Fabrication and solar modulation of thermochromic hydrogel for smart window application

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**FABRICATION AND SOLAR MODULATION OF
THERMOCHROMIC HYDROGEL FOR SMART WINDOW
APPLICATION**

ZHOU YANG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2018

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THERMOCHROMIC HYDROGEL FOR SMART WINDOW
APPLICATION**

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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

Statement of Originality

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

16/Aug/2018

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Zhou Yang

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

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Authorship Attribution Statement

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

Please amend the typical statements below to suit your circumstances.

Chapter 2.3.6 is published as **Y Zhou**, Y Cai, X Hu and Y Long, “Temperature-responsive hydrogel with ultra-large solar modulation and high luminous transmission for “smart window” applications”, *Journal of Materials Chemistry A*, 2014,**2**, 13550-13555. **DOI:** 10.1039/C4TA02287D

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- Dr. Long provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr. Cai and Dr. Long.
- I co-designed the study with Dr. Long and Dr. Cai, and performed all the laboratory work at the School of Materials Science and Engineering. I also analyzed the data.
- All microscopy, including sample preparation, was conducted by me in the Facility for Analysis, Characterization and Testing.

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- I worked as co-author and prepared the manuscript drafts with Dr. Yang together. The manuscript was revised by Dr. Long and Prof. Boey.
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- Dr. Long Yi, Prof. Shlomo and Prof. Boey edited the manuscript drafts
- I worked as first author prepared the manuscript drafts with Dr. Layani together. The manuscript was revised by Dr. Long, Prof. Shlomo and Prof. Boey.
- I designed the study with Dr. Layani, and performed all the experiments related with hydrogel part, such as PNIPAm hydrogel preparation. I also tested all the optical test, such as UV-Vis-NIR testing and response time testing at School of Materials Science and Engineering. I also analyzed the data
- Dr. Layani prepared regular and honeycomb silver grid at Casali Center of Applied Chemistry, Institute of Chemistry, The Hebrew University of Jerusalem, Israel.
- I worked together with Dr. Layani to test the heating efficiency of silver grids and prepared the electro-thermochromic device.
- Dr. Sokolov took the SEM photos of silver grids.

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- Dr. Long Yi, Prof. Shlomo, S Wang, P. Hu, Y Ke edited the manuscript drafts
- I worked as first author prepared the manuscript drafts with Dr. Layani together. The manuscript was revised by Dr. Long and Prof. Shlomo.
- I designed the study with Dr. Layani, and performed all the experiments related with hydrogel part, such as PSAHH gel preparation. I also tested all the optical test, TGA test, SEM, FTIR and viscosity at School of Materials Science and Engineering. I also analyzed the data together with Dr. Layani
- Dr. Layani prepared regular and honeycomb silver grid and printed PSAHH gel through 3D printing at Casali Center of Applied Chemistry, Institute of Chemistry, The Hebrew University of Jerusalem, Israel.
- I worked together with Dr. Layani to prepare the flexiable electro-thermochromic device and thermochromic waveguide.
- Mr. Wang designed and draw the schematic pictures, and 3D-printing design picture.
- Dr. Hu conducted the Raman test.

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Abstract

In the past half decades, hydrogels have received increasing attention, due to their exceptional wide range of promising applications such as drug delivery, sensing, and tissue engineering, etc. A large number of hydrogel products are sensitive to environmental stimuli, such as temperature, pH, etc. Due to the intrinsic properties, different thermos-responsive hydrogels have been fabricated and developed for energy saving smart windows.

Because of the significantly increasing impact from urban heat island (UHI) and global warming, the rising demand for comfortable living and working environments result in serious impact on peak and total electricity demand from building electricity consumption sector. Electrochromic and thermochromic materials are the most promising material applied in smart windows. Compared with conventional thermochromic Vanadium dioxide (VO_2), temperature sensitive hydrogel, one of the organic thermochromic materials has the advantages of low critical temperature (τ_c) (from 32-45 °C), and high luminous transmission (T_{lum}) below τ_c and large solar modulation (ΔT_{sol}) which are highly pursued.

However, there are several drawbacks of traditional hydrogel based thermochromic materials, such as large shrinkage during heating cross τ_c , poor water holding capacity, lack of active control and weak mechanical strength. To solve these problems as well as improve the thermochromic properties of smart windows, three approaches have been adopted to address those issues. Firstly, tungsten doped VO_2 hybridized with cellulose microgel was synthesized, which can block both visible and infrared (IR) light to give a better thermochromic performance. Secondly, by combining with transparent heater, we reported the first flexible electro-thermochromic device, which responded to both temperature and electricity. Lastly, the first carbon and silica-based hydrogel (PNIPAm-Si-Al gel) were hybridized by dispersing poly-(N-isopropylacrylamide) (PNIPAm) microgels into silica-alumina based gel matrix, which gives negligible shrinkage across τ_c , high water-holding ability, and printability as it was able to produce complex structure through a 3D printer. Meanwhile, such hybrid hydrogel films enable fabrication of flexible electro-thermochromic devices with up to 75% of ΔT_{sol} , depending on the film thickness and the

applied voltage, which is among the highest reported results. A flexible smart thermo-sensitive waveguide switch device was also fabricated by such hybrid PNIPAm-Si-Al gel, which will act as temperature sensitive switch for light signal transfer.

