are costly and tend to oxidize easily. NIR active LSPR and UV absorption have been observed and reported for transparent conducting oxides (TCOs) for e.g. aluminium zinc oxide (AZO),⁷⁻⁸ gallium zinc oxide (GZO),⁹ indium tin oxide (ITO)¹⁰ and antimony tin oxide (ATO).¹¹⁻¹⁵ The UV absorption of TCO originates from its intrinsic wide band gap, and NIR absorption occurs as a result of the doping effect.

ATO which has superior stability over its TCO counterparts was chosen as an example to demonstrate its NIR active plasmonic heating on thermally responsive polymers in this thesis. Furthermore, ATO LSPR absorption peak maximum of around 1500 nm, will allow a high visible transmittance to be retained for the thermotropic composite. Consequently, broadband solar modulation in the wavelength region of 250 – 2500 nm could take place without compromising the visibility.

3.1.2 Thermally Responsive Hydrogel – Poly (N-isopropylacrylamide)

PNIPAM hydrogel is a polymeric material that contains around 80% of water and exhibit reversible solar modulation with the change in the surrounding temperature.¹⁶ In comparison to its hydrogel counterpart, cellulose derivative of biopolymer gels such as hydroxypropylcellulose (HPC) shows sign of irreversible flocculation and structural instability during operation.¹⁷⁻¹⁸ Besides, both the structural stability and optical properties of PNIPAM hydrogel, can be preserved even after one year.¹⁹ Therefore, PNIPAM was chosen as the thermotropic candidate in Chapter 4 of this thesis to demonstrate the influence of ATO plasmonic heating on the climate adaptable smart window switching characteristics.

3.1.3 Thermally Responsive Hydrogel – Agarose Hybrid

To resolve the issue of dimensional instability (discrete volume reduction) in hydrogel during LCST transition, agarose was selected as an inactive hydrogel matrix for hosting of thermal responsive non-ionic surfactant. Glycerol as anti-freeze agent was adopted into thermotropic hydrogel system for tuning the thermal sensitivity and to achieve enhance thermal stability.

Solvent containing thermally responsive surfactants could be introduced into the hydrogel to manipulate its thermotropic properties without additional polymerization process.²⁰⁻²¹ The optical switch profile of thermal responsive surfactants is not as abrupt as thermal responsive hydrogels,²²⁻²³ making them more suitable for smart windows applications. Compared to other thermally responsive surfactants, such as poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide), 4-octylphenol polyethoxylate (Triton-X) provides total shielding of harmful UV rays below 300 nm by absorption.²⁴

Agarose was chosen as the inactive hydrogel scaffold since it has a large pore size in the range of 500 – 1200 nm, which allows rapid diffusion of the entrapped solvent.²⁵ Molecular structure of this polysaccharide enables the formation of stable hydrogels even at low

concentrations. The stable hydrogel is formed with suprafibers derived from the aggregation of helices due to its exterior hydroxyl functional groups. More importantly, agarose is a physical gel which dissolves in boiling water to yield random coils and undergoes gelation upon cooling to around 35°C. In comparison to chemical cross link hydrogels, the preparation of physical gel and its composite is facile and cost effective.

Among the various anti-freeze agent, glycerol is non-toxic and assume relatively high boiling point and polarity.²⁶⁻²⁸ Hence, binary solvent containing glycerol could help to enhance the cyclic stability of agarose hydrogel and subsequently lower the technical sealing requirement for hydrogel smart windows.

3.1.4 Thermally Responsive Ionogel – Polyurethane/Ionic Liquid Hybrid

The intrinsic properties of the thermotropic material system is of paramount importance to its operating stability and the choice of non-volatile ingredients including polypropylene oxide (PPO), imidazolium based ionic liquids and hexamethylene diisocyanate is a conscious effort in this thesis. Ionic liquids (ILs) are a vast group of salts with melting temperatures below 100°C.²⁹ Ionogels, namely “gels containing ionic liquids”, are soft semi-solid matters with three-dimensional network percolating throughout IL and can retain IL’s vital properties. What distinctly differentiates ionogel from hydrogels and organogels is the exceptional stability even at high temperatures due to negligible vapor pressure and the intrinsic thermal stability of the IL.

The selection of thermotropic ionogel compositions was based on the following considerations. Firstly, temperature-sensitive interactions such as hydrogen bonding should exist between polymer and IL as shown in **Figure 3.1**. PPO was selected not only for its commercial availability and application in polyurethane-based safety glasses, but also the existence of hydrogen bond acceptance sites. Other ether based polymer such as polyethylene oxide and its derivative are possible, but the increase in polymer polarity, would increase the mixture LCST.³⁰⁻³¹ Secondly, the IL selected should have suitable interaction with PPO and the selection of cations was due to existing critical ‘active’

hydrogens in the imidazolium cation that can construct hydrogen bonding with oxygen in PPO segment.³² Lastly, the selection of [NTf₂] anion is equally important and this anion is tested to form a subtle attraction with cation to balance against the PPO-cation interactions. Other anions with stronger (or weaker) hydrogen bonding tendency would disrupt (or strengthen) hydrogen bonding between cation and PPO, and may annihilate the LCST phenomenon.³²

More specifically, there are four possible hydrogen bonding sites in imidazolium cation which are critical for LCST behaviour with PPO. Other cations such as tetrabutylphosphonium [P₄₄₄₄] and tetrabutylammonium [N₄₄₄₄] were experimentally found to be immiscible with PPO due to the lack of hydrogen bonding capabilities. As for anions, replacing [NTf₂] with stronger basicity [PF₆] result in immiscibility of PPO with imidazolium based IL. This is due to the overwhelm cation-anion interactions, which disrupt the attractions between PPO and cation.

Figure 3.1 The possible hydrogen bonding sites between imidazolium based cation and (a) polypropylene oxide as well as (b) bis(trifluoromethylsulfonyl)amide anion. The different carbon atoms which are connected to the hydrogen bonding atoms are labelled from 1 – 5 accordingly. The hydrogen bonding from the C2 position are indicated with red dotted lines to represent the most active hydrogen bonding site. The above configuration is just a snapshot of one of the other many possible configurations. Note that there is no hydrogen bonding between bis(trifluoromethylsulfonyl)amide anion and PPO. Reprinted with permission from Reference.³³ Copyright 2017, American Chemical Society.

The primary driving force for LCST phase separation mechanism in this system is the hydrogen bonding between the protons of the imidazolium IL cation ring and the solvophilic oxygen atoms of the polymer. Hence, in this thesis, PPO with suitable Lewis basicity was chosen to compete with bis(trifluoromethylsulfonyl)imide anion (Lewis base) in attracting imidazolium cations (Lewis acid) to achieve a plausible LCST.

The participation of the aliphatic triisocyanates cross linker not only enable a free standing robust ionogel film but further endow the ionogel with kinetic stability to prevent bi-phasic separation. However, addition of isocyanate cross linker result in heterogeneous polymer – IL pregel mixture. Hence, ketone based solvent was used as a co-solvent to solubilize isocyanates and PPO. Methyl ethyl ketone (MEK) was chosen over other ketone based solvents due to its appropriate volatility to facilitate both the formation of homogenous ionogel and ease of solvent extraction after the curing process. In addition, MEK dilute the pre-gel mixture to increases the overall LCST which is essential during the curing process to achieve a homogenous ionogel network formation.

3.2 Synthesis Methods

3.2.1 Solvothermal Synthesis of ATO Nanoparticles

The conventional synthesis of continuous ATO dense film are still commonly explored as conductive substrates and IR reflective coatings.³⁴ These ATO coatings are deposited onto substrates *via* deposition techniques such as chemical vapor deposition,³⁵ sputtering³⁶ etc. However, due to the free electron relaxation principle as discussed in Chapter 2, Literature Review (LSPR in Plasmonic TCO), the synthesis and deposition methodology of transparent conducting oxides will indirectly affect their NIR reflection and absorption mechanism. Therefore, different wet chemistry methods to synthesize plasmonic ATO-NP have been considered and their pros and cons are discussed in **Table 3.1**. Briefly, solvothermal method was chosen for the synthesis of ATO nanoparticles because the high temperature post treatment which result in particle agglomeration can be avoided and short process cycle of around 15 minutes could be achieved.

Table 3.1 Comparison of the advantages and disadvantages for different reported synthesis methodology of Antimony Tin Oxide (ATO) nanoparticles.

Synthesis	Pechini ³⁷	Co-precipitation ³⁸	Hydrothermal ³⁹⁻⁴⁰	Solvothermal ⁴¹⁻⁴⁴
Description	Polycondensation of precursor to form an organic matrix scaffold with homogeneous metal cation distribution	Simultaneous Sn and Sb precipitation from supersaturated reagent	Elevated temperature and pressure to increase solubility of precursor in an autoclave with water as medium	Nonhydrolytic reaction with metal halides in an autoclave with alcohol as medium for oxygen source
Pro(s)	Good chemical homogeneity	Scalable process with well controlled stoichiometry composition and particle size	Lower process temperature compared to conventional solid-state reaction	Significantly lower process cycle time compared to hydrothermal. No capping agent required during synthesis
Con(s)	Removal of organic matrix at high temperature of around 500°, which might lead to irreversible hard aggregates	High calcination temperature of around 500°C which might lead to irreversible hard aggregates	Long process cycle time and difficulty of salt precursor ions removal. Repeated cleaning reduces yield.	Relatively expensive to use alcohol as reaction medium

The solvothermal synthesis of nanoparticle with ‘benzyl alcohol route’ is also known as S_N1 reaction in the field of organic chemistry. It involves aromatic benzyl alcohol which can form a stable carbocation intermediate as shown in **Figure 3.2**. Further intervention of a nucleophilic agent, result in hydroxyl leaving group, which act as oxygen source for formation of metal oxides. This is a universal approach where metal precursors are not limited to chlorides, but alkoxides, acetyl acetonates and acetates are suitable as well.^{41, 43}

S_N1 Reaction assisted synthesis of oxides

Figure 3.2 Depicts the S_N1 reactions mechanism between benzyl alcohol and metal salt precursor on the synthesis of metal oxides nanoparticles, proposed by Hu et al. R, R' represent -H and -M- where 'M' refers to metal respectively, or vice versa. Nu stands for nucleophilic agents such as chloride ions, amino, benzyloxy group and others. The reaction mechanism shows the production of oxygen source originated from benzyl alcohol, when used as reaction medium. Reprinted with permission from Reference.⁴² Copyright 2013, The Royal Society of Chemistry.

Generally, solvothermal synthesis temperature can range from 50 – 200°C. Specifically for synthesis of ATO, experimental conditions such as isothermal 100 and 150°C could result in complete reaction time of 20 and 2 hours, respectively.⁴⁴ The increment in temperature significantly reduces the cycle time. Organic entities that are formed at certain stage of the reaction could fulfil the role of a capping agent to prevent irreversible hard agglomerates. Furthermore, modification of existing technique with microwave assisted synthesis have been demonstrated to achieve 3 nm highly crystalline ATO nano particles with just 15 minutes of reaction time.⁴⁵

3.2.2 *In-situ* Polymerization and Physical Gelation of ATO/Polymer Gels Hybrid

The thermally responsive polymer/solvent system becomes turbid when it is heated above the LCST, and further divided by gravity into two optically clear layers upon prolong heating. This will deprive the solution of its optical reversibility.^{19, 46} Therefore, the formation of polymer gel network not only provide mechanical robustness but is also imperative to endow kinetic stability for stable and reversible optical switching. Several

considerations for the preparation of the transparent ATO/polymer gel nanocomposite, should be exercised base on principle of Rayleigh scattering. Rayleigh's law of scattering states that particle diameters should be below 40 nm for transparent nanocomposite. The influence of particle diameter and refractive index matching between polymer and nano particle can be better understand through the following equation:

$$\frac{I}{I_0} = e^{-\left[\frac{3\phi_p x r^3}{4\lambda^4} \left(\frac{n_p}{n_m} - 1\right)\right]} \quad (3.1)$$

where I and I_0 refers to intensity of the transmitted and incident light, respectively. r refers to radius of spherical particles, n_p refers to refractive index of particle and n_m refers to refractive index of matrix. λ refers to wavelength of light, ϕ_p refers to particle volume fraction and x refers to optical path length. From **Equation 3.1**, it is evident that any slight increase in the particle size will cause a significant amount of light scattering, if there is a refractive index mismatch between the particle and polymer matrix.

In this thesis, synthesized and purchased ATO nanoparticles were stabilized mainly by electrostatic repulsion for aqueous dispersion and steric repulsion for MEK dispersion, respectively. Both the synthesized and purchased dispersion of ATO-NP was subjected to standing test and no sedimentation was observed even after half a year. *In situ* polymerization and physical gelation was chosen as the integrated synthesis strategies such that the nanoparticles were always in their well dispersed state, before and after polymeric gel formation. In comparison to other composite synthesis approaches such as melt extrusion or dip coating, *in situ* polymerization and physical gelation allow higher nanoparticle loading, larger degree of mixing and the presence of solvent tends to improve the nanoparticle dispersion during polymer gel formation.

While the physical gelation process of agarose composite, is facilitated by thermally reversible non-covalent interactions including hydrogen bonding and electrostatic interaction of polymer strands, the *in-situ* polymerization procedure involves dispersion of ATO nanoparticles directly in the monomer of NIPAM or PPO solution and subsequent

polymerization of the pregel dispersion with free radical polymerization technique. For the case of polyurethane (PU) ionogel, the presence of IL poses challenge even to dispersion of hydrophobized silane grafted ATO nanoparticles in the pregel mixture. Hence, the pregel nanocomposite solution was placed in a 35°C warm water bath sonicator for 45 minutes prior to filling of the stationary mould for further curing. The viscosity of the pregel mixture increases during this pre-curing thermal treatment to prevent any sedimentation of ATO-NPs during the curing process. Subsequently, the MEK co-solvent for the ionogel synthesis were extracted during the vacuum drying process.

3.3 Characterization Techniques

3.3.1 Electron microscopy

The resolution of a microscope is determined by factors, such as lens quantity, quality as well as wavelength of illumination source. Investigation of nanostructures necessitates the use of electron microscopy (EM) with much shorter wavelength of electron as compare to visible light. Resolution of up to 0.5 Å was reported to be achievable by EM.⁴⁷ Since the primary particle size of ATO is around 15 nm, the two EM techniques that have been utilized in this thesis are namely the scanning electron microscopy and transmission electron microscopy.

3.3.1.1 Scanning Electron Microscopy (SEM)

SEM is a non-destructive testing technique that uses a focused beam of high energy electrons to generate a variety of signals at the surface of the sample. Apart from high resolution, a large depth of field of around 30 mm and high magnification of 10 x – 500,000 x could be achieved. As illustrated in **Figure 3.3(a)**, during electron beam and sample interaction, both elastic and inelastic scattering events occurs, resulting in a variety of secondary emissions. Among the various emissions, secondary electrons, backscattered electrons and characteristic X-rays are commonly harnessed to generate characteristic

information such as material's surface morphology, chemical composition and crystalline structure, respectively.

The depth of the interaction volume for the secondary emissions represent and explains the phenomenon of the observed image. For example, secondary electrons reside at the tip of the interaction volume (c.a. 50 – 500 Å) and hence the topological morphology of the specimen can be well imaged in secondary electron imaging (SEI) mode. As for backscattered electrons (BSE), the interaction volume is relatively much larger and the depth is in the range of several 10's of nm to 100 nm while characteristic X-rays which are responsible for energy dispersive x-ray (EDX) semi-quantitative analysis is in the micron meter range. Secondary electrons are the loosely bound electrons generated from the process of inelastic scattering. These electrons which are more surface sensitive, tends to provide intricate details of the material's surface topology. Therefore, the surface morphology of the solvothermal synthesized ATO were observed by means of SEM, SEI mode in this thesis.

Figure 3.3 (a) Schematic illustrating the electrons specimen interactions within the interaction volume. Image was sourced from the internet. Copyright @ GLA (source: <http://www.gla.ac.uk/>). (b) Schematic representation of the individual components of a typical SEM. Image was sourced from the internet. Copyright @ Wikispace (source: <http://cellularphysiology.wikispaces.com/>).

Characteristic X-rays are emitted from elements when electrons make discrete transitions to lower atomic energy levels. Unique X-rays characteristic for each element thus enable elemental composition analysis to be performed. During operation of SEM in EDX mode, high accelerating voltage of around 20 kV are used to excite the characteristic X-ray of interest, since these continuum X-rays typically lie at the bottom of the interaction volume. For the synthesized ATO-NP, EDX analysis was conducted to semi-quantitatively verify the amount of percentage Sb doping. This allows us to effectively correlate the free electron dopant in ATO to the effect of NIR absorption and its resulting photothermal properties. It is also worthwhile to note that there are some limitations to the EDX technique, such as the inability to separate characteristic X-rays of similar energies and the inability to detect light elements. Therefore, EDX can only be regarded as a semi-quantitative testing technique.

While for operation in backscattered electron imaging (BEI) mode, BSE are produced from the elastic scattering of incident electrons with the interaction volume and re-emitted from the sample towards the backscattered electron detector. With the increase in sample atomic number, backscattering effect of electrons becomes more prominent, resulting in greater contrast. Hence, identification of regions differing in compositions is possible since the intensity of contrast is proportional to the average atomic number of the interaction volume. This imaging mode was not used for materials characterization in this thesis.

A typical SEM includes electron gun, condenser lens, magnetic lens, scanning coil and a sample holder, as depicted in **Figure 3.3(b)** and the operation procedure of the SEM consists of electron production, electron acceleration, electron focusing, electron scanning, electron interaction, signal detection and signal display. Electrons in SEM can be produced *via* thermionic or field emission. Thermionic emission supplies heat energy to the filament (e.g. tungsten or LaB₆) for electrons to overcome the work function of the material while field emission supplies energy in the form of electric field to lower the work function, allowing electrons to ‘tunnel’ out of the source. After production of electrons, they are accelerated towards the sample by applying a voltage to the anode. As electrons travel from the source to sample, they will pass through a series of condenser and objective lenses, which

will help to focus the beam. When the beam of electrons reaches the sample, a scanning process of the sample known as rastering occurs and electron sample interactions give rise to secondary emission which are harnessed for different imaging modes as discussed previously. It is important that the operations of EM are conducted under high vacuum condition to prevent any electron scattering event.

3.3.1.2 Transmission Electron Microscopy (TEM)

Apart from SEM, other state-of-the-art information including crystal structure, size distribution, defects, strain, atomic level chemical information etc., could be obtained with high spatial resolution microscopy such as TEM. High voltage acceleration in TEM allows high speed electrons to exhibit particle and wave duality characteristic while transmitting through thin samples of around 100 nm thick. Resolution at less than 1 nm and magnification of up to 1, 000, 000 times could be achieved in TEM mainly attributed to 2 factors.

Figure 3.4 Schematic outlining the basic operating components in a TEM. Image was sourced from the internet. Copyright @ ETH (source: <http://www.microscopy.ethz.ch>).

Firstly, as observed from the interaction volume in **Figure 3.3(a)**, the amount of primary beam scattering is insignificant and secondly, the usage of high accelerating voltage around 100 – 300 kV. The relation between resolution, accelerating voltage and electron wavelength could be explained with **Equations 3.2 and 3.3**. Where ‘d’ refers to the minimum resolvable distance, λ refers to wavelength and ‘NA’ refers to the numerical aperture.

$$d = \frac{0.61\lambda}{NA} \quad (3.2)$$

$$\lambda = \frac{h}{\sqrt{2meV}} \quad (3.3)$$

while ‘h’ refers to the plank constant, ‘m’ refers to mass of electron and ‘eV’ refers to electron-volts. The application of a large voltage result in a small wavelength which facilitate a very small resolvable distance (i.e. high resolution). However, if the sample is much thicker than 100 nm, then correction for sample density and absorption should be taken into consideration during analysis. Hence, TEM can provide us with information pertaining to ATO primary particle size, crystallinity and its dispersion state in the PNIPAM polymer matrix.

The TEM operation can be classified into electron source, electromagnetic lens system, specimen holder and imaging system, as seen from the various basic components in **Figure 3.4**. Electrons are first produced and accelerated from the source. The electromagnetic lens system then helps to focus the electron beam. Upon electron beam interaction with specimen, scattered electrons are again refocused, magnified and projected onto viewing screen.

Figure 3.5 Schematic illustrating the basic operating component and beam path of a TEM in (a) diffraction mode and (b) imaging mode.

The two operation modes in a TEM that have been commonly used for analysis, are illustrated in **Figure 3.5**. Firstly, with the electrons scattered by the specimen, the objective lens construct diffraction patterns in the back focal plane and ‘consolidate’ them to generate an intermediate image one at the image plane. Hence, both diffraction pattern and image are simultaneously present in the TEM and depending on the focusing of the intermediate lens, the resulting intermediate image two will be magnified by the projector lens system on the viewing screen. The switching between real space image and reciprocal space diffraction can take place easily by changing the strength of the intermediate lens. In the imaging mode, objective aperture can be inserted in the back focal plane to selectively exclude electron beam which would result in different types of final images such as bright field (BF), dark field (DF) and high-resolution TEM (HR-TEM). Similarly, by insertion of a selected area diffraction (SAD) aperture, the region of which the diffraction is obtained can be defined accordingly.

In this thesis, BF-TEM mode was selected for the investigation of ATO primary particle size, crystallographic spacing between adjacent lattice (d-spacing), and the dispersion state of ATO particles in PNIPAM and Agarose. Inherent atomic mass difference between ATO and the polymers result in the optical contrast. ATO which is of higher atomic mass will

scatter electrons more strongly as compare to polymer, hence ATO particles appear darker. This mass contrast BF imaging allows us to effectively identify the individual particle and polymer as well as to evaluate the dispersion state of ATO particles.

3.3.2 UV-Vis-NIR Spectroscopy

The UV-Vis-NIR spectroscopy measure the reflected or absorbed or transmitted rays after illumination of a specimen. The detection region of UV-Vis-NIR spectroscopy typically lies between wavelength of 200 – 2500 nm, identical to that of the solar spectrum, which is why it is commonly utilized for investigation of photovoltaic materials. The detection range are typically classified into three regions where Ultra-violet (UV), Visible (Vis) and Near-infrared (NIR) equivalent wavelength are 200 – 400, 400 – 800 and 800 – 2500 nm, respectively.⁴⁸ The relation between absorbance (A) and transmittance (%T) can be described with the Beer Lambert Law.⁴⁹

$$A = \log(I_0/I) \quad (3.4.1)$$

$$\%T = 100 * I/I_0 \quad (3.4.2)$$

$$A = \log(100/\%T) \quad (3.4.3)$$

$$A = 2 - \log_{10}(\%T) \quad (3.4.4)$$

Where I_0 refers to the incidence ray entering the specimen and I refer to transmitted ray exiting from the specimen. During transmittance and reflectance measurement, the beam path of the ray in the spectrophotometer are as shown in **Figure 3.6**. For transmittance measurement, the specimen is located at the exterior of the integrating sphere and close to the incident beam. On the contrary, specimen should be located at the reflectance port such that integrating sphere interior reflective surface (e.g. Barium sulfate or Magnesium oxide) could allow beam reflection towards detector.