Lay Summary

Normally, a hydrogel is a kind of material contains a large amount of water such as jelly and rice noodle, which is soft and flexible. There are some hydrogel-based materials are “smart”, which will change color, shape or some other properties under external stimuli, such as pH, temperature, etc. Thanks to the intrinsic properties of the hydrogel, different kinds of hydrogel for energy saving smart windows applications have been fabricated and developed during my Ph.D. period.

Urban heat island (UHI) and global warming phenomenon are increasingly alarming in recent years, the rising demand for comfortable living and working environments result in serious impact on peak and total electricity demand from building electricity consumption sector. Correspondingly, numerous researches have been conducted to understand the UHI phenomenon and reduce the demand on air-conditioning systems. These researches have brought innovative designs and technologies such as “Green Buildings” and “Smart Windows”. Thermochromic smart window is a kind of window which will change color or transmittance when the temperature changes. Normally, in winter or at low temperature, the smart window should be transparent and allow solar light to go through, which will warm up the room. In summer or when the temperature is high, thermochromic smart windows need to change to dark color or opaque to block solar light, which decreases the temperature inside the room.

Considering the drawbacks of traditional hydrogel based thermochromic materials, my researches have been continuously enhancing the thermochromic properties and resolving the drawbacks. The thermochromic hydrogel based composite thin film significantly improved the thermochromic property. The new generation smart window, which can respond to both temperature and electricity stimulus, resolves the traditional drawbacks of large shrinkage during the heating process and poor water holding ability. The new synthesized thermochromic hybrid hydrogel solved several drawbacks, such as shrinkage during heating and poor mechanical strength. New applications beyond smart window are also developed, one is to be printed through 3D printing machine for complex display

design, and the other one is to be fabricated into flexible smart thermo-sensitive waveguide switch.

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Abbreviations

AA	Acrylic acid
APS	Ammonium peroxydisulfate
AR	Anti-Reflective
at. %	Atomic percentage
ATO	Sb-doped SnO ₂
ATSB	Aluminum-tri-sec-butoxide
BB	Bromothymol Blue
CAN	Cerium (IV) ammonium nitrate
CVD	Chemical vapor deposition
DI water	Deionized water
DSC	Differential scanning calorimetry
EC	Electrochromic
EDX	Energy-dispersive X-ray spectroscopy
ETD	Electro-thermochromic device
FETD	Flexible electro-thermochromic device
FLIR	Forward-looking infrared
FTIR	Fourier Transform Infrared Spectroscopy
GPTMS	(3-Glycidyloxypropyl)trimethoxysilane
HC	Honeycomb
HCl	Hydrochloric acid
HNO ₃	Nitric acid
HPC	Hydroxypropyl cellulose
IR	Infrared light
ITO	Indium tin oxide
LCST	Lower critical solution temperature
LiCl	Lithium chloride
Lum	Luminous light
M/R	Monoclinic/rutile
MBA	N, N'-Methylene bisacrylamide
MgSO ₄	Magnesium sulfate
MIT	Metal-insulator transitions
N ₂	Liquid nitrogen
NaCl	Sodium chloride
NIPAm	N-isopropylacrylamide
NIR	Near-infrared
NP	Nanoparticles
PCE	Power conversion efficiency
PET	Polyethylene terephthalate
PNIPAm	Poly (N-isopropylacrylamide)
PSAHH	PNIPAm Si-Al hybrid hydrogel

PU	Polyurethane
PVA	Polyvinyl alcohol
PVP	Polyvinylpyrrolidone
SEM	Scanning electron microscopy
Si-Al gel	Silica-Alumina gel
SnO ₂	Tin dioxide
Sol	Solar light
TEM	Transmission electron microscopy
TEMED	N,N,N,N-tetramethylethylenediamine
TEOS	Tetraethyl orthosilicate
TGA	Thermal gravimetric analysis
TiO ₂	Titanium dioxide
T_{IR}	Infrared transmittance
T_{lum}	Luminous transmittance
T_{sol}	Solar transmittance
UHI	Urban heat island
VO ₂	Vanadium dioxide
WO ₃	Tungsten trioxide
W-VO ₂	Tungsten doped vanadium dioxide
ΔT_{IR}	Infrared light modulating ability
ΔT_{lum}	Luminous light modulating ability
ΔT_{sol}	Solar modulating ability

Chapter 1

Introduction

This chapter shows a short background of hydrogels in the thermochromic smart window research area, which introduces the advances and problems of the smart hydrogel in the above research area. Then it followed with the problems: “The intrinsic properties of the pure thermochromic hydrogel, such as passive characteristic, shrinkage, water lost and poor mechanical strength, limited the development of hydrogel smart windows in real life applications” To address the hypotheses, the objectives and scope are divided into three aspects: 1. An electro-thermochromic device was firstly fabricated by PNIPAm hydrogel and silver grid electrolyte, which was sensitive to both temperature and electricity. 2. Hydroxypropyl cellulose (HPC) based microgel and its composite were fabricated, which will not shrink during temperature increasing process and able to regulate both luminous and IR light; 3. A new generation of PNIPAm-Si-Al hybrid hydrogel was fabricated, which shows extremely large ΔT_{sol} and T_{lum} , at the same time, this hybrid hydrogel shows much better water holding ability, negligible-shrinkage during temperature increasing cross τ_c , and also able to be printed through 3D printing method to achieve the complex design.