Figure 3.6 Schematic illustrating the beam path for (a) transmittance and (b) reflectance measurement inside the spectrophotometer equipped with an integrating sphere (green dotted line). Picture obtained from the internet. Copyright @ PerkinElmer.

In this thesis, dispersed plasmonic ATO-NP exhibit steady state absorption in the NIR,¹⁵ while the thermotropic polymer including PNIPAM, Agarose hybrid and PU based ionogel, modulate the solar spectrum in a broadband manner by changing its optical state from transparent to opaque milky white for solar reflection properties.^{33, 50} For a smart window material, the optical property of interest for the hybrid ATO/polymer gel composite is the percentage transmittance as a function of temperature. For measurement of percentage transmittance at equilibrium temperature of 40°C as an example, the peltier heater installed in the spectrophotometer was set to raise the temperature at a rate of 20°C min⁻¹ and isothermal at 40°C for 10 minutes to achieve thermal equilibrium before performing a transmittance measurement. The resulting spectrum at different temperature further allow us to evaluate the integrated visible (T_{lum}), infrared (T_{IR}) and solar transmittance (T_{sol}) according to the following equation:

$$T_{int} = \int T(\lambda) E_{\lambda}(\lambda) d\lambda / \int E_{\lambda}(\lambda) d\lambda \quad (3.5)$$

$T(\lambda)$ refers to the transmittance measured by spectrophotometer. While E_λ can refer to ϕ_{lum} or ϕ_{sol} , which is the standard visible efficiency function of the photopic vision for human eyes as shown in **Figure 3.7** inset,⁵¹ or the solar irradiance spectrum for air mass (AM) 1.5 when the sun is standing at 37° above the horizon as shown in **Figure 3.7**, respectively.

Figure 3.7 ASTM G173-03 reference spectra. Black line, extraterrestrial indicates AM 0, referring to radiation level outside of the earth surface. While red line, direct + circumsolar indicates AM 1.5, refer to the radiation level after passing through the atmosphere 1.5 times.⁵² Inset shows the standard visible efficiency function of the photopic vision for human eyes.⁵³

3.3.3 X-ray Diffraction (XRD)

X-ray has a wavelength of $10^{-8} - 10^{-11}$ nm and is a kind of electromagnetic wave. The wave and particle duality of X-rays enable diffraction to acquire crystallography information of the crystallized samples. When a monochromatic incident X-ray beam strikes on the surface of the specimen, atomic orbital electrons scatter the X-ray and cause an amplitude or phase change. The diffracted X-rays will then interfere in a destructive or constructive manner, where the summation of the scattered X-rays will either cancel each other out in almost all directions or they could mutually reinforce each other, respectively. This X-ray derived energy density distribution is also known as X-ray diffraction (XRD) pattern.

Bragg's law indicates that when a crystal with interplanar spacing 'd' is irradiated by X-ray beam of comparable wavelength, elastically scattered X-ray beams that contribute to the constructive interference will result in specific 2θ angles.⁵⁴

$$n\lambda = 2d\sin\theta \quad (3.6)$$

where n refers to any integer, λ refers to the fixed X-ray wavelength and θ is the diffraction angle measured by the detector. The derivation of Bragg's law can be explained with the geometrical illustration in **Figure 3.8**. There is a difference in distance travelled by the X-ray irradiation striking on the top and bottom plane of atoms. The difference in configuration of atoms could result in the difference in distances which causes phase shift of the reflected X-rays.⁵⁵

Reflected X-rays with constructive interference can be obtained only when,

$$n\lambda = BC + CD \quad (3.7.1)$$

$$BC = CB \quad (3.7.2)$$

$$n\lambda = 2BC \quad (3.7.3)$$

$$\sin\theta = BC/d \quad (3.7.4)$$

$$\text{Hence, } n\lambda = 2d\sin\theta \quad (3.7.5)$$

Figure 3.8 Illustration of incident and diffracted X-rays on two different planes of atoms separated with an interplanar spacing 'd'. The triangle 'ABCD' within the d-spacing allows the derivation of Bragg's law as shown in **Equation 3.7.1 – 3.7.5**.

Figure 3.9 Schematic of (a) XRD instrument with Bragg Brentano $\theta - 2\theta$ configuration. Image is sourced from the internet. Copyright @ UCL (Source: <http://pd.chem.ucl.ac.uk/>). While (b) shows the typical XRD patterns conducted with commercial and synthesized ATO nanoparticles.

The Bragg-Brentano diffraction is a common $\theta - 2\theta$ configuration for XRD analysis. Different modes of operation are possible in a XRD instrument. For example, as shown in **Figure 3.9(a)**, the X-ray source can be fixed while rotating both the specimen stage and detector by θ and 2θ , respectively, or fixing the specimen stage and rotating both the X-ray source and detector by θ simultaneously. Hence, it is essential for a goniometer to be located at the center of the XRD instrument to govern the different mode of rotations.⁵⁵

In this thesis, XRD was employed to provide crystallographic information of synthesized ATO particles. Different Sb atomic% doping in Sn resulted in different primary particle size, and the average of which could be estimated with the aid of Scherrer's equation. Furthermore, the plasmonic property of ATO arises from its free electron carriers which originate from Sb dopant.

Therefore, it is necessary that XRD analysis as shown in **Figure 3.9(b)** could qualitatively provide evidence of Sb dopant entering the Sn lattice. It is worth mentioning that optimal size range of particle powder sample should be around $1 - 5 \mu\text{m}$. Otherwise, peak broadening in XRD pattern could be observed for ATO where the powder size is much smaller.

3.3.4 Differential Scanning Calorimetry (DSC)

DSC is a thermal analytical tool that is widely used to study thermal isotherms such as phase transition or change in heat capacity of materials.⁵⁶ Material properties including oxidative stability, latent heat of fusion, glass transition, crystallization, melting temperature could be evaluated by DSC. The measurement principle of the DSC is to compare the rate of heat flow to the specimen and a reference material when subjected to the same thermal program in a temperature controlled environment. As illustrated in **Figure 3.10(b)**, during a typical thermal program, temperature of the two platinum resistance thermocouples is compared and electrical power would be supplied to individual heater so that both temperature at both specimen and reference side matches that of the program temperature. The amount of energy compensated for the specimen to main zero differential temperature will then be displayed *via* a graph with heat flow as a function temperature.⁵⁷

Materials transitions that are accompanied by a change in specific heat will result in a discontinuous power signal and the corresponding exothermic or endothermic enthalpy changes provide peak areas that are in proportion to the total enthalpy change. For PNIPAM/ATO composite, DSC was employed to verify the photothermotropic properties of the hybrid.

Figure 3.10 Schematic showing a (a) DSC instrument from School of Material Science & Engineering (MSE), Nanyang Technological University (NTU) and (b) its internal operational set-up.

PNIPAM hydrogel has a lower critical solution temperature (LCST) transition temperature of around 33°C,⁵⁶ which correspond to the abrupt optical change from transparent to opaque. Therefore, with addition of plasmonic ATO particles, transition temperature of PNIPAM/ATO composite was determined by DSC to ensure there was no change in LCST. In addition, DSC was also used to characterize the freeze point and enthalpy of Agarose hybrid with different content of glycerol/water binary solvent.

Similarly, the LCST transition of IL/polymer was measured by DSC. The transition temperature measured by DSC is around 5 – 8 °C higher compared to cloud point method and they both show a linear trend. Since the ionogel is intended for smart window application, the determination of ionic liquid/polymer transition temperature should be conducted through optical means. Besides, when PPO ratio increases in the mixture, viscosity increases and inaccurate transition temperature determination by the DSC might result from the minute milligram scale sample size.

3.3.5 Thermal Gravimetric Analysis (TGA)

TGA is another widely used thermal analytical tool to determine thermal stability of a given specimen. Basically, during thermal decomposition and gasification, specimen accurate mass loss is determined by a micro balance as shown in **Figure 3.11(b)** Decomposition profile under pyrolytic or oxidative environment is possible with the selection of either nitrogen or air as the chamber purge gas. Furthermore, by varying the heating rate, different thermal decomposition profile could be generated for investigation of decomposition mechanism and kinetics. TGA data are typically reproducible within the limit of $\pm 1^\circ\text{C}$ and each run only requires 5 – 50 mg of specimen, hence caution should be exercised when evaluating for representative bulk specimen properties. In this thesis, TGA technique was adopted to evaluate the thermal stability of the thermotropic ionogel since the addition of imidazolium based ionic liquid could gradually enhance the onset thermal degradation of the PPO polymer.

Figure 3.11 Picture showing the (a) actual TGA Q500 from NTU MSE. While schematic in (b) illustrate the working components in a TGA. Image is from the internet. Copyright @ Iowa State University of Science and Technology.

3.3.6 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is often used to investigate the chemical functional group of a specimen through infrared absorption which causes molecular vibrational transition. Functional groups exhibit complex vibrations such as twisting, wagging, bending etc., at certain allowed frequencies. When electromagnetic radiation of the corresponding vibrational frequency (infrared radiation) is applied to the molecules, it may be absorbed and leads to transition of the molecular vibrational energy levels. Analogous to our human fingerprint, each functional group has unique frequencies like a chemical fingerprint which are used for their identification. Hence, molecular structure elucidation could be performed with FTIR analysis to identify presence of different functional groups in chemical compounds of different forms, i.e. solid, liquid or gaseous.

The working principle of FTIR is based on interferogram which consist of both constructive and destructive interference, generated by the interferometer. Upon infrared interferogram irradiation, different chemical functional groups in the specimen absorbs a certain amount of incident energy while the remaining energy travel to the detector. With

a laser beam as reference, the detector could compute the variation in energy as a function of time for all wavelength simultaneously. However, a better interpretation of the graph spectra is presented with the aid of Fourier transform where energy vs time spectra is being converted to intensity vs frequency, or commonly seen as transmittance/absorption spectra.

In this thesis, FTIR analysis of the different chemical functional group in the thermotropic ionogel provide us with an insight of the vacuum enabled film curing process. The presence of MEK solvent in the pre-gel mixture during film curing is of utmost importance to achieve a homogeneous state, i.e. transparent and none phase separated. Therefore, retention of MEK and formation of urethane linkage in the ionogel was verified by FTIR.

3.3.7 Photothermotropic Measurement

The optical properties of thermotropic smart windows are usually investigated by UV-Vis-NIR spectrophotometer modified with temperature controller.^{16, 58} This spectroscopy technique coupled with a peltier heater reveal the intrinsic thermal optical property of the chromogenic material. However, for real smart window applications, dynamic solar irradiation is the key driver for the increment in temperature, instead of a static heating source. Therefore, photothermotropic characterization methodology in this thesis was introduced to better elucidate the optical switching behavior of thermotropic materials for the very first time.⁵⁰

The primary purpose of this characterization was to realize a realistic method for evaluating thermotropic smart window optical transitions. Secondly, to investigate the influence of NIR triggered plasmonic heating on the thermotropic ATO/gel hybrid optical properties. Lastly, to provide an effective single wavelength screening and optimizing methodology for thermotropic smart window materials.

As shown in **Figure 3.12**, the distance between the specimen and the solar irradiation source was first determined and set to be one sun, i.e. 0.1 W cm^{-2} . The detecting wavelength was chosen to be 550 nm in the visible region because it is the most sensitive to the human

eyes⁵⁹ and 1700 nm, which is free from hydrogel water absorption interference in the NIR region.⁵⁰ Upon solar irradiation, both the optical power transmittance and temperature could be collected in real time and further used for evaluation of optical switching characteristics such as solar modulation ability and response speed.

It is important to note that this characterization methodology currently only offers a semi-quantitative evaluation of thermotropic smart window optical properties. The detector is detecting the transmitted solar irradiation only at a normal – normal configuration and any form of scattering effects are not accounted for. Therefore, in comparison to results from UV-Vis-NIR spectroscopy, it is only possible to observe similar but not identical data.

Figure 3.12 Picture of (a) modified solar simulator optical system and a close-up view of the (b) sample holder. (c) Schematic illustration of system equipped with (i) a xenon lamp irradiation light source, (ii) sample holder, (iii) visible or NIR photo detector with an attenuator, (v) optical power meter and (iv) is the pyrometer. The hydrogel sample shown in this figure has a dimension of 3 x 2.5 x 0.008 cm. Reprinted with permission from Reference.⁵⁰ Copyright 2017, American Chemical Society.

3.3.8 Energy Saving Model House

Optical characterization techniques such as UV-Vis-NIR and photothermotropic measurements provide us with an insight to the thermotropic materials performance. However, these characterization techniques do not reveal direct evidence of the materials energy saving performance. In this thesis, we designed and constructed a laboratory scale energy saving model house that could be affixed with various smart window materials as shown in **Figure 3.13**. Styrofoam material was chosen for the model house such that heat would build up within the interior during solar irradiation for extended hours. A xenon lamp solar simulator was chosen as the irradiation source with a thermocouple installed in the interior of the model house to provide real time temperature detection.

Figure 3.13 Picture showing the (a) laboratory scale model house. A "NTU" logo was placed in the mini model house for visual check of window transparency during the solar irradiation process. (b) Schematic illustration of the experimental setup for monitoring indoor temperature of model house equipped with windows of various materials and (c) exploded view of the Styrofoam model house affixed with smart window glass panel. Reprinted with permission from Reference.³³ Copyright 2017, American Chemical Society.

3.3.9 Computer Simulation – Molecular Dynamics Simulation (MDS)

MDS techniques are widely employed to investigate the underlying process in applications such as protein solvation and binding, DNA strands dynamics,⁶⁰ membrane processes,⁶¹ drug polymorph and discovery.⁶² MDS resolve classical equations (e.g. Hamiltonian mechanics) for motion of molecules to achieve time evolution of a system. The simulation serve as a bridging link between experimental and theoretical hypothesis and simulation typically involves numerical methods and computers. The typical steps of MDS are namely initialize, forces, motion, properties and summarize. Briefly, initialize consist of setting up the initial system with inputs such as interaction function between various particles (force field), coordinates and velocities. Next, the atomic forces and motion are being computed and parameters such as coordinates and velocities are updated according to the equation of motion. Thus, the statistics and physical properties could be obtained. Lastly, decide if the above process need to be repeated or to generate a final summary. It is worthwhile to note that different types of interactions function include bonded and non-bonded interactions, constitute the force field. Example of bonded interactions refer to bond vibration, angle vibration and torsion potentials while non-bonded interactions refer to short range Van der Waals forces and long ranged electrostatic charge.⁶³

Through MDS, static and dynamic system properties can be obtained. Properties such as kinetic energy, temperature, configuration energy, pressure, specific heat, pair correlation (i.e. radial distribution function) and structural factor could be revealed in the case of static system. Whereas, properties such as mean squared displacement and velocity autocorrelation could be achieved for dynamic system.⁶³ In this thesis, the creation of novel ionogel necessitates the need to investigate and unveil the underlying working principle for its thermotropic origin. Unlike classical PNIPAM hydrogel LCST mechanism, the LCST phenomenon for polymer/IL interactions are rarely discussed. Therefore, we utilized MDS to provide an atomic resolution of the phase separation mechanism. The understanding in interaction of the ionogel constituent enabled us to perform on-demand tuning of its transition temperature.

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Chapter 4

PNIPAM/ATO Dual-Responsive Nanocomposite: Toward Climate-Adaptable Solar Modulation Smart Windows

*In this chapter, a novel fully autonomous photothermotropic material made by hybridizing poly(*N*-isopropylacrylamide) (PNIPAM) hydrogel and antimony–tin oxide (ATO) is presented. The near-infrared (NIR)-absorbing ATO acts as nano heater to induce the optical switching of the hydrogel. Such a new passive smart window is characterized by excellent NIR shielding, photothermally activated switching mechanism, enhanced response speed, and solar modulation ability. Systems with 0, 5, 10, and 15 atomic% Sb-doped ATO in PNIPAM were investigated, and it was found that 10 wt% Sb-doped PNIPAM/ATO exhibits the best response speed and solar modulation ability. Different film thicknesses and ATO contents will affect the response rate and solar modulation ability. Structural stability tests at 15 cycles under continuous exposure to solar irradiation at 1 sun intensity demonstrated the performance stability of such a photothermotropic system. It was concluded that such a novel photothermotropic hybrid can be used as a new generation of autonomous passive smart windows for climate-adaptable solar modulation.*

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4.1 Introduction

PNIPAM hydrogel exhibits excellent optical switching performance and had been of great interest in the field of thermotropic smart windows.¹⁻² The requirements of such thermotropic smart window are multi-fold, including sealing stability,³ thermal and visual comfort control.² However, thermotropic smart windows are still haunted by the incompetency to “intelligently” adjust their transparency in accordance with complex outdoor climate.⁴⁻⁵

The first report on thermotropic smart window switching problem was in 2005,⁴ where optical switching could not take place in cold climates even in the presence of high intensity solar luminance. This is because the thermotropic material in that report is only thermoresponsive, hence switching mostly depends on surrounding temperature despite the intensity of sunlight. Innovative solutions such as lowering transition temperature of hydrogel,³ joule-heating induced switching,⁶ and addition of solar absorber,⁵ had been proposed and investigated. Nevertheless, these strategies are unable to provide climate adaptable optical switching without compromising of thermal optical properties and aesthetic appearance.

In this chapter, the switching behavior problem of hydrogel smart window was resolved by hybridizing PNIPAM hydrogels with dispersed antimony tin oxide (ATO) nanoparticles. Although TCO's photothermal effect has been utilized in photo-catalysis,⁷ ablation therapy,⁸ and laser engraving,⁹ this work is the first to explore its role in thermotropic systems. When PNIPAM-ATO composite hydrogels (PATO) are exposed to sunlight irradiation, as demonstrated in **Figure 4.1**, dimming control could be facilitated and accelerated by plasmonic heating of ATO under glaring sunlight even when the outdoor temperature is far below the transition point of PNIPAM hydrogel. Besides modulation in transparency for dimming control, the addition of ATO also assists in NIR shielding to alleviate air-conditioning burden for cooling in tropical climates. In this chapter, parameters including ATO doping, nanoparticle content and composite hydrogel thickness have been systematically studied and optimized. The findings in this study will provide

further insight into the future research direction required to develop an ‘ideal’ passive glazing.

Figure 4.1 Sketched architecture of the proposed photothermotropic smart window in its (a) clear and (b) translucent state. The size and color fraction of the arrows indicate the magnitude and fraction of transmitted solar spectrum, respectively. Reprinted with permission from Reference.¹⁰ Copyright 2017, American Chemical Society.

4.2 Experimental Methods

4.2.1 Materials

N-iso-propylacrylamide (NIPAM, $\geq 98\%$, purchased from Wako Pure Chemical Industries Ltd), *N,N'*-methylenebis(acrylamide) ($\geq 99\%$, cross-linker, purchased from Sigma-Aldrich), *N,N,N',N'*-tetramethylethylenediamine (TEMED, accelerator, 99%, purchased from Sigma-Aldrich), Ammonium peroxydisulfate (initiator, 98%, purchased from Alfa Aesar), and Multipurpose sealant (Selleys All Clear) were used without further purification. Deionized water (18.2 M Ω) was used throughout the experiments. (ATO) Tin(IV) tetrachloride ($\geq 99\%$, purchased from Sigma-Aldrich), Antimony(III) trichloride ($\geq 99.0\%$, purchased from Sigma-Aldrich), Benzyl alcohol (99%, purchased from Alfa Aesar), Tetramethylammonium hydroxide (TMAH, 2.38% - without surfs, purchased from Kanto Kagaku, Singapore)

4.2.2 Preparation of ATO Nanoparticles

Table 4.1 Formulation of different Sb dopant content in solvothermal synthesized ATO for 10, 15 and 35 wt% aqueous dispersions, used for preparation of the PATO nanocomposite.

Solid Weight (%)	10				15			35		
%Sb	0	5	10	15	0	5	10	0	5	10
ATO (mg)	100	100	100	100	100	100	100	100	100	100
TMAH (μ L)	50	100	150	200	200	250	300	126	156	186
H ₂ O (μ L)	850	800	750	700	367	317	267	60	30	0

Antimony tin oxide of different Sb content doping was synthesized via the benzyl alcohol route.¹¹ Briefly, for a 10 wt% Sb doped ATO, 2.7 mmol of SnCl₄ and 0.3 mmol of SbCl₃ were dissolved in 50 mL of benzyl alcohol. The mixture was then stirred for one hour before being transferred to a Teflon-lined autoclave which was kept at 200°C for 24 hours. The system was cooled to room temperature naturally, and the nanoparticles were separated via centrifugation at 1000 rpm for 15 minutes and three times repeated washing by re-suspending in ethanol. The ATO nanoparticles were then dried in a vacuum oven at 70°C for 24 hours and powdered with agate mortar. The targeted Sb doping content is 0, 5, 10 and 15 wt%. To prepare the aqueous dispersions of different solid weight content, TMAH of different ratio was added accordingly as shown in **Table 4.1**.¹²

4.2.3 Preparation of PNIPAM/ATO – Interlayer Glass Assembly

The nanocomposite was synthesized by *in situ* polymerization of NIPAM in deionized (DI) water with the addition of ATO nanoparticles. Monomer solution, (4.5 mL) containing 410 mg of NIPAM and 32.5 mg of N,N'-methylenebis(acrylamide) was mixed with 46.9 μ L of aqueous ATO dispersion of different solid weight content. ATO in the pre-gel solution has a final concentration of 1.2, 2 and 5 mg mL⁻¹ for 10, 15 and 35 wt% ATO aqueous dispersion respectively. As for GO, same formulation was adopted except that the amount of swelling agent was kept at a constant volume. 1 wt% of aqueous GO was added

at 93.8 and 140.7 μL , which resulted in a concentration of 0.2 and 0.3 mg mL^{-1} for the pre-gel solution, respectively. Based on several PNIPAM formulation trial conducted, a larger volume reduction of hydrogel at temperature above LCST was observed when higher content of methylene bis-acrylamide crosslinker was present in the system. The large volume change of PNIPAM during LCST can be attributed to the high cross-linking density which often result in hydrogel low swelling ratio. Hence, an appropriate amount of methylene bis-acrylamide was chosen such that hydro-gelation of PNIPAM could occur while excessive volume reduction at temperature above LCST could be avoided. For a 0.4 mL of degassed pre gel solution, 40 μL of N,N,N',N'-tetramethylethylenediamine and 14 μL of 5 wt% aqueous ammonium persulfate were added in sequence to initiate the free radical polymerization. The solution was sandwiched in between two clean glass slides and left for reaction to be complete at room temperature for 24 hours. Samples with thickness of 80 and 180 μm were successfully fabricated with the aid of a spacer in between the two glass slides. The edges of the glass slides were sealed with sealant to prevent water evaporation from the swollen hydrogel. Similarly, the same fabrication process was adopted for the neat hydrogel sample except that ATO/DI or GO/DI was not added. For convenience, the symbol of x and y in PATO-x-y represents the corresponding hydrogel with different ATO content and film thickness respectively, for example, PATO-2-80 stands for 2 mg mL^{-1} of ATO content in 80 μm thick PNIPAM film. Same applies for PNIPAM/GO.

4.2.4 Characterization

A) X-ray diffraction (XRD) analysis of ATO were conducted using XRD Bruker D8 (Cu $K\alpha$ radiation at 1.542 $\text{\AA}$). **B) Energy dispersive X-ray spectroscopy (EDS)** of Sb doped ATO was obtained on INCA X-act system attached to JEOL JSM 7600-F FESEM field-emission scanning electron microscope. **C) High resolution transmission electron microscopy (HR-TEM)** JEOL JEM 2010 and **D) Energy filter TEM** equipped with an integrated OMEGA filter (Carl Zeiss LIBRA®) was used for bright field imaging of ATO crystal size and microstructure of freeze-dried composite for ATO nanoparticle dispersion in PNIPAM, respectively. **E) Dynamic shear mechanical tests** were performed with a 25

millimeter parallel plate using a Discovery hybrid rheometer (DHR-3, TA Instruments, USA) at room temperature of 25°C. The linear viscoelastic range was first determined by testing a neat hydrogel gel from 0.001% strain to 1000% strain, and 0.1% strain was chosen to evaluate modulus of gels. Frequency sweep were conducted from 1 rad s⁻¹ to 500 rad s⁻¹ with a fixed gap of 500 μm. **F) Differential scanning calorimeter** (TA Instruments, USA Q10) with ramping rate of 3°C min⁻¹ was used to characterize the specific heat flow of PNIPAM/ATO under N₂ atmosphere. **G) Xenon lamp irradiation** equipped with an AM 1.5 filter was used to evaluate the photothermal effect of ATO in response to solar radiation at 1 sun intensity (100 mw cm⁻²) by measuring the change in temperature of aqueous ATO dispersion with continuous stirring. **H) Thermometer** (FLUKE 54-2 H) and a Fluke 80 PK-1 Beaded K-Type Probe were utilized for this temperature measurement. To verify the photothermal responsive switching mechanism of PATO as well as its response speed and solar modulation ability, a Xenon lamp, Newport 6259, 300W Xenon, UV Enhanced Arc Lamp (Ozone Free), of wavelength (200 to 2400 nm) was utilized as the irradiation light source in the laboratory with a constant room temperature of 21°C. **I) Newport optical detectors** namely, 918D-SL-OD3R (Silicon Detector, 400 to 1100 nm) and 918D-IR-OD3R (Germanium Detector, 780 to 1800 nm) which were set to be detecting at single wavelength of 550 nm (VIS) and 1700 nm (NIR) in the normal-normal configuration, were used to detect any changes in transmittance during the experiment. Any background irradiation detected were zeroed in Newport Optical Power Meter (1918-R) before manually recording changes in power reading during the experiment. **J) Pyrometer (Sentry ST677)** with high 50:1 distance to spot ratio was used to detect the changes in temperature of the prototype window. Detailed experimental setup could be seen from **Figure 4.2** as well as **Figure 3.12**. **K) UV-Vis-NIR spectrophotometer** (Cary 5000, Agilent, USA) at normal incidence was used to collect the transmittance and absorbance spectra in the wavelength range of 250–2500 nm. The spectrophotometer was equipped with a heating and cooling stage (Linkam, PE120).

Figure 4.2 Schematic of modified optical system equipped with (a) xenon lamp irradiation light source, (b) sample holder, (c) VIS/NIR detector with attenuator (d) optical power meter and (e) pyrometer. Reprinted with permission from Reference.¹⁰ Copyright 2017, American Chemical Society.

4.2.4.1 Evaluation of Photothermotropic Properties

The initial transmittance intensity of the solar simulator detected at both 550 nm and 1700 nm were taken to be 100% and subsequent decrease in power intensity during the measurement were linearly converted to percentage transmittance, labelled as %T₅₅₀ and %T₁₇₀₀, respectively. The response rate and solar modulation ability of hydrogel were systematically investigated as a function of time. Solar modulation ability was calculated based on the percentage transmittance change during the irradiation. Average visible transmittance was calculated by taking the average of the initial transmittance of the specimen at (t = 0 s) and final transmittance value at (t = 600 s). Based on **Equation 4.1**, integral transmittance data of the solar spectrum could be calculated.

$$T_{int} = \int T(\lambda) E_{\lambda}(\lambda) d\lambda / \int E_{\lambda}(\lambda) d\lambda \quad (4.1)$$

Where $T(\lambda)$ refers to the transmittance measured by spectrophotometer at wavelength λ and $E_{\lambda}(\lambda)$ is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon). %T₍₃₈₀₋₇₈₀₎ and %T₍₇₈₀₋₂₅₀₀₎ refers to integral transmittance in wavelength ranges of 380 – 780 nm for visible region and 780 – 2500 nm in the infrared region of sunlight, respectively.

Average $\Delta T_{(380-780)}$ were obtained by taking the average of $T_{(380-780)}$ at 20 and 35.5°C. Solar modulation ability, ΔT_{int} were obtained by **Equation 4.2**.

$$\Delta T_{int} = T_{int,x^{\circ}C} - T_{int,y^{\circ}C} \quad (4.2)$$

4.3 Principle Outcomes

4.3.1 Effect of Sb doping in ATO Nanoparticles

In this chapter, 0, 5, 10 and 15 wt% Sb doped ATO was first prepared by solvothermal. From **Figure 4.3**, HR-TEM images of ATO nanoparticles with different wt% Sb doping shows that they are single crystalline and predominantly spherical. ATO nanoparticles with average size of about 12.1, 11.4 and 9.0 nm for Sb doping content of 0, 5 and 10 were observed respectively. Further, from **Figure 4.3(f)**, the interplanar distance for 10 wt% Sb doped ATO particles was measured to be 0.32 Å. This corresponds well with the reported interplanar distance for (110) plane in cassiterite SnO_2 .

Figure 4.3 HR-TEM images of solvothermal synthesized ATO with (a) 0, (b) 5 and (c) 10 wt% Sb doped at 25k magnification and (d) 0, (e) 5 and (f) 10 wt% Sb doped ATO at 60k magnification. Reprinted with permission from Reference.¹⁰ Copyright 2017, American Chemical Society.

Table 4.2 EDX summary table showing nominal and actual Sb doping content for the synthesized ATO. Sb and Sn are normalized in order to determine the actual Sb content present in ATO.

Nominal Sb (wt%)	0	5.0	10.0	15.0
Actual Sb (wt%)	0	3.0	11.5	13.8

The Sb doping was verified with XRD and EDX analysis as shown in **Figure 4.4(a)** and **Table 4.2**, respectively. XRD patterns of different wt% Sb doped ATO shows only presence of one crystalline phase, identified as the bulk cassiterite SnO_2 according to JCPDS card number 41-1445. Average crystallite size of 11.8, 10.3 and 8.9 nm were calculated for 0, 5 and 10 wt% Sb doped ATO according to the Scherrer's equation using FWHM of the (110) plane and they correspond well to the average particle size of 12.1, 11.4 and 9.0 nm as observed in HR-TEM images in **Figure 4.3**.

With the addition of oleylamine as dispersion aid, it was found that 15 wt% Sb doped ATO could not be well dispersed in perchloroethylene for UV-Vis-NIR absorbance test. Hence, aqueous dispersion of the different wt% Sb doped ATO were then used for the preparation of PATO for similar optical characterization. From **Figure 4.4(b)**, ATO absorbs primarily at more than 1500 nm in the NIR region and this absorption can be attributed to the LSPR in ATO as a result of n-type doping.¹³⁻¹⁴ This implies that ATO should absorb the NIR portion of the xenon lamp irradiation and convert it to heat in order to induce PNIPAM optical switching. It is important to note that by increasing the Sb dopant content in SnO_2 till 10 wt%, free electron concentration increases, leading to enhanced NIR absorption efficiency as evidence from **Figure 4.4(b)**.

It was also found that 10 wt% Sb doped ATO generally shows a better NIR shielding effect as compared to 15 wt% Sb doped ATO as seen later in this paper. This phenomenon corroborates with what several authors have commonly reported, where 10 wt% Sb doped ATO is the optimum doping ratio for NIR shielding application.¹⁵⁻¹⁶ Hence, the solar modulation ability as well as response rate of 15 wt% Sb doping was not further investigated. 10 wt% Sb doped ATO was then chosen to investigate its photothermal

heating and serve as the nano heater. As depicted in **Figure 4.4(c)** both pure water and silica aqueous dispersion shows similar mild increment in temperature of about 3 to 4 °C at 100 mW cm⁻² irradiation intensity, whereas the temperature of the 1.2 wt% aqueous ATO dispersion increased from 23.8 to 34.2 °C ($\Delta T = 10.4$ °C). This implies that ATO is capable of converting the absorbed solar irradiation into heat, otherwise known as the photothermal effect. Furthermore, with the increment in ATO content from 0.3 wt% to 1.2 wt%, an increase in the saturation temperature can also be observed. From **Figure 4.4(d)**, the difference in color between different wt% doped ATO powder was observed and this difference in color originated from the electron transfer between different oxidation states of Sb³⁺ and Sb⁵⁺. It has been commonly reported that with an increase in doping content, light absorption intensity increases and darker shades of blue will be observed.¹⁷

Figure 4.4 (a) XRD patterns of synthesized ATO with different wt% Sb doping. (b) UV-Vis-NIR absorbance spectra of 0.025 wt% SnO₂ dispersed in perchloroethylene solvent with Sb doping content of 0, 5 and 10 wt%. (c) Photothermal heating temperature profile for de-ionized water, aqueous dispersion of silica and aqueous dispersion of ATO at different content exposed to irradiation of 100 mW cm⁻². Reprinted with permission from Reference.¹⁰ Copyright 2017, American Chemical Society. (d) Physical appearance of ATO showing darker shades of blue with the increase in wt% Sb doping.

4.3.2 PNIPAM/ATO with varying Atomic% Sb Doping

For comparative and optimization study, single wavelength transmittance, both VIS (%T₅₅₀) and NIR (%T₁₇₀₀) generated from the modified optical system were chosen to evaluate optical properties, such as the switching behavior, solar modulation ability and response rate. The detecting wavelength was chosen to be 550 nm in the visible region since it is the most sensitive to the human eyes, and 1700 nm which is free from hydrogel water absorption interference in the NIR region.

High initial visible transmittance at 25°C for different wt% Sb PATO films can be seen from **Figure 4.5(a)**. This can be attributed to the small ATO nanoparticle size of less than 10 nm as well as the good dispersion state. The 0 wt% Sb doped PATO UV-Vis-NIR spectra overlap well with that of neat PNIPAM especially in the NIR region and shows no enhanced NIR shielding effect as evidence from **Figure 4.5(a)**. Furthermore, with increase in Sb doping content till 10 wt%, SnO₂ transmittance monotonously depressed in the NIR region. However, further increase of Sb doping till 15 wt% result in a higher transmittance in the NIR region. This phenomenon can be attributed to the multivalent nature of Sb dopant which exists in both Sb³⁺ acceptor and Sb⁵⁺ donor states. Higher Sb doping content tends to result in higher concentration of Sb³⁺ ions, creating acceptor states which trap the electrons and reduce the effective charge carrier concentration contributed by Sb⁵⁺ ions.^{11, 15} The 2 prominent peaks observed at 1460 and 1935 nm arise from the hydrogen bond due to the water that is entrapped within PNIPAM.¹⁸

As depicted in **Figure 4.5(b)**, after 10 minutes of solar irradiation, 0, 5 and 10 wt% Sb doped PATO shows a rise of 10.6, 11.4 and 12.5 °C respectively. 10 wt% Sb doped PATO exhibited the largest extent of photothermal heating. This result in 10 wt% Sb doped PATO-1.2-180 film having the best solar modulation ability as well as highest response rate in both visible and NIR region. After irradiation on 10 wt% Sb doped PATO-1.2-180 film for 10 minutes, visible transmittance of the film decreased from 83.0 to 55.3%, ($\Delta T_{550} = 27.7\%$) and 66.9 to 58.2%, ($\Delta T_{1700} = 8.7\%$) for the NIR region, as shown in **Figure 4.5(c)** and **Figure 4.5(d)**, respectively.

Figure 4.5 (a) UV-Vis-NIR spectra of nanocomposite hydrogel film in the clear state at 25°C. and (b) photothermal heating temperature profile of hybrid film, with different Sb doping content. Single wavelength transmittance of nanocomposite hydrogel as a function of (c) time and (d) temperature from solar irradiation at 100 mW cm⁻² for 10 minutes. Graphs above show optical properties of 180 μm hydrogel films incorporated with 1.2 mg mL⁻¹ of ATO with different wt% Sb doping. Reprinted with permission from Reference.¹⁰ Copyright 2017, American Chemical Society.

This indicates that PATO primarily modulates in the visible region rather than in the NIR region, similar to what was observed other studies.¹ For 0 wt% Sb doped PATO-1.2-180 film, visible transmittance only decreased from 81.1 to 64.6%, ($\Delta T_{550} = 16.5\%$) and 75.4 to 68.6%, ($\Delta T_{1700} = 6.8\%$) for the NIR region. Hence, just by changing the ATO doping content from 0 to 10 wt%, a solar modulation improvement of 1.7 and 1.3 times could be observed for the visible and NIR region respectively. Furthermore, an improved response rate of 2 and 1.5 times could also be achieved.

Due to PNIPAM amphiphilic behavior, it is well known that below the LCST, polymer-water interactions such as hydrogen bonding of PNIPAM hydrophilic groups dominate.

Hence, polar swelling agent such as water tends to be good solvent for the PNIPAM chains; causing the hydrogel chains to be extended in water. In this state, the hydrogel appears transparent. However, nearing the transition temperature, destabilization of polymer hydrogen bonding occurs and onset of coil-globule transition takes place. This phase separation between the polymer chains and swelling agent, results in light scattering domains, causing a transparent to opaque change in optical state.

4.3.3 PNIPAM/ATO with varying ATO Content

Figure 4.6 (a) UV-Vis-NIR spectra of nanocomposite hydrogel film with different filler content in the clear state at 25°C. Single wavelength transmittance (%T₅₅₀) of nanocomposite hydrogel as a function of (b) time and (c) temperature from solar irradiation at 100 mw cm⁻² for 10 minutes. Graphs above show optical properties of 180 μm hydrogel films with different filler content of 10 wt% Sb doped ATO. (d) UV-Vis-NIR spectra of PATO in comparison to PGO of different filler content in the clear state at 25°C. Reprinted with permission from Reference.¹⁰ Copyright 2017, American Chemical Society.

Nevertheless, from **Figure 4.5(c)**, even irradiation of PATO with the optimized doping content of 10 wt% Sb and 1.2 mg mL^{-1} ATO filler content at 100 mw cm^{-2} , optical switching still could not take place. Therefore, the filler content of 10 wt% Sb ATO in $180 \text{ }\mu\text{m}$ films was further increased to further enhance the photothermal effect of PATO in order to induce the optical switching. With increasing ATO content in PATO, plasmonic absorption is being enhanced, resulting in a monotonous depression of the transmittance in the NIR regions as observed from **Figure 4.6(a)**.

Although PATO-8-180 shows a relatively high visible transmittance and NIR shielding effect, after irradiation for 10 minutes, a highly opaque state which compromised the visibility could be observed from **Figure 4.7** row 2-d. Hence optical properties of PATO-8 were not further investigated in this study.

Figure 4.7 Photographic images of nanocomposite hydrogel film before and after irradiation for 10 minutes. Columns (a-d) representing ATO content of 0, 2, 5 and 8 mg mL^{-1} respectively. Row (1) and (2) depict nanocomposite hydrogel of $180 \text{ }\mu\text{m}$ in the clear and translucent state, while row (3) and (4) show that of the $80 \text{ }\mu\text{m}$ thick films. Reprinted with permission from Reference.¹⁰ Copyright 2017, American Chemical Society.

The actual degree of transparency before and after irradiation is illustrated by the photographic images as shown in **Figure 4.7**. Before irradiation, the neat PNIPAM appears colorless and transparent; meanwhile PATO is transparent with a slight tint of blue due to the presence of ATO nanoparticles. After irradiation for 10 minutes, higher degree of opacity can be observed with increasing ATO content or film thickness.

The high visible transmittance observed for 180 μm PATO film in the clear state could be attributed to the well dispersed ATO during the *insitu* polymerization of PNIPAM. From the BF-TEM images in **Figure 4.8**, the dispersion state of ATO in hydrogel also concurred with the discussion, where plasmonic NIR absorption occurs in the presence of dispersed ATO, rather than a continuous film. Further, most of the agglomerates only lie within the range of 60–100 nm for hydrogel with 2 mg mL^{-1} of ATO filler content. For hydrogel with 5 mg mL^{-1} of ATO content, agglomeration of 100–450 nm could be observed sparingly from **Figure 4.8(d-f)**.

Figure 4.8 TEM images depicting the dispersion state of nanocomposite hydrogel at 2 mg mL^{-1} (upper row) and 5 mg mL^{-1} ATO filler content (lower row) at magnification of 10k for (a) and (d), 25k for (b) and (e) as well as 50k for (c) and (f). Reprinted with permission from Reference.¹⁰ Copyright 2017, American Chemical Society.

Nevertheless, for PATO-5-180, a high integrated solar $T_{(380-780)}$ of 72.5% and a depressed $T_{(780-2500)}$ of 53.7% was retained in the clear state at 25°C, as calculated from **Figure 4.6a**. Here the subscript indicates the multi-wavelength range, e.g. $\Delta T_{(780-2500)}$ refers to the integrated transmittance difference between 780 and 2500 nm.

With the increase in ATO content, apart from lower visible transmittance in the clear state, significant increment in response rate could be observed from **Figure 4.6(b)**. Comparing the gradient of the transmittance profile for the first 7 minutes reveals a response rate improvement of 2.3 and 4.7 times for PATO-2-180 and PATO-5-180 as compared to neat PNIPAM, respectively. A clearer dependency of the optical switching on the ATO concentration for PATO-5-180 can be further observed in the transmittance temperature profile in **Figure 4.6(c)**. A rapid decrease in % T_{550} at around 33°C also suggests that the LCST of the nanocomposite is preserved. Beside the improvement in response rate, the visible modulation for PATO-2 and PATO-5 is found to be 1.9 and 3.5 times that of neat PNIPAM, respectively. In the NIR region, an improvement of 2.1 and 5.2 times for PATO-2 and PATO-5 as compared to neat PNIPAM can also be observed (see Appendix, **Table A.2**). Hence, the increase of ATO content in PATO will cause a monotonous depression in NIR transmittance and dual responsive PNIPAM optical switching behavior can be achieved.

To enable the dual responsive thermotropic smart window optical switching, nano heater which can effectively convert solar energy to heat is of great importance. By far, only GO has been explored for such application.⁵ In this work, for the first time, plasmonic ATO was introduced as an alternative to GO, to function as a nano heater. Their performance was compared and demonstrated in **Figure 4.6(d)**. Unlike PATO which shows NIR shielding effect, with increasing content of GO, PGO only shows a decrease in visible transmittance and the spectra in the NIR region remains the same as that of neat PNIPAM. In the context of smart window, NIR absorption is an important property for indoor temperature modulation. Therefore, not only visible light transmittance will be sacrificed for GO photothermal effect to take place, but also significant NIR shielding and thermal

insulation could not be achieved by PGO. Hence, in this aspect, PATO will be more competent in comparison to PGO.

4.3.4 Investigation of PNIPAM/ATO Switching Mechanism

Effect of different sun irradiation intensity on the photothermal heating temperature profile was also investigated for neat PNIPAM, nanocomposite hydrogel as well as reference glass slides. From **Figure 4.9(a)**, with increasing irradiation intensity on PATO-5-180, it was found that both the initial rise in temperature as well as the final saturation temperature increase. The temperature profile in the Figure 4.9(a) offers an insight into the behavior of photothermotropic hydrogel system at different irradiation intensity. Hence, one can expect the PNIPAM/ATO photothermotropic hybrid to perform faster optical switching and larger solar modulation capability when the solar irradiation intensity increases.

Figure 4.9 (a) Photothermal heating temperature profile of PATO-5-180 as well as both (b) neat PNIPAM and reference glass slides under xenon lamp irradiation at different sun intensity for 10 minutes. (c) DSC thermogram showing similar LCST values of hydrogel with 0, 2 and 5 mg mL⁻¹ ATO filler content. Reprinted with permission from Reference.¹⁰ Copyright 2017, American Chemical Society.

Furthermore, with the addition of PNIPAM and ATO, a greater increase in temperature could be observed at different sun irradiation intensity, as seen from **Figure 4.9(b)**. This observation can be attribute to the presence of water entrapped within PNIPAM as well as ATO LSPR, which exhibits strong absorption in the NIR region as seen from **Figure 4.5(a)**, leading to the photothermal effect. These results imply that the increment of temperature can be controlled by both ATO content in PNIPAM, as well as light intensity, suggesting the optical switching of this dual responsive nanocomposite can be triggered by both sunlight as well as external temperature.

The mechanism behind the improvement in PATO optical properties was evaluated by means of differential scanning calorimetry (DSC) under flowing nitrogen, and the resulting thermogram is shown in **Figure 4.9(c)**. With addition of 2 and 5 mg mL⁻¹ of ATO filler content, both nanocomposite hydrogel LCST endothermic peaks remained at 33.6°C, which show no significant difference to that of the neat PNIPAM at 33.1 °C. Hence, the overall improvement in the nanocomposite hydrogel optical properties can be ascribed to ATO photothermal effect.

4.3.5 PNIPAM/ATO with varying Film Thickness

It is imperative that new technology developments will strike a subtle balance between thermal properties while maintaining the visual comfort of occupants. PATO-5-180 shows an average T_{550} of 40% with single wavelength measurement which could be further optimized in order to improve on its transparency. Hence, the film thickness was reduced to 80 μm and consequently the average T_{550} increased to 56% with visible modulation of $\Delta T_{550} = 42.6\%$, and NIR modulation of $\Delta T_{1700} = 14.7\%$, which was deem satisfactory. For the 80 μm films, the effects of different ATO filler content on the other optical and thermal properties were then investigated as follows.

Figure 4.10 (a) UV-Vis-NIR spectra of nanocomposite hydrogel film with different filler content in the clear state at 25°C. Single wavelength visible transmittance (%T₅₅₀) of nanocomposite hydrogel as a function of (b) time and (c) temperature from solar irradiation at 100 mW cm⁻² for 10 minutes. Graphs above show optical properties of 80 μm hydrogel films with various filler content of 10 wt% Sb doped ATO. (d) UV-Vis-NIR of optimized sample at different corresponding temperature mapped with solar irradiance spectrum. Reprinted with permission from Reference.¹⁰ Copyright 2017, American Chemical Society.