1.1 Background

Hydrogels are a group of polymeric materials composed of a hydrophilic matrix which enable them to hold large amounts of water in their three-dimensional network [1]. Hydrogels are capable of swelling or de-swelling reversibly in water, which is a dramatic volume transition in response to a variety of physical and chemical stimuli, such as temperature and pH [2]. During the past 60 years from first synthesis hydrogel established [3], hydrogel has become more important and has been used in applications such as drug delivery systems [4], biomedical applications [5, 6], tissue engineering [7], sensors [8] and energy saving applications [9].

1.2 Problem states

Due to human activities, urban heat island (UHI) area with 1 million people or more could be 1–3 °C warmer than its surroundings, which results in higher summertime energy demand, air condition demand, and greenhouse gas emissions [10]. Over exhaustion of energy resources and heavy environmental pollution have been alarming with rapidly growing world energy usage. The global energy consumption contributed from buildings, both commercial and residential, has been steadily increasing and reached figures between 20 and 40% in developed countries, which has overtaken transportation and industrial sectors. Among building services, the growth in air-conditioning system energy use is particularly significant (50% of building consumption and 20% of total consumption in the USA) [11].

Smart windows have received considerable attention because of their potentially significant contribution to the economization of building energy consumption [12, 13]. A window can regulate indoor solar irradiation in a ‘smart’ way, that is, by dynamically and reversibly tuning the transmittance of ultraviolet (UV), visible, and infrared (IR) solar radiation [14-17]. With different stimulated optical response changes, electrochromic, thermochromic and photochromic smart windows are developed to create climate adaptive building to reduce energy consumptions [18-20]. Normally, an electrochromic smart

window has 5 layers including the transparent conductor, counter-electrode, electrolyte, electrochromic material and transparent conductor in sequence [21-25]. While both traditional thermochromic and photochromic smart window require one thermochromic or photochromic materials coating layer on windows [26].

Compared with electrochromic smart window, which needs extra electrical power to active [26], thermochromic materials are advantageous for smart windows [27-32], due to intrinsic properties, which does not require any electrical power to operate and can be fully automated, as well as the large wavelength range transmission modulation, and at the same time, thermochromic smart window has simple configuration resulting in low fabrication and maintenance costs [33-36].

For thermochromic smart window, there are 3 key parameters: (1) the luminous transmittance (T_{lum}), which indicated the amount of visible light transmitted through the smart window; (2) the solar modulation ability (ΔT_{sol}), which indicated the ability to modulate the amount of solar energy pass through the window before and after phase change, it can be expressed by $\Delta T_{sol} = \Delta T_{sol} \equiv T_{sol}(\tau < \tau_c) - T_{sol}(\tau > \tau_c)$, where τ , τ_c donated current temperature and critical temperature of the thermochromic material (3) the critical temperature. Except for the 3 key parameters, other parameters such as luminous light modulation ability (the ability to modulate the amount of visible light energy pass through the window before and after phase change, ΔT_{lum}), solar transmittance (the transmittance for the UV-visible-near IR region of 250-2500nm, T_{sol}), IR transmittance (the transmittance for the near IR region of 780-2500 nm, T_{IR}), and IR light modulation ability (the ability to modulate the amount of near-IR light energy pass through the window before and after phase change, ΔT_{IR}) are also important factors to analyse thermochromic properties of smart window [37].

Compared with vanadium dioxide (VO_2), the most widely studied inorganic thermochromic material [34, 36], smart hydrogels are the caught a lot of attention in recent years in smart window application, which has more advantages. Compared with VO_2 based materials, T_{lum} of thermochromic hydrogels can be easily reached 80% and above at room

temperature, while the highest T_{lum} of VO₂ based materials is just ~ 60%. Compared with ΔT_{sol} , the highest report thermochromic hydrogel based material is up to 36%, while the highest VO₂ based material reported data is 22.3% (Table 1). What makes it even worse is the τ_c of pure VO₂ is 68 °C. For thermochromic hydrogel-based materials, the phase change temperature range from 30 to 52 °C, which is suitable for smart window applications and phase transition temperature is easily tunable [38-41].

Due to the intrinsic properties of the pure hydrogel, there are still several drawbacks limited the development of hydrogel smart windows in real life applications.

- Pure thermochromic hydrogel will shrink during temperature increasing process;
- Thermochromic material is passive, and in certain applications, the active control is required for new generation of thermochromic smart windows.
- The durability of the thermochromic hydrogel is low due to the poor water holding ability;
- The poor mechanical properties of normal thermochromic hydrogels limit them to fabricate complex structure design;
- The thermochromic properties should be further improved.

1.3 Objectives and scope

To address the problems mentioned above, the following studies were made:

- Hydroxypropyl cellulose (HPC) based microgel and its composite was successfully fabricated, which will not shrink during temperature increasing process and able to regulate both luminous and IR light.

- An electro-thermochromic device was firstly fabricated by PNIPAm hydrogel and silver grid electrolyte, which was sensitive to both temperature and electrical stimulus.
- A new generation of PNIPAm-Si-Al hybrid hydrogel was successfully fabricated, which shows improved water holding ability and negligible shrinkage cross τ_c ;
- The pnipam-si-al hybrid hydrogel was able to be printed through the 3D printer to achieve the complex design.
- PNIPAm-Si-Al hybrid hydrogel shows the largest ΔT_{sol} with extremely high T_{lum} compared with reported data.

1.4 Dissertation Overview

Chapter 1 shows a brief background of hydrogels in smart window applications, followed by problems statements, objectives and scope and a summary of the entire doctoral thesis.

Chapter 2 reviews thermochromism, traditional inorganic thermochromic materials including VO₂ based materials and their approaches, organic based thermochromic materials including pure PNIPAm hydrogel and its composites.

Chapter 3 discusses the experimental apparatus and basic principle of characterization techniques. It includes materials purification, different kinds of hydrogels fabrications, ETD and FETD device fabrication, and principles of characterization.

Chapter 4 First HPCA/VO₂ microgel composite thin film was investigated. HPCA microgel thin film was able to control solar light, especially at visible region, while VO₂ can control the IR transmittance (T_{IR}) with temperature change. In order to obtain both large luminous and IR modulating ability with relative high T_{lum} , HPCA microgel, and VO₂ nanoparticles composite is provided.

Chapter 5 Electro-thermochromic device (ETD) was firstly fabricated by PNIPAm hydrogel and silver grid electrolyte, which was sensitive to both temperature and electricity. This new ETD provides active control of passive hydrogel, and at the same time can act as a replacement of electrochromic smart window.

Chapter 6 New generation of PNIPAm-Si-Al hybrid hydrogel was successfully fabricated, which shows extremely large ΔT_{sol} and T_{lum} , at the same time, this hybrid hydrogel shows higher water holding ability, negligible-shrinkage during temperature increasing, and also able to be printed through 3D printing method to achieve the complex design. The new hybrid hydrogel-based devices: flexible electro-thermochromic device and smart thermochromic waveguide switch were also successfully fabricated.

Chapter 7 draws together the study by summarizing the results and suggesting future research directions. The main findings are discussed with reflect in the original problems, which is thus verified.

1.5 Finding and outcome

1. First W-VO₂/HPCA microgel composite was investigated, which will not shrink during temperature increasing process.
2. The new W-VO₂/HPCA microgel composite can regulate both at visible and IR light.
3. Phase change temperature of both materials is nearly the same, which was first achieved.
4. Electro-thermochromic dual response device (ETD) was firstly fabricated by PNIPAm hydrogel and silver grid electrolyte, which was sensitive to both temperature and electricity, while the transparent silver grid provided an active control for the traditional thermochromic smart window. The new ETD can be a cheap replacement of electrochromic smart window.

5. The new generation of PNIPAm-Si-Al hybrid hydrogel (PSAHH) was successfully fabricated, which is the first composite hydrogel with organic micro-pieces in an inorganic matrix.
6. This PSAHH showed largest ΔT_{sol} at 73.5% compared with other reported data, at the same time, the luminous transmittance is more than 80% at room temperature.
7. PSAHH showed much better water holding ability than pure thermochromic hydrogel, negligible-shrinkage during temperature increasing cross τ_c , and also able to be printed through 3D printing method to achieve the complex design.
8. The first flexible electro-thermochromic device was fabricated, which can be bent to 180° and showed the fastest response time compared with other reported data.
9. A thermochromic smart waveguide switch was first fabricated, which could turn light transfer in a waveguide with temperature changing.

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Chapter 2

Literature review

In this chapter, the concept of thermochromism is firstly reviewed. After that, the traditional thermochromic materials including both inorganic and organic materials are introduced. Vanadium dioxide (VO_2) is the most studied candidate for smart windows application, phase change mechanism and different approaches of VO_2 are introduced. Organic thermochromic materials including hydrogel with different mechanisms are introduced. Finally, the recent researches on thermochromic hydrogel and their composites are reviewed.

2.1 Thermochromism

Thermochromism is a kind of property of materials, which will change transmittance and optical properties under temperature change. Once temperature increase above the critical temperature, thermochromic material will modulate light transmittance by changing from a high transmittance state at low temperature to a less transmitting state at high temperature [1].

In general, two kinds of thermochromic materials exist: continuous thermochromic material, and the discontinuous thermochromic material. Continuous thermochromic material demonstrates a gradual color change within a range of temperatures, while discontinuous thermochromism involves a reversible or irreversible structure phase change at the phase change temperature, governed by the thermodynamics of the system [2].

Thermochromic material has high potential in lots of technological applications, including smart windows, temperature sensors, passive radiator, and camouflage devices.

2.2 Inorganic thermochromic material

2.2.1 Metal-insulator transition

Metal-insulator transitions (MIT) means transitions from a metal state to an insulator state with abrupt changes in electrical conductivity, at the same time, large magnitude changing are accompanied. These transitions can be achieved by particular parameters in ambient condition range, such as electrical field, temperature, and pressure etc.

For an insulator, its highest occupied electronic state is within a band gap. As external stimuli provide finite energy on the material to excite the electron from highest occupied electronic state to the lowest accessible state, the material starts to carry electrical current. After electronic bands partially filled, the material starts to show metallic behavior [3].

2.2.2 Vanadium dioxide (VO_2)

Vanadium dioxide (VO_2) is one of most promising candidates for smart windows application, which is sensitive to temperature changes. Vanadium dioxide has many polymorphs, including VO_2 (A), VO_2 (B), VO_2 (M), VO_2 (R), VO_2 (D) and so on [4]. Among these, VO_2 (A), VO_2 (B) and VO_2 (D) are the metastable phase, on the other hand, monoclinic and rutile (VO_2 (M/R)) are thermodynamically stable (**Figure 1**). These two compounds will experience a sharp and reversible first order metal-to-insulator transition (MIT) at nearly 68 °C as temperature increases. As temperature increases, the structure transforms from monoclinic VO_2 (M) (low temperature) to rutile VO_2 (R) (high temperature) companies with a dramatic change in near-infrared optical properties [5].