As seen from **Figure 4.10(a)** UV-Vis-NIR spectra, apart from high T₃₈₀₋₇₈₀ of 78.2%, depressed T₇₈₀₋₂₅₀₀ of 63.5% was shown for PATO-5-80 at 25°C. Further increase to PATO-8 seems to achieve higher degree of NIR shielding effect without compromising the visible transmittance in the clear state. However, after optical switching, the visibility of the PATO-8-80 film is sacrificed as seen in **Figure 4.7**, row 4-d. Moreover, in comparison to both PATO-0 and PATO-2, only PATO-5-80 successfully demonstrated optical switching with the largest extent of solar modulation ability, as observed from **Figure 4.10(b)** and **Figure 4.10(c)**. Therefore, PATO-5 again shows the best comprehensive performance

among the other nanocomposites. With the corresponding saturation temperature from **Figure 4.10(c)**, PATO-5-80 solar spectrum transmittance could be evaluated as a function of temperature as shown in **Figure 4.10(d)**. The increment from 20 to 35.5°C results in an average $T_{(380-780)}$ of 62.7%, $\Delta T_{(380-780)}$ of 35.7% and $\Delta T_{(780-2500)}$ of 18.1%. These optical data are believed to be consistent although not identical to the corresponding single wavelength data (T_{550} of 56%, ΔT_{550} of 42.6% and ΔT_{1700} of 14.7%) due to difference in measurement configuration.

To quantitatively study the effect of ATO addition as well as film thickness on the nanocomposite hydrogel overall performance, improvement in solar modulation ability as well as response rate as compared to 80 μm neat PNIPAM have been listed in **Table 4.3**. With increasing ATO content and film thickness, both solar modulation ability as well as response rate in the visible and NIR regions increase. In comparison to PATO-2-180, PATO-5-80 has a filler content of 2.5 times more, while PATO-2-180 shows a film thickness of 2.25 times that of PATO-5-80. Hence, by taking average of the VIS and NIR values for the solar modulation ability and response rate improvement, it is possible to compare and elucidate the dominant factor behind these improvements. It is interesting to note that both PATO-5-80 and PATO-2-180 show a comparable improvement in terms of solar modulation ability and response rate.

Table 4.3 Summary table depicting the no. of time of improvement in terms of solar modulation ability and response rate improvement for PATO film of different ATO filler content and film thickness as compared to 80 μm neat PNIPAM film. Data were evaluated by means of single wavelength measurement.

Nanocomposite hydrogel	Improvement over PATO-0-80 film (no. of time)					
	Solar Modulation Ability			Response Rate		
	VIS	NIR	Avg	VIS	NIR	Avg
PATO-2-80	1.4	1.2	1.3	1.4	1.2	1.3
PATO-5-80	4.1	2.4	3.3	2.2	1.7	2
PATO-0-180	1.6	1.1	1.4	1.6	1.1	1.4
PATO-2-180	3.1	2.3	2.7	3.7	2.3	3
PATO-5-180	5.7	5.6	5.7	7.7	3.4	5.6

In fact, for a PATO film of lower thickness (PATO-5-80) with higher ATO content, a relatively higher solar modulation can be achieved due to the enhanced photothermal effect. Despite the increase in solar modulation ability with ATO filler content, PATO-2-180 still shows a larger response rate improvement over PATO-5-80.

Figure 4.11 Repeated solar modulation evaluation of 80 μm hydrogel with 5 mg mL^{-1} ATO filler content at T_{550} . Each cycle lasted for 600 seconds under solar irradiation at 100 mW cm^{-2} . Reprinted with permission from Reference.¹⁰ Copyright 2017, American Chemical Society.

In actual field application, it is important for the nanocomposite film to exhibit reversible optical switching. Hence, PATO-5-80 stability was investigated and it was found that both reversible and repeatable optical switching properties could be retained after 15 cycles of irradiation, as shown in **Figure 4.11**. This indicates that the solar modulation ability of this nanocomposite system should be reliable in actual field application.

Admittedly, the stability of such aqueous base gel largely depends on the sealing condition of the glazing system. In the following chapters, improvement in new material systems which endow stability in the photothermotropic system is presented.

4.4 Conclusions

Photothermotropic hydrogel prepared by *in situ* polymerization of ATO in NIPAM has been investigated systematically in this chapter. Through comprehensive analysis of the hydrogel optical switching behavior, the mechanism for the enhanced solar modulation ability and response rate was elucidated by studying various Sb doping and ATO filler content as well as film thickness. Due to the photothermal effect from ATO, the nanocomposite could now serve as a fully autonomous dual responsive solar control glazing that responds to both sunlight irradiation as well as temperature. When exposed to solar irradiation, ATO absorbs photon energy in the NIR region and converts it to heat, facilitating PNIPAM optical switching.

A subtle balance between the thermal comfort and visibility could be realized by employing 5 mg mL^{-1} of 10 wt% Sb doped ATO in $80 \text{ }\mu\text{m}$ nanocomposite film for this study. High $T_{(380-780)}$ of 78.2% and depressed $T_{(780-2500)}$ of 63.5% could be observed in the clear state at 25°C for the optimized sample. This aspect of NIR shielding properties in the clear state will be beneficial when applied for thermal control, such that NIR lights could be shielded off for better indoor comfort environment. Upon optical switching, apart from solar modulation of $\Delta T_{(380-780)} = 35.7\%$, and $\Delta T_{(780-2500)} = 18.1\%$ in both visible and NIR regions, desirable average $T_{(380-780)}$ of 62.7% could still be retained. The solar modulation ability of such nanocomposite film was found to be reversible and repeatable after 15 cycles of irradiation.

For actual application, the degree of photothermal conversion is tunable and achievable based on the same principle, i.e. doping, particle content and the type of nano heater. This work will also serve as a universal guide for TCO application as a thermal driver in any thermally responsive materials related applications.

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Chapter 5

Agarose Hybrid: Hydrogel with Enhanced Stability for Solar Modulation Smart Window

In this chapter, thermotropic hydrogels with enhanced thermal stability was demonstrated with 4-octylphenol polyethoxylate non-ionic surfactant and glycerol/water as binary solvents in agarose. These dimensional stable hydrogels exhibit LCST type optical switch with tunable transition temperature over a range of 40°C. Glycerol as co-solvent widens the operating temperature range, lower swelling requirement and induce gentle optical switch characteristic in the smart hydrogels. Hydrogels with 0, 6, 12, 18 and 24 wt% glycerol contents were investigated and it was realized that 6 wt% glycerol/agarose exhibit the optimum thermal optical properties characterized by lowering of LCST, good solar modulation ability, moderate thermal sensitivity, and negligible thermal hysteresis. Furthermore, hydrogel hybridization with plasmonic ATO endow the composite with climate adaptability and enhanced NIR shielding. These smart hydrogels could emerge as a new generation of autonomous optical shutters for climate-adaptable solar modulation applications.

5.1 Introduction

Thermally responsive hydrogels that exhibit LCST derived solar modulation mechanism is of great interest for thermotropic smart windows because it provides an excellent temperature responsive behavior with a tunable range of transition temperature.¹⁻⁶ However, the volume reduction of these hydrogels during LCST transition hinder the applicability of thermotropic smart window in practice.^{5, 7}

To overcome the dimensional instability of hydrogel during LCST transition, strategies including interpenetrating polymer networks (IPN) formation,⁸⁻¹¹ multi-site polymer chain binding with 2D inorganic material,¹²⁻¹⁴ and inactive polymer scaffold have been investigated.¹⁵⁻¹⁶ Although interesting dual functionality hybrid could be achieved with IPN technology,⁸ yet its synthesise procedure often require tedious multi-step polymerization. Recently, dual functional 2D titania nanosheets and graphitic carbon nitride which can perform as photocatalytic initiators and cross linker were applied in thermal responsive hydrogels to construct multi-site polymer chain binding.¹²⁻¹⁴ Consequently, hydrogel with weak dimensional transition and interesting anisotropy phenomenon was realized. However, the requirement of photo irradiation source for generation of free radicals during synthesis and poor optical transparency of hydrogel composite is undesirable for actual smart window applications.

In this chapter, agarose hydrogel was chosen as an inactive polymer scaffold to facilitate optical switch reversibility and dimensional stability, while solvent containing non-ionic surfactants provides optical switch functionality. Co-solvent containing glycerol (BP: 290°C) as antifreeze agent not only helps to decrease freeze point and volatility of hydrogel, but also enable gradual optical switching characteristics. The thermotropic properties derived from hydrogels thermally responsive interactions hinges on the subtle balance between the hydrophobicity and hydrophilicity of molecules and solvent.¹⁷⁻²⁰ Herein, the effect of glycerol on the thermal optical and thermal stability properties of thermotropic smart window was investigated in this chapter.

5.2 Experimental Methods

5.2.1 Materials

Agarose of molecular biology grade purchased from Vivantis Technologies, (*Non-ionic Surfactant*) Polyethylene glycol *tert*-octylphenyl ether, TX-100 and TX-114 of laboratory grade were purchased from Sigma Aldrich. (*Solvent*) Deionized water (18.2 M Ω), and glycerol of ultrapure grade ($\geq 99.5\%$) purchased from USB Corporation was used throughout the experiments. Multipurpose sealant (Selleys All Clear) were used without further modification. Antimony Tin Oxide (ATO) 40 wt% aqueous dispersion was obtained from NanoMaterials Technology Pte Ltd.

5.2.2 Preparation of Agarose Hybrid – Interlayer Glass Assembly

Stock solutions of 1 wt% agarose and 2 wt% Triton surfactants were first prepared. Different glycerol to water ratio was prepared for the 1 wt% agarose mixture. In a typical synthesis process, the agarose solution was heated at 80°C for 5 minutes to obtain a transparent homogeneous solution before mixing with Triton surfactants at a volumetric ratio of 1:0.7. The resulting mixtures were injected into glass panels with steel spacer of different thickness (1.2, 1.8 and 2.4 mm) and transparent hydrogels were obtained upon cooling to room temperature. The glass panel with prepared hydrogels in between them were sealed with multipurpose sealant and kept at 15°C for 12 hours prior to characterization.

5.2.3 Characterization

A) Differential scanning calorimeter (DSC) (Q10, TA Instruments, USA) with ramp rate of 5°C min⁻¹ was employed to characterize specific heat flow of specimens under N₂ protection. **B) UV-Vis-NIR spectrophotometer** (Cary 5000, Agilent, USA) at normal incidence, collected the transmittance spectra in the wavelength range of 250 nm – 2500

nm. **C) Peltier heater/cooler** (Linkam, PE120) was equipped to the spectrophotometer for temperature control. Integral transmittance data were evaluated per **Equation 5.1**.

$$T_{int} = \int T(\lambda) E_{\lambda}(\lambda) d\lambda / \int E_{\lambda}(\lambda) d\lambda \quad (5.1)$$

Where $T(\lambda)$ refers to the transmittance measured by spectrophotometer at wavelength λ and $E_{\lambda}(\lambda)$ is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon). T_{sol} refers to integral transmittance in wavelength ranges of 250 nm – 2500 nm, while T_{lum} and T_{IR} are in the wavelength ranges of 380 nm – 780 nm for visible region and 780 nm – 2500 nm in the near infrared region of sunlight, respectively. Average luminous transmittance was evaluated through averaging the value of T_{lum} from two different temperatures. Solar modulation ability, ΔT_{sol} were obtained by **Equation 5.2**.

$$\Delta T_{sol} = T_{sol,x^{\circ}C} - T_{sol,y^{\circ}C} \quad (5.2)$$

Transition temperature of TX surfactants containing aqueous solution were characterized by cloud point method. The thoroughly stirred solution mixture was sealed in the glass vial and subjected to gradual heating in a water bath at a rate of $0.2^{\circ}C \text{ min}^{-1}$ from 25 to $65^{\circ}C$. When turbidity of solution mixture was detected by naked eyes, the corresponding temperature was recorded as the LCST. **D) Dynamic shear mechanical tests** were performed with a 25 millimetre parallel plate using a Discovery hybrid rheometer (DHR-3, TA Instruments, USA) with an Environmental Test Chamber (ETC). The linear viscoelastic range was first determined by testing a neat agarose gel from 0.001% strain to 1000% strain, and 0.1% strain was chosen to evaluate modulus of gels. The dependence of modulus on temperature was recorded from 26 to $50^{\circ}C$ at a ramping rate of $2^{\circ}C \text{ min}^{-1}$, with a frequency of 1 Hz and fixed gap of 500 μm .

5.3 Principle Outcomes

The commercial trade name of the thermal responsive non-ionic surfactants used in this chapter is Triton-X and this family of octylphenol ethoxylates and their micellar properties are strongly affected by the length of its polar ethylene oxide (EO) group. When temperature of surfactant solution increases and approaches LCST, dehydration of polyoxyethylene (POE) chains occurs because of its conformational change. Subsequently, micelle-micelle interaction overwhelms micelle solvent interaction, resulting in formation of giant micelle aggregates which result in to optical turbidity.²¹⁻²² In comparison to TX-100 which has an average of 9.5 EO units per molecule, TX-114 has an average of 8 EO units. The presence of more hydrophilic EO units result in a higher LCST for TX-100.

5.3.1 Dimensional Stability of Thermotropic Agarose

The dimensional stable thermotropic system shown in **Figure 5.1(a)** consist of agarose as inactive polymeric scaffold containing thermal responsive surfactant and aqueous solvent. Agarose dissolution occurs at around 80°C and forms physical gel upon cooling to embody the solvent containing surfactant at around 36°C.

Figure 5.1 Schematic showing a typical heat and cool cycle of a laminated (a) agarose hybrid and (b) PNIPAM hydrogel. Both hydrogels optical transition temperature is around 32°C. Complete optical reversibility was observed for agarose hybrid and not PNIPAM due to volume reduction and irreversible shrinkage during LCST transition. The agarose hybrid and PNIPAM shown in this figure has a sample dimension of 3.3 x 2.3 x 0.24 cm and 3 x 2.5 x 0.018 cm, respectively.

The non-ionic surfactant containing solvent endow agarose with thermotropic properties *via* reversible thermal responsive interactions, while agarose polymeric network enables optical switch reversibility and dimensional stability. On the contrary, reversibility could not be obtained in PNIPAM due to its discrete volume reduction during LCST transition, as shown in **Figure 5.1(b)**.

Based on the experimental trial, volumetric ratio of agarose to surfactant stock solution was fixed at 1:0.7 since lower surfactant content ratio will result in a lower solar modulation and higher transition temperature of around 1.5°C, while stable agarose gel formation could not be achieved at higher surfactant ratios. Concentration for surfactant stock solution was 2 wt% as non-homogenous turbidity was observed in hydrogel when surfactant concentration was 5 wt% or higher. These agarose hybrid film thickness should be in millimeter scale instead of micron meter scale. The trial with a 180 μm thick film result in heterogeneous turbidity and insufficient optical switch above its LCST. (see Appendix, **Figure A.3**)

FE-SEM of freeze-dried hydrogel in **Figure 5.2** shows fibrillar structure of agarose with pores in sub-micron meter scale. Since thermal reversible interactions between surfactant and solvent occurs within the porous structure of agarose, the mechanical integrity of the fibrillar scaffold remains undisrupted.

Figure 5.2 FE-SEM images shows the internal porous microstructure of agarose hydrogel under (a) 10k and (b) 25k magnification. The agarose hydrogel was freeze dried and sliced to observe the cross-section microstructure.

The LCST of 1 wt% TX-114 and TX-100 in aqueous solution was reported to be around 25 and 67°C, respectively and this corroborated with the experimental findings.²³ The addition of electrolyte for tuning of LCST in non-ionic surfactant system have been commonly explored and unfortunately, the presence of counter-ions not only render electrostatic stabilization mechanism of nanoparticles futile but also a relatively large amount of salts is needed to sufficiently tune the LCST for actual applications.²³ Moreover, addition of electrolytes in large quantity could result in the poor mechanical properties of hydrogel.²⁴ Hence, in this chapter, transition temperature tunability of agarose hybrid was demonstrated with surfactant mixtures consisting of TX-100 and TX-114 in different ratios.

5.3.2 Agarose Hybrid Transition Temperature Tunability

As seen from **Figure 5.3**, mixture of nonionic surfactant containing TX-100 and TX-114 enable transition temperature range of hydrogel to be extended from 27 to more than 60°C. Both aqueous surfactant mixture solution and agarose hybrid shows a linear increase in transition temperature when the content of TX-100 increases in surfactant mixture. (see Appendix, **Table A.4**)

Figure 5.3 Hydrogel transition temperature tunability in the range of 27 – 64 °C was demonstrated with 2.4 mm thick agarose hybrid film containing different ratio of TX-100 and TX-114 surfactants. The inset illustrate flexibility and optical visualization of the thermotropic hydrogel film below and above transition temperature. The flexible agarose hybrid sample in this figure has a dimension of 3.3 x 2.3 x 0.18 cm.

More specifically, an increment of around 5°C was found for every 10% increase of TX-100 in surfactant mixture. Similar linear transition temperature trend of mixed TX surfactant had been reported.²⁵

5.3.3 Agarose Hybrid with varying Glycerol Content

Different content of glycerol was introduced in agarose to replace aqueous solvent. The influence of glycerol co-solvent on the thermal optical characteristic of agarose hybrid was further investigated. The dielectric constant of glycerol and water is 46.5 and 80.1, respectively at 20°C.²⁶ Due to its hydrophobic glyceryl group, the addition of glycerol can reduce the hydrophilic interactions below LCST. While the presence of its polyhydroxyl structure will reduce the hydrophobic interaction above the LCST. Hence, both hydrogen bonding below LCST and hydrophobic interaction above LCST can be weakened with the addition of glycerol, resulting in gradual and restrained aggregation – disaggregation transition of the micelles. Hence, an optimum content of glycerol content in agarose hybrid is required to realize good solar modulation capability and enhance thermal stability for thermotropic smart window application.

5.3.3.1 Effect of Glycerol on Transition Temperature

The transition temperature was found to decrease by around 2°C for every 6 wt% increase in glycerol content. (see Appendix, **Table A.5**) The effect of various additives such as electrolytes, alkanes, alcohols, ionic and non-ionic surfactants on the phase separation properties in non-ionic surfactants have been investigated.²² Co-solvent trifluoroethanol (TFE) was investigated for its hydrophobicity enhancement of 4-octylphenol polyethoxylate micelles.²⁷ Similar to the glycerol structure, TFE is a proton donor which could interact with surfactant oxyethylene group at the palisade layer to replace water molecules. The low hydrogen bond forming capability of TFE decreases the solubility of surfactant, while fluorinated group of TFE enhances the hydrophobic character of the palisade layer to favor phase transition.²⁸

Figure 5.4 Shows the integral visible transmittance as a function of temperature for agarose hybrid containing different wt% content of glycerol (of total hydrogel). The surfactant mixtures in these 1.2 mm thick hydrogels consist of 25% TX-100 & 75% TX-114. The transmittance measurement at every individual temperature point was performed after isothermal holding for 5 minutes to achieve thermal equilibrium.

Similarly, the decrease in agarose hybrid LCST in this work can be attributed to two factors. Firstly, glycerol molecules preferentially solubilize *via* interfacial absorption between micelle and water. Hence, the hydration level of micelle (hydrogen bonding) is decreased. Secondly, replacement of water molecules with alcohol at micelle surface, decreases the dielectric constant which lowers the solubility of micellar aggregates, leading to a decrease in LCST.

5.3.3.2 Effect of Glycerol on Solar Modulation Performance

The effect of glycerol on the solar modulation ability of agarose hybrid was investigated with 1.2 mm thick films, and the luminous transmittance spectra obtained in **Figure 5.4**, shows a slight decrease of ΔT_{lum} (20°C - 50°C) from 48.3 to 46.6% and 48.3 to 35.5% when 6 and 12 wt% of glycerol was present in the hydrogel system, respectively. It should be

mention that the transition temperature for agarose hybrid containing 0, 6, 12 and 24 wt% glycerol is 42.0, 39.7, 38.2 and 32.6°C, respectively. Since the polarity of glycerol is lower than that of water, the aggregated micelles should experience an increase solubility in the presence of glycerol. Hence, the turbidity at temperature above LCST is lowered for glycerol/water system as compared to that of pure aqueous solvent.

5.3.3.3 Effect of Glycerol on Thermal Sensitivity

A more gradual optical switching transition could be achieved with the increase of glycerol content in agarose hybrid as shown in **Figure 5.4** inset, heating slope comparison. A decrease in the optical thermal sensitivity of 0.74 times and 0.47 times compared to pure thermotropic hydrogel could be achieved in the presence of 6 and 12 wt% glycerol for a 1.2 mm thick agarose hybrid film, respectively.

The thermal sensitivity of agarose hybrid is affected by the micelle aggregation and disaggregation micro dynamics. During the heating phase, hydrophilic POE group gives up their hydrogen bond with water and subsequently, the micelles diffuse and aggregates. Hydrogen bonds form between the micelles to stabilize the aggregates. From **Figure 5.4**, the abrupt reduction in the transmittance is due to dehydration of POE chains while the lagging end is due to micelle aggregation transition. During dehydration of POE, interactions between the glyceryl group and POE delay the transition and lower the degree of micelles aggregation. While for the cooling process, aggregated micelle disaggregates by breaking hydrogen bonds between them and form hydrogen bonds with solvents. The presence of glycerol as a co-solvent reduces the hydrogen bond forming capability between solvent and micelle. These restrained transitions during heating and cooling result in a reduced thermal sensitivity of the glycerol/water surfactant system. This co-solvent strategy for lowering thermal sensitivity of optical switching is suitable for smart window applications and easier to implement compared to tuning of the hydrophobicity and hydrophilicity ratio in thermal responsive systems.²⁹

5.3.3.4 Effect of Glycerol on Thermal Hysteresis

The 1.2 mm thick hydrogels investigated shows negligible thermal hysteresis profile, even with the presence of up to 24 wt% glycerol as evidenced from **Figure 5.4**. The hydrogel containing 6 wt% glycerol was chosen for further evaluation since not only could it perform gradual optical switch, but also increases the stability of hydrogel with minimal deterioration in solar modulation ability.

Interestingly, tuning the magnitude of scattering domains *via* film thickness control could result in different end applications such as smart window or privacy glass. The thermal optical properties of agarose hybrid containing 6 wt% glycerol in different thickness of 1.2, 1.8 and 2.4 mm was investigated, as shown in **Table 5.1**. It was found that films of 1.2 mm thick would be more suited for smart window since its average T_{lum} remains well above 70% even after optical switch. While hydrogel films of 2.4 mm thick could be suitable for privacy glass when integrated with conductive substrates for joule heating up to 50°C, to achieve low T_{lum} of below 30% upon optical switch. For actual application, the desired T_{lum} upon optical switch could be tuned by manipulating the hydrogel transition temperature and film thickness.

Table 5.1 Integral optical properties for agarose hybrid of different film thickness. All hydrogels contain 6 wt% glycerol and surfactant mixture of 90% TX-114 and 10% TX-100.