Figure 1. Crystal structures of VO_2 (M) (left) and VO_2 (R) (right), the O_1 and O_2 stand for oxygen atom that occupies two different Wyckoff position: $\pm (x, y, z)$ and $\pm (x, \frac{1}{2}-y, \frac{1}{2}+z)$, respectively. [6]

During the process of converting VO_2 from monoclinic to rutile, a decrease of resistivity happened with the magnitude of 10^4 to 10^5 theoretically, and the Infrared transmittance decreased dramatically [7].

At low-temperature region, VO_2 behaves like a semiconductor or insulator, which allows a large amount of IR light transmitted through. As temperature increase above the critical

temperature, VO_2 will behave like metal, which will near IR light. The infrared region contains the nearly half heat energy carried by solar light.

Due to the intrinsic properties mentioned above, VO_2 was applied for a wide variety of technological applications, such as smart windows and field-effect devices (such as switches, transistors, sensors) [8]. For smart windows application, **Figure 2** shows a typical spectrum of VO_2 film, while Table 1 summarizes the best VO_2 optical properties by experimental and simulation.

Figure 2. Typical VO_2 thermochromic performance below and above τ_c .

Table 1. Different approaches to enhance both ΔT_{sol} and T_{lum} of VO_2 -based thermochromic materials including doping, porosity, nanocomposite, anti-reflective and gridded structure [9]

		ΔT_{sol}	T_{lum}	Remark
Doping	Experimental	6.9%	45.1%	W doping, τ_c decrease to 48 °C [10]
	Experimental	6.7%	53.8%	Eu doping, τ_c decrease to 47.5 °C [11]
	Experimental	10.6%	54.2%	Mg doping, τ_c decrease to 54 °C [12]
Porosity	Experimental	14.1%	43.3%	Polymer-assisted deposition [13]

	Experimental	14.7%	50%	Freeze Drying [14]
	Simulation	20%	45%	155nm Thickness [13]
Nanocomposite	Experimental	12%	59.1%	VO ₂ /Si-Al nanocomposite foils [15]
	Experimental	11.7%	51.4%	Sb: SnO ₂ (ATO)/PU matrix [16]
	Experimental	22.3%	42.8%	VO ₂ /PU nanocomposite foils [17]
	Simulation	20%	67%	Sphere nanoparticle [18]
Anti-Reflective	Experimental	14%	22%	Si-Al gel AR coating [19]
	Experimental	43.5%	12%	Five-layered TiO ₂ /VO ₂ /TiO ₂ /VO ₂ /TiO ₂ films [20]
Gridded structure	Experimental	14.9%	43.3%	Micro-patterned [21]
	Experimental	13.2%	46.0%	Nanoparticle array [22]
	Simulation	14.0%	76.5%	Grid Nanoparticle array [23]

Vanadium dioxide is the most intensively studied solid-state thermochromic material, **Table 1** shows the highest performance of thermochromic properties achieved by different strategies. Although the thermochromic performance of VO₂ based materials has largely improved compared to the intrinsic VO₂, it is still on hold for commercial or industrial applications due to its intrinsic problems. Firstly, the critical temperature of VO₂ is 68 °C, which is too high to be applied in smart windows for daily life usage. Secondly, the T_{lum} VO₂ is around 50% or less, which is too low to be used for smart windows application in daily life. For the most important problem, the modulation of the solar energy throughput between the then temperature below and above critical temperature modest [18]. Besides, the cost is also another problem. Though VO₂ film has an effect on solar energy control, the production cost is too high for industrial applications. At the same time, it is also hard to scale up. Thermostability of VO₂ is poor, which is easy to be oxidized when it is in a high temperature environment or exposed to air for a long time.

Doping with other elements is commonly used to moderate its high critical temperature, as this can modify both physical and chemical parameters of VO₂, and the different doping effects were achieved through different dopants. Transition temperature (τ_c) of VO₂ can be changed directly by doping other elements to replace V⁴⁺ and O²⁻ ions [24]. The best-known dopant for reducing τ_c is tungsten (W) [25], transition temperature can be decreased at a range of 21 to 28°C per 1 at% [26, 27]. VO₂ films with W doping, which has τ_c of 30.0 °C and 38.5 °C were reported in the reference [28] and [29], respectively.

Compared with V⁴⁺, doping cations with larger valance and radius, such as W⁶⁺, Mo⁶⁺, Nb⁵⁺, and Ta⁵⁺, which can decrease VO₂'s critical transition temperature. Doping anions, which tend to replace O²⁻, such as F⁻ and P³⁻ [30, 31], is another way to decrease the critical transition temperature of VO₂.

Although W-doping is one of the most effective candidates for reducing τ_c , its sacrifice other optical properties such as T_{lum} and T_{sol} . Therefore, other dopants such as Eu and Mg [11, 12] were employed to reduce the τ_c and improve thermochromic properties at the same time. As the Eu- and Mg-doped VO₂ achieved a balance among τ_c , T_{lum} and T_{sol} , they are more competitive than W-doped VO₂ for the smart window application.

The multi-layer structure is another research area tend to improve the T_{lum} of VO₂ thin films [32, 33]. And the VO₂ film with the multi-layer structure to improve solar energy modulation has also been achieved [1, 34], even it is not very effective. Instead, the addition of new materials to generate composites, which have novel effect in improving optical properties and energy saving, should be used.

Beside transition temperature, there are still two more problems restrict VO₂ film's immediate use in the solar control area. Firstly, the integrated luminous transmission (T_{lum})

for VO₂ (M) is only ~40% with a noticeable magnitude of solar modulation (ΔT_{sol}) < 20% which is insufficient for windows coating applications [35]

VO₂ nanopowders can solve the above-mentioned problems. Based on experiment and calculations, when nanoparticles dispersed well in a dielectric host, they have both higher T_{lum} and ΔT_{sol} compared with VO₂ thin films [7, 36]. Size of VO₂ can affect the phase transition behavior: the size of VO₂ nanoparticles decreased, the width of the hysteresis curve (loop) increased during the MIT, meanwhile, the transition temperature will decrease. Both in direction of benefiting smart windows applications.

VO₂ nanopowders can be easily incorporated into thin plastic thermochromic films and smart windows with a relatively low cost.

Composite materials are the materials which combine two or more materials with different physical or chemical properties together to achieve advanced properties. For example, SiO₂/VO₂ composites with a core/shell structure can be put into a solution to make transparent, stable and flexible VO₂-based composite films. VO₂ powders stability is poor in dry air, for example, they may be oxidized to V₂O₅ after long time storage or affected by acid. Converting VO₂ powders into composite can expand their applications [37]. **Figure 3** shows the process of making the SiO₂/VO₂ core-shell composites and pigments.

Figure 3. Process to make SiO₂/VO₂ core-shell composites. [37]

2.3 Organic thermochromic material

2.3.1 Temperature-sensitive hydrogel

The temperature-sensitive hydrogel is a kind of chromogenic material, which will change its optical properties under temperature changes. There are 3 kinds of chromogenic hydrogel able to control solar light [38]: thermotropic hydrogel, thermochromic hydrogel and some chromogenic hydrogel with both thermotropic and thermochromic properties [38-46].

2.3.2 Thermotropic hydrogels

Thermotropic hydrogels have reversible transmittance control of the optical properties in respect with temperature. Below the critical temperature, thermotropic hydrogels are transparent and colorless [39, 40]. Once temperature increased above the critical transition temperature, the thermochroic hydrogel will turn to opaque. The color changing transition is reversible.

Normally, the transition temperature of some thermotropic hydrogels can be adjusted by changing the concentration of polymers. **Figure 4** shows the difference of the critical temperature with different polymer concentrations [40].

Lots of polymer matrixes and their composites have reversible transmittance control property, such as aqueous polyalkoxy derivative, aqueous LiCl-containing buffer solution, and polyvinyl methyl. In the transparent state, these hydrogels will allow the solar light transfer, while at opaque state, these hydrogels will reflect and scatter most visible light, which made thermotropic hydrogels able to be applied for solar energy control systems.

Figure 4. DSC curves of aqueous polyether samples with polyether/water mixing ratios of 5:1, 4:1 and 3:1. [40]

2.3.3 Thermochromic hydrogels

Thermochromic hydrogels will change their transmittance and color with temperature changing.

Firstly, during the gel-sol-gel transition process [41, 42], thermochromic materials can exhibit reversible color changes, due to their scattering effect [38]. A lot of hydrogel and

their composites including 3 wt% isotactic polypropylene dissolved benzene non-aqueous gel and gelled poly (1-butene) solved tetra-chloroethylene and belong to this group. [43]

Secondly, with temperature increasing, poly (phenylenevinylene) color changes from red to yellow, while this thermochromism process is not fully reversible [38].

For the last material, a suitable pH-sensitive indicator was dispersed into a hydrogel matrix which has a reversible pH changing with temperature changing. For example, phenolphthalein (with a color transition from colorless to red at pH8.3-10.0) was embedded in the transparent polyvinyl alcohol (PVA)/borax/surfactant gel network. **Figure 5** shows the color change of polyvinyl alcohol (PVA)/borax/surfactant gel network with phenolphthalein from 20°C to 70°C, from transparent clear state to transparent red [44].

Figure 5. a Photograph of the gel between two glass plates (2 mm thickness) at 20 °C; b Photograph of the gel at 70 °C. [44]

2.3.4 Chromogenic gel networks

Chromogenic gel network is kind of hybrid hydrogel for both color and transmittance control with temperature. Chromogenic gel network can be changed from a transparent colored state into an opaque colored state during temperature increasing process. Such gel

networks can change both their transmittance and color due to a temperature change at a constant volume. [45, 46]

This type of hydrogel is a mixture of an aqueous LiCl-containing buffer solution and polyalkoxy derivative, which is mixed with a suitable pH-sensitive indicator dye such as bromothymol blue. The color and transmittance behavior of the pH-sensitive indicator dye-doped gel networks is shown in **Figure 6**.