Film Thickness (mm)	T_c (°C)	T_{lum} (20°C)	T_{lum} (38°C)	T_{lum} (50°C)	Avg. T_{lum} (20°C - 38°C)	ΔT_{lum} (20°C - 38°C)	ΔT_{lum} (20°C - 50°C)
1.2	33.0	86.8	62.4	49.5	74.6	24.4	37.3
1.8	31.0	86.2	52.9	37.2	69.5	33.3	48.9
2.4	30.5	85.7	42.9	26.9	64.3	42.8	58.8

5.3.3.5 Effect of Glycerol on Thermal Stability

Figure 5.5 (a) DSC thermogram showing depression of both freeze point and enthalpy change with increase of glycerol content from 0 to 24 wt% (of total hydrogel) in agarose hybrid. The volatility of agarose hybrids was evaluated with the (b) mass loss profile of agarose hybrid in a glass vial when exposed to air in 60°C environment. The hydrogel used in (a) and (b) contains surfactant mixture of 90% TX-114 and 10% TX-100.

The presence of glycerol antifreeze agent widens the operating temperature range of the agarose hydrogel and lowers the sealing requirement of the hydrogel based smart window. As shown in **Figure 5.5** and **Table 5.2**, both the freeze point and evaporation profile decreases with increase of glycerol content. The freezing enthalpy of agarose hybrid without glycerol is much less compared to that of water (333.5 J g^{-1} at around 0°C), which implies that freezing of water had been suppressed by hydrogen bonding of agarose and water.²⁶ Furthermore, lowering of freezing enthalpy with addition of glycerol can be attributed to the decreasing amount of water that are not bonded with glycerol in the hydrogel. Specifically, for 6 wt% glycerol containing agarose hydrogel, the freeze point depressed by 62% from -5.8 to -9.4°C and its specific enthalpy decreases by 18% from 265.2 to 217.5 J g^{-1} , indicating the possibility for the material to operate in cold weather climate. The 6 wt% glycerol containing hydrogels were exposed to air in a 60°C oven and the degree of solvent evaporation decreases by 17% from 5.6 to 4.6 wt%. While, further increase of glycerol content did not result in significant decrease of solvent evaporation.

Table 5.2 Specific enthalpy and freeze point of agarose hybrid with different content of glycerol. All values were obtained through analysis of hydrogels freezing exotherm from DSC thermogram.

wt% glycerol in hydrogel	0	6	12	18	24
Specific Enthalpy (J/g)	265.2	217.5	197.2	165.0	151.4
Freeze Point (°C)	-5.8	-9.4	-11.5	-17.1	-18.9

Although water in hydrogel is a good absorber of near infrared, the NIR shielding and climate adaptability features of agarose hybrid could be enhanced with plasmonic ATO, nano heating effect introduced in Chapter 4. **Table 5.3** shows the hybrid films of different thickness with less than 10 % of near infrared modulation and T_{IR} remain above 20% after optical switching at 38°C for a 1.2 mm hydrogel film. As demonstrated in Chapter 4, plasmonic ATO-NP could perform as localized nano heater in thermal responsive systems not only to enhance both solar modulation and response speed, but also to induce optical switch in the event of insufficient thermal energy.

Table 5.3 NIR transmittance and modulation properties of agarose hybrid films of different thickness. The hydrogels contain 6 wt% glycerol (of total hydrogel) and surfactant mixture of 90% TX-114 and 10% TX-100.

Hydrogel Thickness (mm)	T_c (°C)	T_{IR} (20°C)	T_{IR} (38°C)	ΔT_{IR} (20-38°C)
1.2	33.0	26.0	20.4	5.6
1.8	31.0	24.8	17.5	7.3
2.4	30.5	23.9	15.4	8.5

5.3.4 Agarose/ATO Nanocomposite

Agarose/ATO hydrogel exhibit fibrous porous network structure, similar to pure agarose. From the FE-SEM images in **Figure 5.6(c)** and **Figure 5.6(f)**, ATO nanoparticles residing on the fiber of agarose was observed in the range of 15 to 30 nm. This well disperse state of ATO in agarose can be attributed to the electrostatic stabilization mechanism of ATO nanoparticles in aqueous dispersion prior to physical gelation of agarose.

Figure 5.6 FE-SEM images depicting the internal porous microstructure and dispersion state of Agarose/ATO hydrogel with 0.2 wt% (a – c) and 0.4 wt% (d – f) nanoparticle content. Magnification of images were taken at 10k for (a) and (d), 25k for (b) and (e), 50k for (c) and (f). Yellow and red arrows indicate the location of ATO nanoparticles in 0.2 wt% and 0.4 wt% Agarose/ATO nanocomposite, respectively.

Different ATO contents were hybridized with agarose hybrid containing surfactant mixture of 90% TX-114 and 10% TX-100. The transition temperature of hydrogels with different content of ATO remained at around 33°C with no significant changes (**Table 5.4**), while both T_{lum} and T_{IR} of the hydrogels depressed monotonously, as shown in **Figure 5.7**. It should be mention that the actual climate and position of thermotropic smart window with different solar irradiation conditions will result in different saturation temperature.

Figure 5.7 UV-Vis-NIR transmittance spectra of agarose hybrid with (a) different plasmonic ATO particles content at 25°C and (b) 0.2 wt% ATO particles thermal optical response at different temperatures. Inset shows the change in optical transparency of Agarose/ATO hybrid film before and after switching. The 1.2 mm thick hydrogel films contain 6 wt% glycerol (of total hydrogel) and surfactant mixture of 90% TX-114 and 10% TX-100.

For example, upon solar irradiation, consider an equilibrium temperature of 40°C for a 1.2 mm thick agarose hybrid with 0.2 wt% ATO, 6 wt% glycerol and surfactant mixture of 90% TX-114 and 10% TX-100. This result in an average T_{lum} of 64% while other thermal optical properties depicting the thermal insulation capability of this hydrogel based smart window are ($T_{lum40^{\circ}C} = 51\%$), ($\Delta T_{lum} = 26\%$) and ($T_{IR40^{\circ}C} = 12.4\%$). It is important to realize that the desired thermal optical behavior of the agarose nanocomposite could be tuned on demand by optimization of surfactant mixture, glycerol and plasmonic nanoparticle content.

Table 5.4 Integral optical properties of agarose hybrid with different ATO content. These 1.2 mm thick hydrogel films contain 6 wt% glycerol (of total hydrogel) with surfactant mixture of 90% TX-114 and 10% TX-100.

wt% of ATO in agarose hybrid	T_c (°C)	T_{lum} (20°C)	T_{IR} (20°C)	T_{sol} (20°C)
0	33.3	86.8	26.0	73.0
0.2	32.6	77.0	16.7	58.0
0.3	33.0	71.8	13.3	51.7
0.4	32.8	67.5	11.1	47.0
0.5	32.6	63.0	9.3	42.7

The presence of glycerol as co-solvent in agarose has been reported to enhance the hydrogel mechanical properties.³⁰ More specifically, the compression properties which facilitates physical handling of the hydrogels could be improved and this corroborated with the experimental observation. When subjected to dynamic shear mechanical analysis, modulus of agarose hydrogels and its hybrids typically remain unchanged throughout the testing temperature range of 25 – 50°C, shown in **Figure 5.8**. The storage modulus is higher than loss modulus for all hydrogels, indicating a stable gel during application.

Figure 5.8 Dynamic shear mechanical plot of pure aqueous agarose, glycerol containing agarose and agarose/ATO hybrid hydrogels showing their storage (G') and loss (G'') modulus as a function of temperature.

With the addition of 6 wt% glycerol, storage modulus of agarose hybrid increases from around 2500 to 3000 Pa. However, hybridization with 0.2 wt% ATO nanoparticles in hydrogel result in a decrease of storage modulus from around 3000 to 2750 Pa. Similar phenomenon was observed in previous work for PNIPAM/ATO nanocomposite, and a possible underlying reason could be due to the decrease in crosslinking density during the hydrogelation process.

5.4 Conclusion

In conclusion, stability enhanced thermotropic hydrogels based on agarose, non-ionic surfactants and binary solvents was demonstrated. Mixed non-ionic surfactant with wide tunable optical transition temperature range were contained within agarose scaffold which endow optical switch reversibility and dimensional stability. The variation of solvent composition, glycerol effect on thermotropic hydrogel thermal optical and thermal stability properties was extensively elucidated and the underlying mechanism was discussed in the perspective of surfactant thermal transition micro dynamics. A decrease in LCST by 2°C, gradual thermal optical sensitivity with 0.74 times that of pure agarose hybrid and negligible thermal hysteresis could be achieved with the presence of 6 wt% glycerol in 1.2 mm thick thermotropic agarose hybrid. Furthermore, a subtle balance between hydrogel solar modulation ability and thermal stability could be realized simultaneously. Agarose hybrid containing 6 wt% glycerol successfully demonstrates a reduction of 62% and 17% for freeze point and solvent mass evaporation, respectively. Through engineering of hydrogel film thickness, magnitude of scattering domains can be adjusted for different end applications such as smart window and privacy window. The versatility of these thermotropic hydrogels was demonstrated through hybridization with plasmonic nanoparticles for enhanced NIR shielding features. It was envisaged that such approach of smart materials design for enhance stability will be relevant and useful for future developments of other thermally responsive hydrogels for various applications.

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Chapter 6

Polyurethane Ionogel: A New Class of Tunable Thermotropic Materials with Super Cyclic Stability for Solar Modulation Smart Window

In this chapter, a new class of thermally responsive polyurethane based ionogels, has been synthesized. These mechanically robust ionogels exhibit LCST-type optical switching with no dimensional change upon heating. The optical switching temperature is tunable from sub-zero to over 100 °C. Molecular dynamic simulation was used to provide further mechanistic understanding. Freezing point and volatility are absent in these ionogels and they demonstrated optical cyclic stability after 5000 heat-cool cycles with no volume change, detectable liquid leaching and performance deterioration. Furthermore, a range of functional additives, such as organic dyes and photothermal plasmonic nanoparticles was hybridized with the ionogel to endow multifunctionality for their intended application. Energy saving effort was demonstrated by a model mini-house affixed with ionogel containing glazing, which shows an indoor temperature reduction of 20 °C over normal float glass.

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6.1 Introduction

Polymeric based thermotropic materials, exhibit broadband and high solar modulation ability. Polymeric thermotropic composites are usually multi-component and are being commonly explored for optical applications such as temperature sensors, light valves and smart windows.¹⁻³ Generally, at temperatures below the optical switch point, all constituents are either homogeneously mixed at molecular level or possess similar reflective index (RI) so that high visibility is observed. With increase in temperature, phase transition or separation causes RI mismatch which results in opacity.⁴

Among the various polymeric thermotropic candidates, PNIPAM hydrogels have commonly been explored as smart windows for its excellent thermal optical performances, such as negligible hysteresis and high solar modulation ability.⁵ Yet, thermotropic hydrogels still suffer from intrinsic disadvantages of poor mechanical integrity, water evaporation and freezing, discrete volume change and liquid expulsion during phase separation. Therefore, issues pertaining to reversible cyclic stability hinder the applicability of hydrogel material for actual smart window application.

Ionogel containing ionic liquids in the semi-solid state, have been intensively sought after in various critically important areas including membranes for gas separation, sensors, actuators, energy storage and conversion devices.⁶⁻⁸ It is important to realize all these prior arts of utilizing ionogels relies on IL's inherent functionalities while mechanical support was derived from the three-dimensional network. By far, thermotropic property that originate from switchable interactions between IL and network has yet to be reported.

In this chapter, thermal responsive polyurethane (PU) ionogels were synthesized by crosslinking polypropylene oxide (PPO) diol in the presence of various imidazolium ILs. The outstanding thermotropic properties which arise from the intriguing interactions between PPO and IL were extensively investigated. On demand tuning of transition temperature could be achieved in a wide temperature range from sub-zero to over 100°C, which is unattainable by any previously reported thermotropic materials.

Figure 6.1 (Left) materials candidate explored for the thermotropic ionogel in this chapter and (Right) operating principle of thermotropic ionogel optical transmittance change in response to temperature. Above transition temperature, light scattering at interfaces of IL and PU domains occurs and decreases the ionogel optical transparency. Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

Further, thermal cycling for at least 5000 times between highly transparent and opaque optical states can be performed without compromising the ionogel's solar modulation ability, dimensional and thermal-optical stability. Different material constituents in the thermotropic ionogel system and its phase separation mechanism for solar modulation smart window are illustrated in **Figure 6.1**.

6.2 Methods

6.2.1 Molecular Dynamics Simulation

(A collaboration with Dr. Sadiye and Professor Chew Jia Wei)

Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) was employed for all molecular dynamic simulations in this chapter.¹⁰ Molecular visualization and analyses are performed with Visual Molecular Dynamics (VMD) packages.¹¹ Force field parameters of polypropylene oxide (PPO) reported earlier had been adopted.¹²⁻¹⁴ These

parameters are compatible with the Optimized Potentials for Liquid Simulations-All Atom (OPLS-AA) framework.¹⁵ PPO repeated unit has an atactic tacticity that were randomly generated with probability of a chiral inversion of 0.5. Same OPLS-AA¹⁵ force field was used for the ionic liquids (ILs), but specific parameters developed by Lopes *et al.*¹⁶⁻¹⁷ was adopted to encompass the entire IL homologous series. Packmol software is used to generate the initial configurations of the simulations.¹⁸ According to the size of the unit cell, cut-off distance for non-bonded interactions is adjusted as 8 and 12 Å. SHAKE algorithm are used to constrain the bond distances involving hydrogen atoms in IL. Nosé–Hoover thermostat is used to control the temperature to the targeted value with a coupling time constant of 100 fs, while Nosé–Hoover barostat maintained the pressure at 1 bar with a coupling time constant of 500 fs. The simulation time step is set to 1 fs.

Firstly, PPO initial configurations were allowed to relax with zero-temperature minimizations for 1 ns, followed by preliminary NpT (isothermal – isobaric ensemble) runs at 30 K for 1 ns, after which the temperature was gradually raised to 298 and 363 K within 5 ns, respectively. Next, 5 ns of NVT (canonical ensemble) and 10 ns of NpT runs were performed at specified temperatures to equilibrate the system before any statistics are collected. Lastly, trajectories of the equilibrated systems were generated at 298 and 363 K for 200 and 800 ns, respectively, with configurations recorded every 2000 fs time steps. With the detailed atomistic model matrices generated, conformational characteristics such as radius of gyration (Rg), hydrogen-bonding (h-bonding) and radial distribution function (RDF) were estimated. The Rg value indicates the molecular conformation behaviour of polymer chains, which reveal the size of the polymer coil and therefore solvent capability in solvation of polymer.

Hydrogen bonding is defined based on the distance between donor and acceptor atoms which is less than 3.2, 4.2, 2.4 Å and the angle is greater than 130, 110 and 110° for O–H...O,¹⁹ C–H...O,²⁰ and X–H...F,²¹ hydrogen bonding, respectively. RDF provide the probability of locating an atom with a distance to the specific site in comparison to another given atom. One PPO chain consist of 30 repeat units instead of short chains. Hence, the effect of end groups is not accounted for in this simulation work.

Figure 6.2 Illustrate the chemical structures of imidazolium cation $[C_4mim]$, bis (trifluoromethylsulfonyl) imide $[NTf_2]$ anion, and repeating unit of polypropylene oxide (PPO) with the preferential interaction sites labelled accordingly. For cation $[C_4mim]$, top and bottom hydrogen atoms (HCR and HCW), first carbon atom (Ci) connected to the phenyl ring and hydrogen atom (HC) at the end of alkyl chain. For anion $[NTf_2]$, oxygen (OBT), fluorine (F1) and sulfur atoms (SBT). For PPO, oxygen atoms (OP) in PPO backbone, hydrogen atoms (HP) and carbon atoms (CP3) of methyl group. Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

As shown in **Figure 6.2** hydrogen bonding in *cation-anion* is defined based on hydrogen atoms (donor), HCR and HCW, with oxygen atoms (acceptor), OBT for $C-H\cdots O$ and fluorine atoms (acceptor), F1, for $C-H\cdots F$ hydrogen bonding in the anion, respectively. In addition, the hydrogen atoms linked to first carbon atom (Ci) connected to imidazolium cation phenyl ring is also chosen as a donor in hydrogen bonding between *cation-anion* and *cation-PPO*.²²

Cation-PPO hydrogen bonding is defined based on hydrogen atoms (donor), HCR, HCW, and hydrogens linked to Ci with oxygen atoms (acceptor), OP, in the backbone of PPO chain. While *PPO-anion* hydrogen bonding is defined based on hydrogen atoms (donor), HP, at the end groups of PPO chain with anion oxygen atoms (acceptor), OBT for $O-H\cdots O$ and fluorine atoms (acceptor), F1, for $O-H\cdots F$ hydrogen bonding in the anion, respectively. Only non-bonded inter-molecular potential energy such as Van der Waals, coulomb and long-range energy are considered for the interaction energy between selected pairs. Any bonded interactions or intra-molecular interactions are excluded.

6.2.2 Experimental Method

6.2.2.1 Materials

The reagents used in this chapter include Hexamethylene Diisocyanate trimer (Tolonate™ HDT-90, Vencorex Chemicals), Polypropylene Oxide (PPO) (Diol type, $M_n = 4000$ Da, Sigma Aldrich), Dibutyltin dilaurate (95%, Sigma Aldrich), 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_4mim][NTf_2]$, Sigma Aldrich), 1-Butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_4dmim][NTf_2]$, Merck), 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2mim][NTf_2]$, Tokyo Chemicals), 1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_6mim][NTf_2]$, Tokyo Chemicals) and Methyl Ethyl Ketone (MEK, HPLC grade, Tedia®). All ionic liquids were dried under vacuum at 60°C before using. Brilliant green, rhodamine B and methyl orange organic dyes were purchased from Sigma Aldrich while Antimony Tin Oxide (ATO) dispersion in MEK was obtained from NanoMaterials Technology Pte Ltd.

6.2.2.2 Preparation of Thermotropic Ionogels

The ionogels were synthesized by crosslinking PPO with diisocyanate trimer in the presence of ionic liquids. In a typical procedure, 0.18 g Tolonate™ HDT-90 was mixed with 1.40 g of PPO (mole ratio of NCO/OH = 1.2) and 0.72 g MEK to obtain a homogeneous colorless solution. 1.40 g ionic liquids mixture including $[C_4mim][NTf_2]$ and another ionic liquid, e.g., $[C_4dmim][NTf_2]$, of different weight ratios was then added to the PPO solution, followed by 0.1 g Dibutyltin dilaurate catalyst solution (10 wt% in MEK). This mixture was stirred and degassed for 30 minutes before filling into a cavity between PTFE plate and a steel spacer. The curing reaction took place at 45 °C for 24 hours within the mould in an airtight condition to achieve a transparent homogeneous ionogel. Upon curing, the ionogel was subjected to vacuum to remove MEK. The film thickness in this study is in the scale of millimeter (1.7 ± 0.1 mm) thick, which is comparable to that of conventional non-responsive polyurethane elastomers used in safety glass laminates. The

millimeter thick ionogel films provide sufficient mechanical robustness and adequate solar modulation performance required for smart window applications. This chapter mainly focuses on the investigation of thermotropic ionogel intrinsic properties. Hence, the detailed study on effects of extrinsic engineering parameters such as thickness was not conducted. Nevertheless, one could expect an optimum thickness to achieve the desired optical and mechanical properties.²⁻³ Characterization of the ionogel was performed either in its freestanding form or sandwiched between glass panels and sealed with epoxy adhesive for optical properties testing. Neat polyurethane film was synthesized by the same procedure without the addition of ionic liquids. Similarly, ATO containing ionogels were synthesized by adding ATO – MEK solution with known concentration before curing. For aesthetic modification, freestanding ionogels were further dip coated in respective aqueous organic dyes solutions for 12 hours and dried in vacuum to obtain colorful ionogel film.

6.2.2.3 Characterization

A) Differential scanning calorimeter (DSC) (Q10, TA Instruments, USA) with ramp rate of 5°C min⁻¹ was employed to characterize specific heat flow of specimens under N₂ protection **B) Thermogravimetric Analysis (TGA)** was performed with Q500 (TA instrument) under nitrogen atmosphere from 25 to 850°C with heating rate of 10 °C min⁻¹. **C) UV-Vis-NIR spectrophotometer** (Cary 5000, Agilent, USA) at normal incidence, collected the transmittance spectra in the wavelength range of 250 – 2500 nm. **D) Peltier heater/cooler** (Linkam, PE120) was equipped to the spectrophotometer. Integral transmittance data were evaluated per **Equation 6.1**.

$$T_{int} = \int T(\lambda) E_{\lambda}(\lambda) d\lambda / \int E_{\lambda}(\lambda) d\lambda \quad (6.1)$$

Where $T(\lambda)$ refers to the transmittance measured by spectrophotometer at wavelength λ and $E_{\lambda}(\lambda)$ is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon). T_{sol} refers to integral transmittance in wavelength ranges of 250 – 2500 nm, while T_{lum} and T_{IR} are in the wavelength ranges of 380 – 780 nm for visible region and 780 – 2500 nm in the near infrared region of sunlight, respectively.

Average luminous transmittance was evaluated through averaging the value of T_{lum} from two different temperatures. Solar modulation ability, ΔT_{sol} were obtained by **Equation 6.2**.

$$\Delta T_{sol} = T_{sol, x^{\circ}C} - T_{sol, y^{\circ}C} \quad (6.2)$$

PPO/IL mixtures phase separation temperature were characterized by the cloud point method. Firstly, PPO and ILs were directly mixed in argon filled glove box and thoroughly stirred. The mixture solution sealed in the glove box was subjected to gradual heating in a water bath at a rate of $0.2^{\circ}C \text{ min}^{-1}$ from 25 to $95^{\circ}C$. When the naked eyes detected the solution to be turbid, the corresponding temperature was recorded as the phase separation temperature. **E) Xenon lamp**, Newport 6259, 300W Xenon, UV Enhanced Arc Lamp (Ozone Free), of wavelength 200 to 2400 nm was utilized as the irradiation light source in the laboratory (constant room temperature of $25^{\circ}C$) to demonstrate the photo-responsive switching mechanism of ionogel composite. **F) Single wavelength optical detector**, 918D-SL-OD3R (Silicon Detector, 400 to 1100 nm) set to be detecting at single wavelength of 550 nm (VIS) in the normal-normal configuration, was used to detect any changes in transmittance during the experiment. **G) Optical Power Meter** (1918-R, Newport) convert the captured signal from the optical detector to power reading. Existing background irradiation detected in the scale of nW were zeroed before any measurement of power reading. **H) Pyrometer** (Sentry ST677) with high 50:1 distance to spot ratio was used to detect the changes in temperature of the prototype window. Detailed experimental configuration could be seen from **Figure 4.2** and **Figure 3.12**. The initial transmittance intensity of the solar simulator detected at 550 nm were taken to be 100% and subsequent decrement in power intensity during the measurement were linearly converted to percentage transmittance. **I) Dynamic shear mechanical tests** were performed with a 25 millimeter parallel plate using a Discovery hybrid rheometer (DHR-3, TA Instruments, USA) with an Environmental Test Chamber (ETC). The linear viscoelastic range was first determined by testing from 0.001% strain to 1000% strain, and 1% strain was chosen to evaluate modulus of gels. The dependence of modulus on temperature was recorded from 26 to $70^{\circ}C$ at a ramping rate of $2^{\circ}C \text{ min}^{-1}$, with frequency of 1 Hz and a set gap of 1700 micrometers.