As temperature increases, three color states of the net gel can be shown in turns at different temperature. Based on **Figure 6**, the net gel is in the transparent green state when the temperature is lower than 32 °C. As temperature increases, this gel system will change to transparent yellow state; and into higher temperature range, the color becomes opaque yellow in a reflective state. In this thermochromic process, the green to yellow transition is primarily caused by pH change due to temperature increase. The significant decrease in transparency is caused by phase separation process which is typical for such polyalkoxide/LiCl/water gel systems. [38]

Figure 6. Transparency and color behavior of a Bromothymol Blue (BB) doped gel network in respect for the temperature at 750 nm wavelength of light. (Layer of thickness: 1 mm, [BB] = 1.9×10^{-4} mol/L). [38]

2.3.5 Transition temperature (lower critical solution temperature) of hydrogel

The most thermochromic hydrogel is synthesized by polymerization of a monomer in DI water. The lower critical solution temperature (LCST) of the hydrogel can be tuned by selecting thermal sensitive monomers. Such as hydroxypropyl cellulose with LCST at around 55°C, NIPAm with LCST at around 32°C, and poly (N-vinylcaprolactam) with LCST at around 30°C. PNIPAm has the most wide applied due to its narrow transition temperature range. The LCST of PNIPAm hydrogel can be adjusted by copolymerization with the second component. In general, copolymerizing with hydrophilic component would increase the LCST, especially for those ionic species; while copolymerizing with hydrophobic component (like MMA) would reduce the LCST. One point needs to be noted is that overdosing of ionic species would cause the disappearance of LCST. For example, when the molar ratio of NIPAm to sodium acrylate is smaller than 4, the thermal sensitivity disappears [47].

The PVA introduced constructed the hydrophilic tunnels to release water, especially when the hydrogel dimension is large. This is because when the bulk hydrogel is subject to external heat, the surface always become hydrophobic first and the water inside would be entrapped if no PVA is added [48]. The PVA and PNIPAm form semi-IPN structure and the presence of PVA would not significantly influence the LCST.

2.3.6 Poly (N-isopropylacrylamide) (PNIPAm) hydrogel

Poly (N-isopropylacrylamide) (PNIPAm) is a widely investigated hydrogel, with a lower critical solution temperature (LCST) around 32 °C [49, 50], is a temperature-responsive polymer, which has variety applications in tissue engineering [51, 52], drug delivery [53, 54] and smart windows [55]. As shown in **Figure 7**, when the temperature is below LCST, PNIPAm hydrogel is transparent, and at this state, the phase of PNIPAm hydrogel is homogeneous, while polymer chain hydrogel is connected with water molecular through hydrogel bond (intramolecular hydrogen bonds). Once temperature increased above LCST, intramolecular hydrogen bonds start to break, and intermolecular hydrogen bonds

generated. At the same time, the homogeneous phase starts to separate and the PNIPAm hydrogel start to turn opaque to block solar light.

	Optical property	Micro structures
Below LCST < 32 °C		Intramolecular hydrogen bond
Above LCST > 32 °C		Intermolecular hydrogen bond

Figure 7. Optical properties and microstructure changes of PNIPAm. [55]

Y Zhou et al [55]., investigated pure PNIPAm hydrogel thin films, as the thickness of the hydrogel thin film increased from 26 to 200 μm and the testing temperature increased from 20 to 60 $^{\circ}\text{C}$, the T_{lum} decreased and the ΔT_{sol} increased. The potential of the PNIPAm hydrogel thin film to be used in smart window applications is related to the hydrogel's thickness.

Figure 8a, b showed the optical properties of PNIPAm hydrogel thin films with different thickness. The thin film with 52 μm thicknesses, which was transparent at room temperature, with T_{lum} of 87.9%, while became translucent at 40 $^{\circ}\text{C}$, with an acceptable T_{lum} of 59.9%. At the same time, 52 μm thicknesses thin film provided 20.4 % ΔT_{sol} . It was found that T_{lum} of PNIPAm hydrogel thin film was not changed with thickness increasing at room temperature (below LCST), while underwent a monotonous reduction from $\sim 80\%$

(26 μm) to 1% (200 μm) when the temperature above LCST, which is totally opaque (**Figure 8c**). Stability and durability of PNIPAm hydrogel thin film was also tested, the optical properties were not changed after 20 cycles of measurement (**Figure 8d**).

Figure 8. a Optical transmittance spectra of the three samples with different thicknesses between 20 and 40 °C; b Trend of ΔT_{sol} , ΔT_{lum} , ΔT_{IR} and T_{lum} at 40 °C for different sample thicknesses; c Smart hydrogel thin films at room temperature (left) and in sunshine at 35 °C (right) with thicknesses of a 26 μm , b 52 μm , c 78 μm and d 200 μm ; d Durability test of hydrogel with thickness of 36 mm between 20 and 40 °C. [55]

2.3.7 Hydroxypropylcellulose (HPC) based material

Another hydrogel based on HPC was generated by YS Yang et al [56]., which is a green organic thermochromic material with tunable LCST by adding NaCl. Pure HPC hydrogel is transparent at room temperature (below LCST) and will become translucent when the temperature increased from 20 to 44 °C, with negligible IR transmittance change. Once

temperature increased above 50 °C, HPC hydrogel will become opaque and block whole solar wavelength (250 to 2500 nm) (**Figure 9a, b**).

Figure 9. an Optical transmittance spectra of the 0.35 mm HPC sample with temperature from 25 °C to 50 °C. b Pictures of various temperatures of HPC. [56]

Figure 10a, b showed micro-structure of freeze-dried HPC hydrogel at both 20 and 70 °C, the polymer chain size decreased from 10 μm to 2 μm , and pores size between polymer chain also reduce from more than 20 μm to less than 10 μm , while temperature increased from 20 to 70 °C, the much smaller pores and closed packed polymeric web structure act as a scattering center to block the visible light and result in opaque status above LCST.