6.3 Principle Outcomes

6.3.1 LCST of PPO and Ionic Liquid Solution Mixture

Figure 6.3 (a) Average radius of gyration for PPO chains in different ionic liquids with 30 and 40 wt% concentrations at 25°C. (b) Hydrogen bond number between cation-PPO, cation-anion and anion-PPO as a function of $[\text{C}_n\text{mim}]$ alkyl chain length at 25°C. (c) Average interaction energy between anion-PPO, cation-PPO and anion-cation, at 25 and 90°C. The simulations were conducted for 40% PPO in solution mixture, and the negative sign indicates attraction forces. (d) Radial distribution functions, $g(r)$, between the C2 hydrogen atom in the imidazolium cation ring and oxygen atoms in the PPO for ILs of different alkyl chain length at 25°C. Inset shows a snapshot of PPO chain surrounded predominantly by $[\text{C}_4\text{mim}]$ cations (blue cloud) rather than $[\text{NTf}_2]$ anions (red cloud). Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

In comparison to polymers that show temperature-dependent solubility in water or organic solvents, polymer/IL systems were less often explored, not to mention with a Lower Critical Solution Temperature (LCST) around atmospheric temperature.²³⁻²⁴ The underlying interactions between polymer and IL which give rise to its thermoresponsive behavior remains unclear, although it is generally known that LCST originates from a subtle and balanced interaction between polymer and solvent. Molecular Dynamic Simulation (MDS) aided in the understanding of molecular interactions between polymer and IL which accounts for ionogel transition temperature tunability and its dimensional stability.

Figure 6.3(a) shows that at temperatures below T_t , PPO radius of gyration increases in an IL with a longer alkyl chain in cation. This indicates that imidazolium IL with a longer alkyl chain is a better solvent for PPO and PPO/IL solution should have a higher T_t , if not complete miscibility. Higher content of PPO results in lower radius of gyration and lower T_t as expected, which is in good agreement with the experimental result in **Table 6.1** and **Figure 6.4**.

It is known that the LCST-type phase separation occurs only when both ΔS_{mix} and ΔH_{mix} are negative, and hydrogen bonding is a common predominant factor for this thermally responsive interaction. As seen in **Figure 6.3(b)**, molecular dynamic simulation reveals that a longer alkyl chain in imidazolium cation results in more hydrogen bonds, which is counterintuitive when considering the steric hindrance effect of long alkyl chain. A longer alkyl chain electron-donating group results in less localized positive charge in cation due to super-conjugating effect and consequently suppressed Coulomb interactions to boost hydrogen bonds.²⁵⁻²⁷ Hence, it was postulated that hydrogen bonding and Coulombic forces are considered “defects” in each other’s network.

It is interesting to observe the different developing trends of hydrogen bonding and interaction energy between cation and anion at temperatures below T_t from **Figure 6.3(b)** and **Figure 6.3(c)**, respectively. Therefore, the mere factor of hydrogen bond could be insufficient to elucidate the polymer/IL increasing T_t with longer alkyl group in cation,

since the hydrogen bond increment between cation and anion is more pronounced than between cation and PPO. It is possible that other interactions such as Coulomb force and dispersive force could participate in T_t tuning. More contributions to anion-cation interaction originate from hydrogen bond and dispersive force as the alkyl chain length in cation increases. In comparison to [C4mim][NTf₂], the reduced hydrogen bond capacity in [C4dmim][NTf₂] explain its immiscibility with PPO and ability to lower T_t . Nevertheless, the stronger anion-cation interaction with a longer cation alkyl chain ($n > 4$) support the argument that IL tends to assemble into more ordered structures, and the reduced entropy in neat IL results in a smaller decrease in entropy of mixing and consequently higher transition temperature.²⁸⁻²⁹

Simulation further revealed that the most ‘active’ hydrogen atom was located at C2 position of the imidazolium ring. As depicted in **Figure 6.3(d)**, at below T_t , the simulation of radial distribution function between C2 hydrogen atom and oxygen atoms in the PPO demonstrates that solvation shell of cation with a longer alkyl chain is statistically closer to PPO. This suggest a stronger interaction and more completed solvation shell that needs higher temperature to break (i.e. higher T_t). This is also corroborated by interaction energy simulation that the PPO-cation interaction strengthens with a longer alkyl chain in cation **Figure 6.3(c)**. Therefore, when the imidazolium alkyl chain is long enough (e.g. $n > 8$), the cation-PPO interaction could be so strong that cannot be broken by kinetic energy from high temperature. Thus, LCST properties would appear to be annihilate since PPO would be “permanently” wrapped by IL cation shell. With the understanding of various interactions between PPO and ILs from MDS, it is possible to experimentally perform an on-demand tuning of T_t by variation of PPO and binary IL content as demonstrated in **Table 6.1** for neat IL and **Figure 6.4** for binary IL system. When sufficient thermal energy is provided for temperature to rise above T_t , PPO - cation interaction and the solvation shell are interrupted due to breakage of hydrogen bonds. However, the residual IL/PPO attractive interactions, such as dipolar force and dispersive force, would help constrain the magnitude and rate of phase separation. This ‘residual forces’ mechanism could be translated to the thermotropic ionogel, to realize a dimensional stable system with no presence of liquid expulsion during phase separation.

Table 6.1 Summary table of PPO-IL mixture LCST determined by cloud point method.

LCST (°C)		Imidazolium based ILs of different alkyl chain length			
		[C ₁ mim][NTf ₂]	[C ₂ mim][NTf ₂]	[C ₄ mim][NTf ₂]	[C ₆ mim][NTf ₂]
PPO (wt%)	5	33.2	37.0	72.5	> 95.0
	10	30.0	31.5	66.5	> 95.0
	20	Immiscible	Immiscible	53.5	> 95.0
	30	Immiscible	Immiscible	43.6	> 95.0
	40	Immiscible	Immiscible	33.0	83.0
	50	Immiscible	Immiscible	Immiscible	71.5
	60	Immiscible	Immiscible	Immiscible	61.0
	70	Immiscible	Immiscible	Immiscible	57.0
	80	Immiscible	Immiscible	Immiscible	53.5

Figure 6.4 Tuning of thermotropic PPO/IL solution mixture transition temperature by adjusting both polymer and binary IL content. Transition temperature was determined by cloud point method. Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

6.3.2 Attributes of Thermotropic Ionogels

6.3.2.1 3D Polyurethane Network for Optical Switch Reversibility

Figure 6.5 Shows the heat – cool cycle of (a) thermotropic IL/PPO solution with irreversible performance. The weight ratio of PPO to $[C_4mim][NTf_2]$ is 1:1 and upon prolonged heating, biphasic separation of PPO in the upper region and IL in lower region of mixture solution could be observed. While (b) shows thermotropic ionogels with reversible performance even after 12 hours heating. The laminated ionogel are sealed with epoxy adhesive. The ionogel sample in this figure have an area size of 3 x 2 cm. Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

As depicted in **Figure 6.5(a)**, the PPO/ $[C_nmim][NTf_2]$ solution becomes turbid when it is first heated above the LCST. With isothermal heating, the solution mixture further divided by gravity into two clear layers that deprived the solution of its optical reversibility. Some prior arts of aqueous solution/colloids thermotropic systems probably also suffer from this problem.³⁰⁻³¹ Therefore, the formation of network is imperative to endow kinetic stability that guarantees stable and reversible optical switch in the ionogel.

As illustrated in **Figure 6.5(b)**, the ionogel is highly homogeneous and transparent at room temperature. Increasing temperature switches the subtle interaction balance between IL and PU network in favour of molecular repulsion resulting in a well-defined phase separation to form IL-rich domains which causes light scattering and reduced optical transmittance.

Conversely, decreasing temperature enhances the IL and PU network affinity, resulting in complete phase mixing and high optical transmittance. The light transmittance of ionogel depends on the solvation conditions of the polymeric network in IL. While the thermal-optical switch also applies for ionogels, the transition temperature (T_t) of ionogel differ from that of solution's LCST and this is probably due to the difference in constituent diffusivity. In contrast to polymer/IL solution mixture, the ionogel maintained its opacity even after prolonged heating.

According to experimental trial, free-standing ionogel can be formed with up to 70 wt% IL and above which only viscous solution might be obtained due to dilution effect. Although ionogel mechanical integrity could be improved with higher content of polymer and cross linker. Both the cross linker and the polymer should be added in moderate amount, to prevent 'weak' optical transition in ionogel. In fact, low optical contrast and sluggish optical switch was observed when the ILs account for 30 wt% or lesser of the ionogel. Therefore, the IL weight in ionogel is fixed to be the same with PPO (47 wt%) throughout this chapter to achieve balanced mechanical and optical properties.

Besides reversible thermal optical performance, it is also worth mentioning the thermal mechanical properties of the ionogel. Shear dynamic mechanical analysis between 25 and 65°C in **Figure 6.6(a)** show that the ionogels are indeed in the gel state with $G' > G''$. G' values remains largely unchanged within the temperature range exhibiting a typical rubber plateau like behavior of an elastomeric material. No distinct change of G' was detected below and above the LCST. More importantly, the ionogel's thermotropic properties are retained during stretching **Figure 6.6(c)** and bending, inset of **Figure 6.8(a)**.

Figure 6.6 The mechanical robustness of thermotropic ionogel with binary IL of 30 wt% $[C_4dmim][NTf_2]$ and 70% $[C_4mim][NTf_2]$ was investigated. (a) Dynamic shear mechanical analysis depicts the storage and loss modulus of ionogel at various temperatures. (b) Stress strain properties of the ionogel was tested at 10 mm min^{-1} and (c) reversibility of optical switch could be observed after 50 cycles of heat stretch cool and relax. Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

6.3.2.2 Transition Temperature Tunability

For the case of ionogel optical transition temperature, a plot of transmittance against temperature was first generated as shown in **Figure 6.7(a)**, and T_t could be evaluated as the temperature with a transmittance drop of 20% from the highest value at 550 nm. T_t for ionogel containing neat $[C_4mim][NTf_2]$ is about 68°C which is high for smart window applications. Modifying the network composition by copolymerization is possible but tedious for tuning T_t .³² Alternatively, the on demand tuning of T_t could be realized easily and precisely by introducing a second IL into ionogel to form a binary IL system with $[C_4mim][NTf_2]$. For instance, T_t can be shifted within a wide range between 20 and over 100°C by doping $[C_2mim][NTf_2]$ or $[C_6mim][NTf_2]$ as shown in **Figure 6.7(b)**.

[C₄dmim][NTf₂], which has the C2 proton in cation replaced by methyl group, is able to reduce T_t even to sub-zero degrees when it accounts for $\geq 50\%$ in the binary IL.

Figure 6.7 (a) Illustrate how a typical T_t is determined for an ionogel containing 33% [C₄dmim][NTf₂], through % transmittance at 550 nm versus temperature graph. (b) Influence of different binary ionic liquids and composition on the ionogel optical transition temperature. Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

6.3.2.3 Solar Modulation Performance

Figure 6.8(a) presents the transmittance spectra of ionogel at various temperatures below and above T_t . The transmittances change quite gradually with temperature in visible and infrared ranges and the ionogel is still “hazy” or translucent at temperatures a few degrees above T_t . In contrast, smart window composed of PNIPAM hydrogel with the same thickness of 1.7 mm would witness a large optical contrast around T_t within 1°C. It is desirable for smart window to gradually control light transmittance with temperature otherwise only full transparent or totally opaque states are available.³³ This intrinsic ability of thermotropic ionogel was postulated to originate from the constrained phase separation, which interestingly corresponds with the wider endothermic peaks in DSC, **Figure 6.9(a)** inset. The ionogel finally turns opaque if the temperature is far above T_t . For an ionogel with T_t of 33°C which is a typical transition temperature for smart window, the solar transmittance decreased from 77.7% at 25°C to 10.9% at 60°C demonstrating excellent

solar modulation ability. A summary of ionogel optical properties in relation to temperatures could be found in **Table 6.2**.

Figure 6.8 (a) The transmittance spectra of ionogel containing 33% [C₄dmim][NTf₂] and 67% [C₄mim][NTf₂] as the binary ILs, at various temperatures. The T_i is about 33°C and insets show the transparent, translucent and opaque states of the flexible ionogel. (b) The optical performance reversibility of ionogel during 5000 cycles. Each cycle between transparent and opaque states contains heating, holding, cooling and holding steps. The ionogel for ageing test contains 35% [C₄dmim][NTf₂] and 65% [C₄mim][NTf₂] for the binary ILs and the T_i is about 31°C. Luminous and solar transmittance refers to the integral value from 380 – 780 and 250 – 2500 nm, respectively. The modulation is obtained from the difference of transmittance values at 15 and 40°C. Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

Table 6.2 Ionogel's optical properties including the integral transmittance and modulation at different temperature. The ionogel contains 33% [C₄dmim][NTf₂] and 67% [C₄mim][NTf₂] as the binary IL and has a T_i of 33°C.

Temperature (°C)	15	25	35	45	60
T _{lum} (%)	87.8	86.7	76.6	10.6	7.7
T _{IR} (%)	70.8	70.8	69.7	38.7	15.5
T _{sol} (%)	78.5	77.7	70.8	23.4	10.9
ΔT _{lum} (15°C-X°C) (%)	0	1.0	11.2	77.1	80.0
ΔT _{IR} (15°C-X°C) (%)	0	0	1.1	32.1	55.4
ΔT _{sol} (15°C-X°C) (%)	0	0.8	7.7	55.1	67.7
Average T _{lum} (15°C-X°C) (%)	87.8	87.3	82.2	49.2	47.8

Furthermore, the ionogel's thermotropic properties are highly repeatable. As shown in **Figure 6.8(b)**, the ionogel's optical parameters including luminous transmittance (T_{lum}), luminous transmittance modulation (ΔT_{lum}) and solar transmittance modulation (ΔT_{sol}) varied within 5% after 5000 heating-cooling cycles. It is worth mentioning that no thermotropic material with phase-separation mechanism has reported such impressive performance reversibility. Hence, the thermotropic ionogel's light modulation ability is reliable and stable in an actual field application for an extended period of time.

6.3.3 Underlying Mechanism for Ionogel Stability

6.3.3.1 Ionogel Thermal Stability

Other characteristics that advantageously distinguish this ionogel from previous thermotropic hydrogels include the thermal and dimensional stability.

Figure 6.9 (a) DSC graph of neat [C₄mim][NTf₂], ionogel and PNIPAm hydrogel between -50 to 150°C. Inset shows the spectra enlargement of the phase separation characteristics between 20 to 75°C. **(b)** The TGA spectra of neat PU film and ionogels with different PPO to ionic liquid weight ratio. The ionic liquid used here is [C₄mim][NTf₂] and thermal stability of ionogel improved with the addition of IL. Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

Differential scanning calorimetry (DSC) tests in **Figure 6.9(a)** shows that, although neat IL has a freezing point of -3°C close to that of water, yet interestingly it was depressed to below -50°C , if not vanished, in ionogel. The similar confinement effect on the freezing points of ILs had been reported in nano-porous silica matrices and explained by Gibbs-Thomson model.³⁴ Hence, the nano-scale confinement mechanism in the ionogel could be attributed to IL-PU physicochemical affinity and its large PU fraction, since micro-scale confinement preserved the freezing point of bulk IL.³⁵ The undetectable freezing and negligible volatility of IL imparted the ionogel with excellent thermal stability between -50 and 150°C .

In addition, TGA spectra in **Figure 6.9(b)** shows that the ionogel does not thermally degrade till 250°C . The 5% weight loss observed around 284°C is due to neat polyurethane while a second onset of around 300°C could be observed in the presence of IL. The addition of IL result in an increase of thermal stability of PU. These thermal analyses indicate that besides smart windows, this thermotropic ionogel can also function in harsh conditions such as overheating protector for solar collectors.

6.3.3.2 Ionogel Dimensional Stability

The underlying reason for the ionogel superior cyclic performance was scrutinized by optical microscopy as shown in **Figure 6.10**. As temperature increased above the T_t , isolated domains of IL emerged as a result of micro-phase separation from PU matrix, and the ionogel became opaque as light scatters at the interfaces. However, the IL domains are always contained by crosslinked and aggregated PU walls in ionogel, which prevented the micro-phase separation from escalating into macroscopic scale phase separation. In addition, the ionogel has self-storage properties in that the micro-scale domains serve as IL reservoir within the opaque ionogel. Thus, the ionogel can be used as a solid device and exempts IL supplement to maintain responsive properties. When the temperature dropped below T_t , mutual affinity dominates the PU-IL interactions. The phase-separated IL, which is still contained within ionogel, diffuses into PU network to regain the ionogel's homogeneity and transparency. The large contact area between the two phases, the low

viscosity of IL as well as the entropic elasticity of PPO segments facilitate the diffusion process such that the ionogel's optical switching could be achieved within a few seconds. There was no change in the ionogel volume during the heat cool cycle as shown in **Figure 6.10** inset. From **Figure 6.9(a)** inset, ionogel dimensional stability may be associated with the much lower ΔH than that of PNIPAM hydrogel, during phase separation, since a large enthalpy change always implicates a large scale phase separation coinciding with liquid expulsion.³⁶ In fact, the volume reduction is not exclusive for responsive hydrogels and all the shrinkable gels happen to contain a tremendous amount of liquid phase to be functional.³⁷⁻⁴⁰ Based on Flory-Huggins theory, it was postulated that the large volume fraction of cross-linked PU is also responsible for the ionogel's negligible volume change during optical switch.

Figure 6.10 Optical microscope images of ionogel during heating from (a) 25°C (below T_g) to (b) 34°C (above T_g) to (c) 40°C (above T_g) and cooling back to (d) 25°C (recovery). Insets are the corresponding photos of the ionogel lying on a glass substrate and heated by a peltier heating stage. The T_g of the 1.7 mm thick ionogel is about 33°C and the light spot on ionogel came from microscope. Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

According to Flory-Huggins theory, the second derivatives of Helmholtz mixing free energy per lattice site is,

$$\frac{\partial^2 \Delta F_{mix}}{\partial \phi^2} = kT \left(-2\chi + \frac{1}{1-\phi} + \frac{1}{N\phi} \right) \quad (6.3)$$

where ϕ is the PU volume fraction, k is Boltzmann constant, T is Kelvin temperature, N is repeating unit number of PU and χ is Flory interaction parameter.⁴¹ The third item in bracket is insignificant since N is very large. When temperature is below T_i , IL is good solvent for PPO and $\chi < 0.5$ makes $\frac{\partial^2 \Delta F_{mix}}{\partial \phi^2} > 0$ regardless of polymer fraction, thus ionogel is stable and homogeneous. However, when ionogel undergoes phase separation ($\chi > 0.5$ and $\frac{\partial^2 \Delta F_{mix}}{\partial \phi^2} < 0$), a larger polymer fraction can minimize the absolute value of $\frac{\partial^2 \Delta F_{mix}}{\partial \phi^2}$ and diminish the released free energy used for liquid expulsion, thus restraints the extent of unfavourable phase separation.⁴²

6.3.4 Versatility of Thermotropic Ionogels

Besides tunability of transition temperature and stability of thermotropic properties, the ionogel also shows great versatility potential. Unlike conventional reflective coatings/films that are always dark blue, the ionogels can be easily dyed to different colors due to good affinity between ILs and organic dyes. As shown in **Figure 6.11(a-c)**, the ionogel's aesthetic superiority does not compromise the thermotropic properties. In **Figure 6.11(d)**, the optical switch was electrically triggered by joule-heating, and the implementation is much easier than the thermo-responsive hydrogel counterparts⁴³ owing to absence of liquid expulsion in ionogel and IL's physicochemical stability.

Figure 6.11 Photographs show the optical transition of ionogels doped with (a) methylene blue, (b) rhodamine B and (c) methyl orange organic dyes. The ionogels were located a few centimeters from the background pictures. (d) Possibility of electro-thermotropic smart window was demonstrated with a free standing ionogel ($T_t = 30^\circ\text{C}$) placed on single piece of ITO glass and joule-heating of specimen triggered by electricity. The temperature indicated on the thermal tape refers to the reading of the thermocouple in the OFF and ON state, respectively. DC voltage applied in this demonstration is 3 V. All the ionogels samples in this figure have an area size of 3 x 2 cm. Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

6.3.4.1 Ionogel/ATO Energy Saving Performance

Further, antimony tin oxide (ATO) nanoparticles was introduced into thermotropic ionogel to impart dual responsivity, which enable the ionogel smart window to adjust its transparency in accordance with a complex outdoor climate, especially low temperature but high solar luminance intensity. It can be seen from **Figure 6.12 (a – c)** that the transition temperature of the ionogel remains almost unchanged with the addition of different ATO content and their respective solar modulation profile at different temperature could be better visualized through **Figure 6.12 (d – f)**.

Figure 6.12 (a – c) Shows insignificant change of ionogel composite T_t with different plasmonic ATO content, while (d – f) illustrate the solar modulation profile of these composite in response to temperatures. The ionogels in (a – f) contain 33% [C₄dmim][NTf₂] and 67% [C₄mim][NTf₂] as binary IL. Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

From **Figure 6.13(a)**, it was observed that the surface temperature increment of neat ionogel under one sun irradiation was insufficient to trigger the optical transition. However, the composite ionogel temperature could rise by 15°C within 30 minutes to realize autonomous anti-glaring properties owing to ATO plasmonic resonance heating as demonstrated in **Figure 6.13(b)**.⁴⁴⁻⁴⁵

When solar irradiation is off, ATO-ionogel compatibility preserves a rather high luminous transmittance for smart window as shown in **Figure 6.12(d – f)**. In fact, ATO perfectly matches with this thermotropic ionogel in that neat ionogel modulates more remarkably in visible range while ATO predominantly absorbs near infrared (NIR) light. Hence, the presence of ATO in ionogel not only facilitates and accelerates the dimming control, but always shield the NIR irradiation to alleviate indoor air-conditioning burden. To quantitatively evaluate the thermotropic ionogel's performance for autonomous solar energy blocking in real situation, a heat-insulating styrofoam model house was built and an artificial sunlight source, which mimics the real application better than IR lamp or halogen lamp was used for the energy saving evaluation experiment.^{31, 46}

Figure 6.13 (a) Shows the profiles of surface temperatures and normal-normal transmittances at 550 nm for ionogels with different contents of antimony tin oxide (ATO) nanoparticles under solar irradiation. (b) The transmittance of ionogel with 0.1 wt% Antimony Tin Oxide (ATO) before and after 1 sun solar irradiation mapping with the solar irradiance spectrum. It shows the ionogel can be triggered by solar irradiation. Insets are the photos of neat ionogel and composite ionogel before and after irradiation taken by infrared camera. The T_i of ionogel is about 33°C. Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

Figure 6.14 (a) Schematic illustration of the experimental setup for monitoring indoor temperature of model house equipped with windows made of various materials. The photographs show the model house (front view) equipped with smart window of 0.15 wt% ATO composite ionogel before and after solar irradiation, respectively. The “NTU logo” in the mini model house is used for visual check of window transparency. The inner dimension of the model house is 0.22 x 0.22 x 0.19 meters and wall thickness is 0.03 meter. The energy distribution for the solar source is 5, 45 and 50% in UV, visible and NIR range, respectively. (b) The temperature profiles of an indoor sensor behind windows under solar irradiation. The T_i of ionogel is about 24°C. Reprinted with permission from Reference.⁹ Copyright 2017, American Chemical Society.

As depicted in **Figure 6.14(b)**, thermotropic ionogels and non-smart materials show different temperature profiles under irradiation. For non-smart windows, the indoor temperature would rapidly increase monotonously before reaching a plateau; while for smart ionogels the indoor temperature would decrease before slowly increasing to saturation. This is because the optical switch of ionogel makes the indoor sensor’s energy collection rate suddenly lower than the rate of energy dissipation to air. After that, indoor temperature increases much slower due to the slashed energy input. The state-of-the-art tungstate based coating for NIR shielding can help achieve an indoor temperature reduction of about 7°C compared with normal float glass. However, this widely used non-smart material is not able to modulate the energy carried by visible light, which accounts for roughly half of sunlight energy. On the other hand, the thermotropic ionogel achieved a 17°C temperature deduction due to the ability to modulate in both NIR and visible range. The synergic effects from ATO and ionogel help the composite achieve the largest

temperature reduction of about 20°C compared to float glass. Therefore, these thermotropic ionogels successfully proved to adapt dynamically to outdoor environment and achieve better indoor cooling performance than current state of the arts.

6.4 Conclusions

In summary, a new class of polyurethane based thermotropic ionogel with highly stable, reversible and tunable temperature-dependent optical performances was demonstrated in this Chapter. The constrained reversible phase separation within the ionogel is responsible for transparency-opacity switching without liquid expulsion. By variation of ionic liquid compositions, ionogel's optical transition temperature could be tuned between sub-zero to over 100°C for various application scenarios, and the underlying mechanism was extensively elucidated by molecular dynamic simulations. The ionogels showed high transparency ($T_{\text{lum}} = 87\%$) and luminous modulation ($\Delta T_{\text{lum}} = 80\%$) below and above the transition temperature, respectively; and these performances decayed negligibly even after 5000 heating-cooling cycles. Due to the modulation ability in both visible and NIR range, the ionogels can reduce indoor temperature by up to 20°C compared with float glass. In addition, ionogel's versatility was illustrated by incorporation of plasmonic nanoparticles that endowed thermotropic ionogels with dual responsivity. The promising approach of harnessing tunable IL/polymer interactions could be a powerful tool in creation of next generation flexible optical switching materials used in wearable electronics and micro optical sensors.

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Chapter 7

Discussion and Future Work

This chapter summarizes the idea behind this thesis. The first section of this chapter draws together the tread of this thesis and discuss on the implications and impacts of experimental findings. The extent of design target fulfilment based on hypotheses raised in Chapter 1 will be discussed. The second section of this chapter discuss the outstanding questions for future work. Possible future opportunities will be highlighted with suggested strategies.

7.1 General Discussion

In conclusion, this thesis explores three types of polymer gels, which achieve the main objective of climate adaptability and cyclic-stability in thermotropic smart window. The inability to perform optical switch in cold climate is because the hydrogels are only thermally responsive while its poor cyclic stability can be attributed to the high content of aqueous solvent (c.a. 90%) and large enthalpy change during LCST transition. Three simple and effective approaches have been demonstrated. Firstly, hybridization of thermal responsive PNIPAM hydrogel with plasmonic ATO nanoparticles, realized the concept of fully autonomous photothermotropic smart window and overcome the limitations of optical switching in the event of insufficient thermal energy for LCST transition. The presence of plasmonic nano heater in thermotropic hydrogel further enhance the solar modulation ability and response speed *via* photothermal effect. Next, binary solvent strategy consisting of glycerol and water in a dimensional stable thermotropic Agarose hybrid reveals potential to improve its cyclic-stability with a substantial reduction of 62 and 17% for freeze point and volatility, respectively. The experiment results reveal the thermal optical response of polyoxyethylene based surfactant in a binary solvent system, which is of paramount importance for enhanced stability of LCST based hydrogel smart window. Lastly, a new class of cyclic stable thermochromic ionogels was unveiled and this PU-based ionogel comprises of intrinsically stable ionic liquids and PPO. The options of multiple tuning parameters provide a broad range tuning of ionogel transition temperature while its versatility with plasmonic ATO enabled its superior energy conservation feature, when applied as an interlayer material for smart window. In this summary chapter, main findings of individual attempts which could effectively facilitate real life applications of thermotropic smart windows are recapped in the following section.

7.1.1 Discussion for Hypothesis #1 – PNIPAM/ATO Nanocomposite

In Chapter 4, application of the simple and scalable plasmonic heating strategy successfully leads to a fully autonomous photothermotropic composite.¹ The inability to perform optical switch in the absence of sufficient thermal energy was resolved. Solvothermal synthesized nanoparticles preserves the crystal structure of SnO₂, while the presence of Sb dopant endows ATO with NIR active plasmonic absorption. The ATO-NP with dimension of around 10 nm were uniformly dispersed in PNIPAM hydrogel matrix by *insitu* polymerization and the TMAH pre-treatment of ATO dispersion facilitates de-agglomeration of the particles in matrix of the composites. It is of interest that the pre-gel mixture should not contain any additives that could compromise the electrostatic stabilization mechanism of ATO-NP.

The optimization of the photothermotropic properties had been conducted with consideration of wt% Sb dopant, ATO-NP content and thickness of the hydrogel film. ATO nano heater exhibit the best photothermal effect when optimized with 10 wt% Sb dopants. Average T_{lum} was targeted at 60% for visibility after optical switch since increasing either particle content or film thickness will result in enhanced ΔT_{sol} , at the expense of lower visible transparency. In general, increasing the particle content demonstrates better thermal insulation properties than increasing film thickness because the former can induce more pronounced decrement of T_{IR} due to plasmonic absorption in the NIR region. It is worth mentioning that the dominant factor for the improvement of response rate and solar modulation ability can be attributed to the increase of film thickness and ATO particle content, respectively. The optimize composite with 5 mg mL⁻¹ ATO content in 80 μ m film thickness assume a high T_{lum} of 78.2% and depressed T_{IR} of 63.5% at 20°C. The saturation temperature of 35.5°C upon solar irradiation results in optical switching with $\Delta T_{lum} = 35.7$ and $\Delta T_{IR} = 18.1$, while preserving an average T_{lum} of 62.7% for visibility.

This material design strategy and its unique set of thermal optical properties surpasses the contemporary results of other thermotropic composites.²⁻⁴ Furthermore, the method of

applying nano heating via NIR active plasmonic would be universal for any other thermally responsive systems.

7.1.2 Discussion for Hypothesis #2 – Agarose Hybrid

As an alternative of PNIPAM which exhibit a large volume reduction during its LCST transition, a facile strategy of dimensional stable agarose hydrogel containing thermal responsive polyoxyethylene based surfactant was adopted. The presence of 6 wt% glycerol in binary solvent of hydrogel was found to be optimum and could lower the sealing requirement of smart window by substantially improving agarose thermal stability with a reduction of 62 and 17% in freeze point and volatility, respectively. The transition temperature of the hydrogel hybrid was observed to decrease by 2°C for every 6 wt% increase in glycerol, implying that binary solvent strategy could exhibit synergistic effect with plasmonic ATO for climate adaptable smart window. In fact, the use of less volatile alcohol for tuning of transition temperature, could also aid in achieving mechanically robust hydrogel. Due to the restrained micelle aggregation-disaggregation micro dynamics, a gradual optical switch of 0.74 times that of pure hydrogel was obtained and the response speed of optical switching could now be easily tuned on demand with plasmonic heating and binary solvent approach. Thermal hysteresis during a heat-cool cycle was found to be negligible, since the agarose hybrids managed to achieve thermal equilibrium after five minutes of isothermal holding. The solar modulation ability for ΔT_{lum} slightly deteriorated with a decrease of 1.7% upon optical switching, which should not affect the thermotropic smart window since a large ΔT_{lum} is not necessary during operation, unlike that of a privacy window. When coupled with plasmonic nano heating approach introduced in Chapter 4, this new hybrid could serve as a stability enhanced fully autonomous photothermotropic smart window. The understanding of micelles transition micro dynamics in binary solvent of alcohol/water from this work, will aid in future developments of smart hydrogels for various applications.

7.1.3 Discussion for Hypothesis #3 – Polyurethane based Thermotropic Ionogel

The purpose of the PU based thermotropic ionogel is to achieve cyclic stability gel for solar modulation based on LCST mechanism.⁵ Based on intrinsically stable ionic liquids and polyurethane, the ionogels assume optical switch functionality with critical zero-volume change, non-freezing and non-volatile properties. Polymerization of polypropylene glycol with isocyanate cross linker resulted in 3D polyurethane network structure which ensure ionogel fully reversible and repeatable optical switch of 5000 cycles. This indicates the presence of thermally reversible interactions between IL cation and ether group of polyurethane, creating additional avenue for this material to be explored in novel solid-state applications such as smart electrolyte,⁶⁻⁷ smart membrane⁸ and many others. From DSC thermogram, a broader and smaller enthalpy change was observed for ionogel as compared to the steep and sharp enthalpy change of PNIPAM hydrogel, during phase separation transition. This broadening of transition implies a smaller size of IL domain compared to PNIPAM,⁹ which could be attributed to the various attractive forces of IL cation and anion and the large fraction of polyurethane cross-linked chains. The nano confinement effect was observed with a significant shift in melting point from -3°C in ionic liquid to more than -50°C in the ionogel, due to the large polyurethane fraction of around 50%. The new class of thermotropic ionogel demonstrated in Chapter 6 offers a competitive edge over all other contemporary thermotropic systems in terms of cyclic stability and thermal optical properties. Intrinsic stable and non-volatile characteristics of ILs and PPO enabled this new class of thermal responsive ionogel to be applied in applications for various environmental settings.

7.2 Outstanding Question / Future Work

7.2.1 Multi-Functional Smart Window

The requirements of window glazing for both buildings and automotive are multi-fold and these includes comfort, safety and stability features. For practical application of

thermotropic smart window in both buildings and automotive, safety glass and noise control features are necessary for personal protection and acoustic comfort purposes.

7.2.1.1 Adhesion Property

As seen from **Figure 7.1(a)**, interlayers such as polyvinyl butyral (PVB),¹⁰⁻¹¹ ethylene vinyl acetate,¹²⁻¹³ and thermoplastic polyurethane¹⁴⁻¹⁵ had been commonly explored as polymer adhesive to improve laminated safety glass post breakage behavior and impact properties, which is critical for anti-theft and prevention of shattered glass injury.

Figure 7.1 Schematic illustrating (a) typical setup of a laminated solar control glazing and its (b) interfacial adhesion properties on glass substrate with various CuS film configuration. The labelling ‘h’ and ‘S’ of the specimens indicates the duration of chemical deposition at room temperature and number of PET side coated with CuS. Reprinted with permission from Reference.¹⁶ Copyright 2012, Springer Nature. While (c) shows the underlying hydrogen bonding mechanism for PVB adhesion with glass substrate.¹⁷ Image was sourced from the internet. Copyright @ Techno Galss (source: <http://technoglass.com.sa/>)

Among the various properties of a polymeric interlayer, interfacial adhesion of interlayer with glass substrate appears to be one of the key performance requirement, as shown in **Figure 7.1(b)**.¹⁶⁻¹⁸ There is a need to strike a balance between compliance and adhesion properties for interlayer material depending on the end application. Interlayer with high compliance tends to deliver better impact resistance while high adhesion result in firm adhering of glass fragments after shattering.¹⁷⁻¹⁸ Hydrogen bonding is often a dominant factor for adhesive application and the mechanism for PVB to glass bonding could be visualized from **Figure 7.1(c)**. PVB consists of non-polar butyral group and highly polar vinyl alcohol group. The hydrogen bonding that is formed between PVB vinyl alcohol group and the polar silanol group on the glass substrate is responsible for its good interfacial adhesion properties.

During physical handling, surface of the synthesized thermotropic ionogels and neat PU from Chapter 6, were found to be very tacky. In principle, the highly polar urethane groups of these PU-based ionogels should form strong hydrogen bond with the glass substrate for good adhesion properties. This promising observation in ionogels should lead to the possibility of a multi-functional smart window with noise reduction feature, in addition to its thermotropic optical switching. The adhesion properties of ionogel will be evaluated according to both standard compressive shear test and industrial pummel test.¹⁷⁻¹⁸

7.2.1.2 Energy Damping

Beside optical switch and safety glasses, acoustic control to mitigate noise pollution is also important and the energy damping mechanism which endow various materials systems with acoustic control have been investigated extensively.¹⁹⁻²¹ Among the various materials system, elastomer material exhibit excellent energy damping as it could easily adopt new conformations to relief the vibration energy.²² A part of the vibrational energy is dissipated as heat and this hysteretic solid damping mechanism could be characterize by the loss modulus and profile of the tan delta peaks. Several important factors such as polymer viscoelasticity, T_g and use of fillers will affect tan delta profile. More specifically, the T_g of the polymer for energy damping should be close and below the application operating

temperature range. As shown in **Figure 7.2**, various strategies such as formation of IPN,²³ use of organic,²⁴ and inorganic fillers²⁵ to shift and broaden the effective damping temperature range have been demonstrated.

Figure 7.2 Graphs showing the importance of tan delta profile (loss factor) for energy damping properties. (a) Loss factor for pure PU in comparison to pure epoxy and its IPN structures. Reprinted with permission from Reference.²³ Copyright 2017, MDPI Publisher. While figure (b) shows that different processing method for blending of ethylene-vinyl acetate organic fillers result in shifting and widening of tan delta peak. Reprinted with permission from Reference.²⁴ Copyright 2017, Elsevier.

The thermotropic ionogels are PU-based elastomer *insitu* polymerized with ILs.⁵ The presence of IL changes the viscoelastic properties of PU. Theoretically, an increase of IL should lead to a decrease of E' and increase of E'' , which result in an increase of energy damping properties for acoustic control. Since the energy damping has an inverse relation to resilience, an in-house modified drop impact test was designed and set up to determine the damping ratio of the thermotropic ionogels with varying IL content. It is worth mentioning that the modified drop impact test is designed to resemble the commercial bayshore resilience test method.

The synthesized PU and ionogels films of 30 x 20 x 1.45 mm were first subjected to vacuum drying at 50°C for 4 hours to remove the MEK cosolvent. The films were then sealed in airtight polyethylene bag to eliminate any possible surface induce effect from the films. A steel ball of 5 mm in diameter and 0.5g in weight was dropped vertically from a height of

0.8 m onto the sample through a quartz tube and the rebound distance was captured and recorded by a camera in slow motion mode. The drop impact test for each sample were repeated for 5 times (different spot of the sample) at room temperature of 25°C. Subsequently, the damping ratio of each samples at different temperature is calculated based on the following modified **Equation 7.1** and **Equation 7.2**.

$$R = D_r / D^* \quad (7.1)$$

$$\zeta = 1 - R \quad (7.2)$$

where R is the rebound resilience, D_r is the rebound distance, D^* is the baseline for rebound distance without any sample and ζ is the loss ratio or damping ratio which is an indicator of hysteretic energy loss during deformation and recovery of the material.²² The energy damping characteristics for the ionogels increases with IL content at temperature below LCST, as shown in **Figure 7.3**. The increment of E'' with IL content will be further investigated with a dynamic shear mechanical analyzer.

Figure 7.3 Illustrate the relative energy damping characteristic of commercial PVB, as synthesized PU and the thermotropic ionogels (Ig). The ionogels with varying IL content, contain 35 wt% [C₄d₃mim][NTf₂] and 65 wt% [C₄mim][NTf₂] as the binary IL. The transition temperature of the ionogels is around 32°C. Damping ratio of the specimens was evaluated with a modified steel ball rebound test, depicted in equation 7.1 and 7.2.

Furthermore, the glass transition temperature range of the thermotropic ionogels could be tuned by adjusting the polymer to IL ratio. Dynamic shear mechanical analysis would be adopted to compare the tan delta profile of the synthesized ionogels with neat PU and commercial energy damping materials. Tunable damping properties of the ionogel should be achievable with different kind of ILs, polymer to IL ratios and different polyurethane backbone chemistry. Further experimental investigation will be conducted on the above hypothesis to check for possibility of multi-functional smart window.

7.2.2 System Integrated Smart Window for Energy Harvesting

A sustainable and green concept for smart building can be further realized through hybridization of energy conservation and energy harvesting technologies. The idea of integrating different smart window systems with photovoltaic have been discussed and reported. These include systems such as thermochromic,²⁶⁻²⁷ electrochromic,²⁸⁻²⁹ thermotropic,³⁰⁻³² and suspended particle glazing.³³ The idea of a thermotropic/PV integrated system seems very attractive since solar irradiation could be harnessed by reflection of solar luminance from the thermotropic layer.

Figure 7.4 Schematic illustration of the working mechanism for building integrated concentrating photovoltaic (BICPV) smart window system during (a) summer and (b) winter. The thermotropic layer used in this reference literature is a HPC based hydrogel with tunable transition temperature in the range of 25 – 60 °C. Reprinted with permission from Reference.³⁰ Copyright 2017, MDPI Publisher.

Ideally, the thermotropic/PV system will autonomously adapt to climate changes to achieve a balance between electricity generated from PV and the amount of solar irradiation permitted through the building, as shown in **Figure 7.4**. The possibility of locating solar cells at the edges of the pane for reflected ray absorption and a cover glass for total internal reflection had been investigated with the aid of computer 3D ray tracing simulation.³² As seen in **Figure 7.5(a)** and **Figure 7.5(c)**, the efficiency of PV was explored with different solar incidence angle and total energy output was simulated for a sunny day from 8 am to 4 pm, with a thermotropic layer of 99% luminous reflectance, respectively. The exposure area was 1.44 m² with 100 modules each with dimension of 12 x 12 x 0.6 cm. A maximum electrical output of 57 W could be generated at 11 am on that day. This magnitude of power generation could be useful for powering a small fraction of home electrical appliance.

Unfortunately, the proposed design of thermotropic/PV system was only hypothesized and discussed by means of simulation thus far. The actual efficiency of energy generation could not be investigated and implementation of the system would not be possible, due to the limitation of aqueous based thermotropic hydrogel layer including formidable freezing and volatility. Furthermore, a simulated 60°C only result in a maximum of around 47% luminous reflection from HPC hydrogel, shown in **Figure 7.5(b)**.

Hence, there is an opportunity to explore the cyclic-stable thermotropic ionogel for BICPV application. The effect of system integration design, configuration of glass panes and solar incidence angle on the PV power generation efficiency could be evaluated experimentally and reliably. In principle, the presence of ATO plasmonic particles in thermotropic layer could further aid in facilitating higher solar luminance reflectance to achieve improve PV power generation performance.

Figure 7.5 (a) Showing the total internal reflection possible light path simulated by 3D ray tracing technique. A portion of the reflected ray reaches the PV cell located at four edges of the glazing after multiple scattering events. While (b) shows the percentage of transmittance and reflectance before and after LCST transition of the thermotropic HPC hydrogel. Reprinted with permission from Reference.³¹ Copyright 2016, Elsevier. Simulation reveal the (c) electrical output that could be generated by BICPV smart window system at different time of the day. Reprinted with permission from Reference.³² Copyright 2016, Elsevier.

7.2.3 Influence of Moisture on Polymer – IL Interactions

(A collaboration with Dr. Sadiye and Professor Chew Jia Wei)

The ILs used for the synthesis of thermotropic ionogel described in Chapter 6 are common hydrophobic imidazolium based ILs. Based on experimental observation and reported literatures, these hydrophobic ILs are hygroscopic and they tend to absorb a certain amount of water from air under normal operation conditions. The presence of water in IL, changes its properties such as viscosity,³⁴⁻³⁶ density,³⁷ and surface tension,³⁸ in a drastic manner. For example, the viscosity of [C₄mim][NTf₂] had been reported to decrease by 30%, when only 1.2% of water was present in the IL.³⁵ From previous study in Chapter 6, it was realized that the presence of water will affect the optical switch transition temperature of

the thermotropic ionogel. Hence, it is of importance to understand the role of water in a thermally responsive polymer and IL system for further technological developments. Moreover, thermally responsive interactions derived from polymer and IL are also hotly pursued in other trendy technologies including smart gating and smart electrolyte systems.⁶⁻⁸ To date, no simulation or experimental studies have reported the effect and micro dynamics of water on the LCST behavior of polymer and IL. Zhou et al. conducted a simulation study with molecular dynamics to elucidate the effect of water (0 to 10%), on the viscosity and various interactions parameters in imidazolium based IL with different anions.³⁹

Figure 7.6 The graphs in (a) and (b) depicts the radial distribution function of cation-anion and anion-anion, respectively. While the (c) spatial distribution function illustrates the three-dimensional probability distribution of water (yellow) and cation (cyan) around the [Ac]⁻ anion. The water content used was 4 wt%. (d) Shows the trending of hydrogen bond interaction as a function of water for the cation-anion, anion-water and overall system. All the simulation in this work was conducted for system consisting of only water and IL, with no influence of heat. Reprinted with permission from Reference.³⁹ Copyright 2017, John Wiley & Sons.

Firstly, the simulated radial distribution function shown in **Figure 7.6(a)** and **(b)** reveal that water tends to interact with anion instead of cation and this interaction increases with water content. Secondly, the spatial distribution function illustrated by **Figure 7.6(c)** further demonstrate the shielding of cation from anion by the water molecules. Lastly, the specific interaction of water with cation and anions was exemplified by the trending of hydrogen bonding as a function of water content as seen in **Figure 7.6(d)**. The hydrogen bond interaction between anion and water was observed to increase with water content in the system. Hence, it is definite that more complex multi-dimension interactions between polymer and IL will occur in the presence of water. It was postulated that the presence of water can disrupt the hydrogen bonding between cations and the ether functional groups from PPO, which facilitate the recombination of cation and anion to enable phase separation at lower temperature. However, cloud point determination of the solution mixture containing PPO, [C₄mim][NTf₂] and water in **Table 7.1** shows that the solution mixture LCST tends to increase with water content. This indicate that the water molecules might not disrupt the hydrogen bond interactions between cation and PPO, but rather a more complex interaction involving the anions is highly possible.

Table 7.1 Showing the influence of water on the LCST of [C₄mim][NTf₂] and PPO system. The nominal value for PPO was kept at 10 wt% while varying both IL and water content.

[C ₄ mim][NTf ₂] (wt%)	PPO (wt%)	H ₂ O (wt%)	Cloud Point (°C)	Remarks
89.4	10.6	0	65.3	NIL
89.6	10.0	0.4	78.6	NIL
88.5	10.7	0.8	80.0	NIL
88.3	10.0	1.7	86.4	NIL
88.0	10.0	2.0	90.1	NIL
87.5	10.0	2.5	101.5	NIL
87.0	10.0	3.0	NIL	Partially Immiscible
86.0	10.0	4.0	NIL	Immiscible

Figure 7.7 Illustrate the effect of water content on the experimental determined LCST values and its correlation with PPO radius of gyration determined *via* molecular dynamics simulation. The PPO content used for both experiment and simulation was set to be 10 wt%.

Based on Zhou et al. findings and the conducted experimental cloud point determination, it is possible that the LCST increases with water content, since water can function as a molecular shield to prevent cation and anion recombination. Alternatively, preliminary simulation results shown in **Figure 7.7** state that the PPO radius of gyration increases with water content and LCST. This suggest that water molecule could disrupt the bonding between cation and anion and subsequently, anion could hydrogen bond with PPO to increase the LCST. These possibilities would be further investigated by considering parameters including interaction energies and radial distribution function between different components in the systems.

7.2.4 Thermally Responsive Smart Electrolyte

(A collaboration with Dr. Sadiye and Professor Chew Jia Wei)

Thermally responsive polymer which exhibit LCST behavior in water or IL had been demonstrated as a responsive polymer electrolyte (RPE). These RPE modulates the conductivity and/or resistance of battery at desired ‘shut-off’ temperature to prevent thermal runaway in the event of overheating.^{6-7, 40-42} More specifically, Jesse et al.

demonstrated RPE in lithium ion battery with polymer and IL system consisting of PEO/[C₂mim][BF₄] and PBnMA/[C₂mim][NTf₂]. The thermally responsive polymers used in those studies ranges from 5 to 20 wt% and their different working mechanism had been elucidated.⁶⁻⁷ At temperature above the phase transition temperature, biphasic separation of IL and polymer occurs which result in the formation of polymer coating onto the porous electrode. Beside generating an increase in internal resistance at the interface of electrode and electrolyte, decrease in ion conductivity of RPE upon phase separation is another possible working mechanism.

Jesse et al. also investigated the influence of electrode surface area, polymer molecular weight, polymer to IL composition and Li ion doping on the RPE performance as shown in **Figure 7.8**. Unfortunately, the addition of polymer to IL always coincide with a decrease in conductivity. A drastic decrease in conductivity by more than 10 times could be observed in **Figure 7.8(b)** where PEO accounts for 80% in the RPE.

Figure 7.8 Shows the temperature dependence of ionic conductivity for the responsive polymer electrolytes. (a) Illustrate the difference in conductivity between different PEO to [C₂mim][BF₄] ratios for PEO molecular weight of 1.5K and 20K. While (b) and (c) shows the influence of Li ions on the conductivity for PEO to IL ratio of 80:20 and 50:50, respectively. The ionic conductivity for the various samples were measured via electrochemical impedance spectroscopy (EIS). Reprinted with permission from Reference.⁶ Copyright 2015, The Royal Society of Chemistry.

The viscosity of IL had been reported to display an inverse relation to its diffusivity, which is indirectly related to the conductivity.⁴³ While the viscosity of IL had been commonly reported to decrease with water content, i.e. the diffusivity of the ions should increase in the presence of water.³⁴⁻³⁶ Based on Zhou et al. study, the presence of water in ionic liquids result in hydrogen bond formation between anion-water and water molecules itself.³⁹ The water molecules acts as a diluent in the system which leads to lowering of IL viscosity. Hence, the addition of water in minute content of 1 – 5 wt% should increase the diffusivity of RPE to achieve comparable conductivity to that of neat IL.

A preliminary trial to investigate the conductivity of IL at room temperature of 25°C was performed *via* both experiment and molecular dynamics simulation as shown in **Table 7.2** and **Figure 7.9**, respectively. In the presence of 2 wt% water, the experimental conductivity of the RPE was found to be even high then that of neat IL, as shown in **Table 7.2**. The IL used in these conductivity measurements only consist of [C₄mim][NTf₂]. The conductivity of solution mixture was measured by Metrohm conductivity electrode (Metrohm, with Pt 1000 temperature sensor) coupled to conductivity module 856. The electrode was freshly calibrated with standard solution prior to the measurement.

Furthermore, the contribution from individual components in RPE was investigated by means of simulation and depicted in **Figure 7.9**, where the conductivity of the overall system was found to increase and this corroborate well with the experimental findings. It is worth mentioning that the PPO chain was not accounted for during the calculation of diffusion coefficient for the entire liquids (water, cation, and anion). However, it directly affects the diffusion coefficients of solutes due to interactions. For ion-conductance, the self-diffusion coefficients of cations and anions was considered in the Nernst-Einstein relation. The content of PPO used for simulation was 10 wt%.

Table 7.2 Shows the difference in ionic conductivity between neat IL, PPO – IL (binary) and PPO – IL – H₂O (ternary) systems.

Specimen (solution)	Ionic Conductivity ($\mu\text{S cm}^{-1}$) at 25°C
Neat [C ₄ mim][NTf ₂]	3183
90% IL – 10% PPO – 0% H ₂ O	1918
89% IL – 10% PPO – 1% H ₂ O	2893
88% IL – 10% PPO – 2% H ₂ O	3460

It is worthwhile to note that through IL structural modification, the hydrogen bond capability of imidazolium cation at the C2 position could be altered to tune the phase transition temperature.^{5, 44} This should enable a facile and on-demand tuning of the RPE ‘shut-down’ temperature, as demonstrated in **Table 7.3**. It was also reported that upon phase transition at the shut-down temperature, the polymer and IL based RPE did not manage to restore its conductivity even after one week.⁶⁻⁷ This implies an irreversible phase separation behavior which could be resolved with the thermotropic ionogel that was introduced in Chapter 6 of this thesis.

Figure 7.9 Illustrate the simulated change in (a) diffusion coefficient for the anion, cation, water and total system as a function of water concentration in the solution mixture. While (b) shows the changes in both experimental and simulated conductivity of the solution mixture as a function of water concentration.

Table 7.3 Demonstrate the LCST tunability of solution mixture with binary IL strategy. The cloud point temperature could be tuned on demand to obtain desirable ‘shut-off’ temperature for the responsive polymer electrolyte.

[C ₄ mim][NTf ₂] (wt%)	[C ₄ dmim][NTf ₂] (wt%)	PPO (wt%)	H ₂ O (wt%)	Cloud Point (°C)	Remarks
54.0	36.0	10.0	0	30.5	NIL
53.5	36.0	10.0	0.5	50.5	NIL
53.0	36.0	10.0	1.0	62.5	NIL
52.5	36.0	10.0	1.5	66.0	NIL
52.0	36.0	10.0	2.0	68.3	NIL
51.5	36.0	10.0	2.5	72.5	NIL
51.0	36.0	10.0	3.0	76.6	Partially Immiscible
50.0	36.0	10.0	4.0	78.5	Immiscible

From **Figure 6.10** optical microscope images, the formation of isolated IL droplets upon phase transition could lead to a decrease in conductivity at the desired ‘shut-down’ temperature. While a less cross-linked PU network could be adopted to endow irreversibility in the RPE. In principle, the IL to PPO ratio could be adjusted to obtain a subtle balance between conductivity and reversibility.

There are few important characterizations to be conducted for RPE systems doped with Li ions. This includes electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV), modified with temperature control. Beside Nyquist plot which could reveal the resistance, the conductivity of RPE could also be determined indirectly by EIS. While CV would help to determine the electrical double layer capacitance of cells with RPE, which depends on the accessible surface area and ion concentration. It is worthwhile to note that the shape of the CV graph could provide insight into the working mechanism of RPE. For example, a rectangular profile would indicate that ion diffusion is not a limiting factor and that an *insitu* formation of polymer coating onto the electrode could have occurred, which result in an increase of resistance.

7.2.5 Plasmonic Thermal Regulated Textile

In recent years, tremendous amount of efforts has been invested in the development of nanotechnologies in functional textile and important properties that focus on comfort and hygiene of textile user had been realized. Examples of these functionalities endowed by the nano moieties include stain repellence, wrinkle-free, anti-static and electrical conductivity.⁴⁵⁻⁴⁶ Thermal management in functional textile is an important attribute and various studies had been conducted in this aspect. The properties of interest investigated are typically moisture management,⁴⁷⁻⁴⁸ thermal regulation,⁴⁹⁻⁵⁰ and thermotherapy.⁵¹⁻⁵²

Conventionally, moisture management *via* fast drying could be achieved when certain multi-layered structure arrangement is adopted in the textile to facilitate moisture transport through wicking mechanism.⁵³ A typical multi-layered structure could be in the following order: skin > absorption/wicking layer (e.g. polyester or other wicking fibers) > wicking/spreading layer (e.g. polyester micro fibers) > absorption/evaporation layer (e.g. cellulosic, cotton or other hydrophilic fibers).

While thermal regulation studies which focus on the user body temperature have been exemplified with phase change materials (PCM) such as paraffin waxes microcapsules, and vanadium dioxides (VO₂).⁴⁹⁻⁵⁰ The objective of these thermal regulation textiles is to enable thermal insulation (retain heat) in cold climate while keeping the body cool during warm climate. Unfortunately, when the phase transition of paraffin wax microcapsules is completed, further increment or decrement in temperature will continue to result in heating or cooling, respectively. While the development of VO₂ is still currently in the research phase with various limitations such as limited range of transition temperature tunability, poor oxidative stability and low solar modulation ability.

Numerous intensive research efforts had been devoted to the developments of wearable thermal management devices, derived from flexible electrically conductive textile. These wearable conductive textiles had been explored for thermotherapeutic application based on its joule-heating ability. Candidates that were considered in conductive textiles includes

poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS),⁵¹ and more often, inorganic materials such as carbon nanotubes,⁵⁴ graphene,⁵⁵ and metallic nanowires.⁵⁶⁻⁵⁷ Although joule-heating facilitate active control of wearable thermal device, its implementation is hard to realize, since conducting polymer does not exhibit sufficiently high conductivity, while carbon rich nano material requires expensive vacuum environment and toxic chemical process to enhance conductivity, and metallic nanowire requires complex fabrication method, passivation and typically have low aspect ratio.

Based on the understanding of NIR plasmonic mechanism in transparent conducting oxides (TCOs) discussed and investigated in previous Chapters, an interesting concept of using plasmonic TCO for thermal management of functional textile is hypothesized and proposed as future work in this thesis. Although nano plasmonic had been demonstrated in textile application, its focus was only on the aesthetic and sensing aspects.⁴⁵ Moreover, plasmonic sensing in functional textile had only been proposed and yet to be demonstrated. Matsui et al. had demonstrated tuning of NIR plasmonic response of nano ITO by manipulating the inter-particle distance of ITO to achieve plasmon couplings.⁵⁸ Surface modification of the ITO NP facilitated the manipulation of inter-particle distance which result in selective IR reflection or absorption mechanism. Similarly, Dong et al. demonstrated the formation of electrically conductive network of polyethylene-imide (PEIN) treated ATO NP in PAN spin fibers during the drawing process to achieve anti-static property.⁵⁹

Hence, it could be postulated that the creation of thermal management textile with IR absorption or reflection mechanism would be possible by controlling the inter-particle distance of embedded or coated plasmonic TCO NP. The manipulation of plasmonic TCO plasmon couplings during the processing of fibers *via* drawing ratio would be intriguing from a fundamental point of view, while practically, plasmonic textile which could exhibit NIR absorption or reflection could result in functional textile with fast drying and thermotherapy attribute or anti-static with thermal insulation properties, respectively. Furthermore, the intrinsic photocatalytic property of wide band gap (c.a. 3.3 eV) zinc oxide based TCO such as gallium zinc oxide (GZO) could impart self-cleaning and anti-bacterial attributes to the plasmonic textile.⁶⁰⁻⁶¹

The key characterizations of these novel plasmonic textiles includes quantification of moisture retention and dye degradation as a function of solar irradiation time, anti-bacterial *via* adenosine triphosphate (ATP) and cell culture, UV-Vis-NIR spectroscopy to elucidate UV and NIR shielding mechanism, tensile test to evaluate mechanical integrity and FE-SEM to observe fiber morphology and nano particle dispersion state.

A modified solar irradiation set-up was established to evaluate the fast-drying properties of the plasmonic textiles. Firstly, PVA-1799 was dissolved in 80°C DI water to form a 2.5 wt% stock solution. Next, different content of 20 wt% of GZO aqueous dispersion were added to the PVA stock solution such that the final plasmonic textile contains 0, 3.5, 6.5 and 9.5 wt% of coated GZO nanoparticles. The prepared textiles of 3 cm by 3 cm were dipped coated with aqueous PVA/GZO dispersions and dried in an air oven at 60°C for an hour. Both the coated and uncoated textiles were then soaked with water and suspended with a clip for solar irradiation to test for fast-drying property. The weight loss of the absorbed water by the textiles were measured as a function of irradiation time, as shown in **Figure 7.10(a)**.

As compared to the neat cotton and PVA coated cotton (CPVA) which took around 65 mins to achieve complete drying, the plasmonic textile with 3.5, 6.5 and 9.5 wt% of coated GZO only requires 50, 40 and 30 mins to reach complete drying, respectively. This indicates an accelerated drying of up to 2.2 times could be achieved with only 9.5 wt% of plasmonic GZO nanoparticles. The corresponding temperature raise over time could be seen from **Figure 7.10(b)** where the plateau indicates the time taken for complete drying, while the subsequent raise in temperature could possibly be harness for photo thermotherapy to ease body discomfort like muscle ache.

Figure 7.10 Shows the photothermal characteristic and physical appearance of PVA/GZO coated cotton textile. (a) Illustrate the fast-drying attribute of the plasmonic textile with different content of GZO, upon solar irradiation at one sun condition (1000 W m^{-2}). While (b) shows the corresponding temperature raise of the plasmonic textile.

The mechanism of plasmonic heating by GZO nanoparticles on the solar irradiated textile were verified by means of thermal imaging as shown in **Figure 7.11**.

Figure 7.11 Shows the thermal images of the wetted cotton and plasmonic textiles taken by the forward looking infrared camera (FLIR) during the solar irradiation at one sun condition. The cross hair in the thermal images indicates the position of the textile where the temperature was captured and recorded. Note that the textiles were infused with around 0.3g of water (17°C) and irradiated in an environment with surrounding temperature of 21°C . All the textile sample in this figure have an irradiated area size of $3 \times 3 \text{ cm}$.

For example, after 30 minutes of solar irradiation, the cottons appear blue as it is still wet, while the effect of plasmonic heating could be clearly observed for CPVA/6.5wt% GZO and CPVA/9.5wt% GZO, which result in accelerated drying. Moreover, very uniform heat distribution of plasmonic heating could be observed for CPVA/9.5wt% GZO which could be further exploited to develop other functional textiles with stimuli-responsive or thermotherapy features.

Preliminary investigation of the plasmonic textile anti-bacterial property was conducted by measurement of the adenosine triphosphate (ATP) where a lower ATP value basically indicates a better anti-microbial property. Firstly, the textiles coated with different content of PVA/GZO were cut into 1 cm by 1 cm and sterilized with UV irradiation to disinfect the surface prior to antibacterial evaluation. Next, 50 μL of E Coli bacteria solution (10^6 cfu mL^{-1} in PBS) was drop casted onto the surface of the textiles. The textile samples were then incubated at 37°C for 24 hours. After incubation, the textile samples were immersed into 1.5 mL PBS solution and vortex mixed to dislodge the bacteria from the textile into the PBS solution. Both total and free ATP found inside the solutions were then measured using the Hygenia SystemSURE Plus ATP meter using AquaSnap™ Total and AquaSnap™ Free sampling consumables. It is worth mentioning that the AquaSnap™ Total measures both free ATP in solution and microbial ATP while AquaSnap™ Free measures ATP that is free in solution. The value of microbial ATP (alive) is obtained from the difference of total and free ATP measured experimentally.

Table 7.4 Shows the measured ATP in relative light units (RLU) for both coated and uncoated textiles.

Sample	Free/Dead (RLU)	Total (RLU)	Alive (RLU)
Neat Cotton	63	77	14
CPVA/6.5wt% GZO	5	6	1
Neat Polyester	24	30	6
PPVA/6.5wt% GZO	4	5	1

An enhanced anti-microbial property could be observed for the plasmonic textiles as shown in **Table 7.4**. Further quantification evaluation of the anti-microbial property will be conducted with the cell culture plate count method.

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APPENDIX

Chapter 4 – Supplementary Information

Table A.1 Effect of different Sb dopant content on solar modulation for PATO-1.2-180 films.¹

180 μm PATO films	VIS Modulation (%)			NIR Modulation (%)		
	200 s	400 s	600 s	200 s	400 s	600 s
Neat	7.2	12.2	16.7	3.0	5.0	6.5
0 wt% Sb	6.6	12.3	16.5	2.8	5.0	6.8
5 wt% Sb	8.2	16.8	23.5	3.3	5.8	7.4
10 wt% Sb	11.5	23.4	27.7	2.8	6.2	8.7

Table A.2 Effect of different ATO content on solar modulation for 180 μm PATO films.¹

180 μm PATO films	VIS Modulation (%)			NIR Modulation (%)		
	200 s	400 s	600 s	200 s	400 s	600 s
Neat	7.2	12.2	16.7	3.0	5.0	6.5
PATO-2	12.2	25.4	32.1	5.0	9.5	13.9
PATO-5	25.6	54.4	58.9	5.1	27.4	33.9

Table A.3 Effect of different ATO content on solar modulation for 80 μm PATO films.¹

80 μm PATO films	VIS Modulation (%)			NIR Modulation (%)		
	200 s	400 s	600 s	200 s	400 s	600 s
Neat	3.9	7.8	10.3	2.8	4.5	6.1
PATO-2	5.1	11.4	14.4	2.8	5.1	7.4
PATO-5	6.2	24.3	42.6	3.7	6.8	14.7

Figure A.1 Photothermal heating temperature profile of (a) PATO-1.2-180 (c) PATO-x-180 (e) PATO-x-80 and single wavelength T₁₇₀₀ graph for (b) PATO-1.2-180 (d) PATO-x-180 (f) PATO-x-80 from solar irradiation at 100 mW cm⁻² for 10 minutes. Reprinted with permission from Reference.¹ Copyright 2017, American Chemical Society.

Figure A.2 Rheology plot of PATO, showing all the specimens storage modulus (G') are higher than the loss modulus (G''), indicating they are indeed cross-linked hydrogels. Reprinted with permission from Reference.¹ Copyright 2017, American Chemical Society.

Chapter 5 – Supplementary Information

Figure A.3 Insufficient and inhomogeneous turbidity could be observed in 180 μm thick agarose hydrogel film containing 100% TX-114, above its transition temperature of around 29°C.

Table A.4 Transition temperature of 2.4 mm thick pure aqueous agarose and LCST of 2 wt% aqueous solution mixtures with different fraction of TX-100 and TX-114 surfactant.

Fraction of TX-100 in surfactant mixture with TX-114 (%)	Transition temperature of 2.4 mm aqueous hydrogel (°C)	LCST of 2 wt % solution mixtures (°C)
0	27	29
10	33	34
20	37	39
30	42	44
40	48	48
50	53	52
60	58	57
70	64	62

Table A.5 Transition temperature of 2.4 mm thick agarose hybrid hydrogels with different glycerol content. The surfactant mixture in these hydrogels consist of 80% TX-114 and 20% TX-100.

Fraction of glycerol content (%)	Transition temperature (°C)
0	37.5
6	35.4
12	33.2
18	30.8
24	28.8

Chapter 6 – Supplementary Information

Figure A.4 (a) FTIR spectra monitoring ionogel synthesis reaction after 0, 6 and 24 hours. After 6 hours of curing, the characteristic peak of -NCO group at 2270 cm^{-1} almost vanished, indicating a completion of reaction. (b) FTIR spectra of ionogel and various chemicals for ionogel synthesis. After 24 hours reaction in airtight mould, the solvent MEK still remains in ionogel, to ensure a phase-separation free curing reaction while the transparent ionogel also indicates a homogeneous reaction with the presence of MEK. Reprinted with permission from Reference.² Copyright 2017, American Chemical Society.

Figure A.5 (a) Probability distribution of radius of gyration for 30 wt% PPO/IL solution at 90°C over 800 nanoseconds. Both (ai) and (aai) show the iso-surface plots based on volumetric occupancy of $[\text{C}_4\text{mim}][\text{NTf}_2]$ at the average radius of gyration between $7 - 8\text{ Å}$ and $14 - 15\text{ Å}$, respectively. The blue and red colour clouds represent the cation and anion, respectively. Reprinted with permission from Reference.² Copyright 2017, American Chemical Society.

Figure A.5 displays results for a temperature of 90°C and presents no clear difference between cations with various alkyl chain length, which is presumably due to being close to or above the phase separation temperature and not being stable at that temperature, consequently exhibiting different configurations. The inset snapshots show that when the PPO is in the folded form (i.e., lower radius of gyration), it is surrounded both with anions and cations. However, when it is in the unfolded form (i.e., higher radius of gyration), the anions are closer in proximity to PPO, which reveal the dominance of the anion in the solvation process. This agrees with earlier studies which reported that the most important physicochemical properties can be controlled through anion exchange.³⁻⁴ Our experiments also show that imidazolium based ionic liquids with anions like halides and BF_4^- do not show LCST phenomenon with PPO.

Figure A.6 UV-Vis-NIR spectra of ionogel/ATO hybrid based on different corresponding saturation temperature obtained from xenon lamp irradiation experiment. These ionogel/ATO hybrid contains 33% $[\text{C}_4\text{dmim}][\text{NTf}_2]$ as binary IL and (a) 0, (b) 0.05, (c) 0.1 and (d) 0.15 wt% ATO plasmonic nanoparticles.

Table A.6 Summary table depicts the integral optical properties of different ionogel/ATO hybrid based on their corresponding saturation temperature from xenon lamp irradiation experiment.

50 PPO - 50 BIL 33% [C₄d₃mim][NTf₂]	0 wt% ATO		0.05 wt% ATO		0.1 wt% ATO		0.15 wt% ATO	
Temperature	25.0	30.6	25.0	34.6	25.0	37.9	25.0	41.1
T_{lum}	87.7	84.1	76.4	64.7	65.5	37.3	45.3	6.4
T_{IR}	71.6	71.3	48.7	54.2	34.9	30.0	24.8	8.2
T_{sol}	78.6	76.0	61.8	47.1	49.3	32.4	34.0	7.1
ΔT_{lum}	3.5		11.7		28.2		38.9	
ΔT_{IR}	0.3		1.6		4.9		26.9	
ΔT_{sol}	2.5		7.6		16.9		16.6	
Average T_{lum}	85.9		70.6		51.4		25.8	

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