Figure 10. SEM image of freeze-dried HPC hydrogel at (a) 20 °C and (b) 70 °C. [56]

The LCST of pure HPC is around 45 °C, which could be reduced to 30 °C with the addition of NaCl up to 5%, as NaCl weaken the hydrogen bonds between HPC and water (**Figure**

11a, b). The ΔT_{sol} , ΔT_{IR} , ΔT_{lum} were all increased with increasing NaCl concentration (Figure 11c, d). The most suitable hydrogel is HPC/NaCl (0.5%) sample, the ΔT_{sol} is 25.7% with high averaged T_{lum} at 67.4 % at 0.35 mm thickness.

Figure 11. a Hysteresis loop for the temperature-dependent transmittance of the HPC/NaCl (0-5%) samples with 0.7 mm thickness at a wavelength 580 nm and the curve of LCST vs NaCl concentration (wt%); b DSC spectra of pure HPC and HPC/NaCl samples. c Optical transmittance spectra of 0.35 mm HPC/NaCl samples at both 20 and 45 °C. d Concentration effects on ΔT_{sol} , ΔT_{lum} , ΔT_{IR} , and T_{lum} at 45 °C. [56]

2.3.8 Thermochromic hybrid material VO₂/PNIPAm hydrogel thin film

One thermochromic hybrid with the dual thermochromic function of both VO₂ nanoparticles and PNIPAm matrix was successfully fabricated by Y Zhou et al. in 2015

[57]. During this research, the phase transition of PNIPAm hydrogel controlled the luminous modulation, while VO₂ nanoparticles contribute to the infrared modulation, which provides extremely high $\Delta T_{\text{sol}} \sim 35\%$, while still maintained a high average $T_{\text{lum}} \sim 60\%$. **Figure 12** showed the mechanism formation of the laminated VO₂/hydrogel hybrid thin film.

Figure 12. Solar modulation mechanism of the VO₂/hydrogel hybrid. [57]

Pure PNIPAm hydrogel is colorless and transparent (**Figure 13a**) at room temperature, meanwhile the VO₂/hydrogel hybrid is brownish and transparent due to the presence of the VO₂ nanoparticles (**Figure 13b**) and once temperature increased above 35 °C (above the LCST), the composite starts to appear translucent (**Figure 13c**) within one minute.

Figure 13. a Pure hydrogel thin film at room temperature (25 °C), b VO₂/hydrogel hybrid at room temperature, c VO₂/hydrogel hybrid at 35 °C. [57]

Ball milled VO₂ nanoparticles are non-spherical, irregular, and well dispersed inside the matrix as shown as TEM images at different magnifications (**Figure 14**).

Figure 14. TEM image of VO₂ nanoparticles at (a) 31500× and (b) 50000×. [57]

The thickness effects of this VO₂/hydrogel hybrid composite were also studied (**Figure 15a, b**). The ΔT_{IR} and ΔT_{sol} increased with increasing thickness (**Figure 15b**), which is due to the combined effects of increased scattering effect from the PNIPAm hydrogel and IR absorption from VO₂ nanoparticles at the temperature above LCST.

Figure 15. a Optical transmittance spectra of the three samples with different thicknesses between 20 °C and 80 °C; b trend of ΔT_{sol} , ΔT_{lum} , ΔT_{IR} , and average T_{lum} between 20 °C and 80 °C for different thickness. [57]

Compared with same thickness (52 μm) pure hydrogel, VO₂/PNIPAm hybrid thin film had slight lower T_{lum} at both 20 and 90 °C, due to the VO₂ nanoparticles introduced, but IR modulating ability was dramatically increased, which lead to the high $\Delta T_{\text{sol}} \sim 34.7\%$.

Figure 16 showed the UV-Vis spectra for pure hydrogel, VO₂ nanoparticles thin film, and hydrogel/VO₂ nanoparticles hybrid. Pure hydrogel demonstrates a large contrast in visible range while pure VO₂ only shows the contrast in the near infra-red (IR) range. The large contrast in the hybrid structure (blue lines) occurs in both visible and IR range gives an improved ΔT_{sol} while maintaining moderate T_{lum} .

Figure 16. UV-Vis spectrums of pure hydrogel (black), pure VO₂ (red) and VO₂/hydrogel hybrid (blue) at low and high temperature, the grey area indicates the normalized values of the luminous (light) and IR (dark) spectra spectral irradiance. The light cyan area with sparse slashes is the luminous transmission difference and the light yellow area is the IR transmission difference of VO₂/hydrogel hybrid. [57]

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Chapter 3

Experimental Section

In this chapter, the experimental apparatus and basic principle of characterization techniques will be introduced. It includes: 1. Materials purification method and apparatus; 2. Preparation of HPCA microgel thin film and W-doped VO₂/HPCA microgel composite films; 3. Preparation of the transparent electrical grid 4. Preparation of PNIPAm hydrogel electro-thermochromic devices; 5. Preparation of liquid PNIPAm-hydrogel; 6. Preparation of Si-Al gel; 7. Preparation of PNIPAm Si-Al hybrid hydrogel; 8. Characterization method: UV-Vis-Nir, powder X-ray diffraction, single crystal X-ray diffraction, Infrared spectroscopy, Raman spectroscopy, thermogravimetric analysis, rheometer, scanning electron microscope, and vibrating sample magnetometer.

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2. **Y Zhou**, M Layani, F Y C Boey, I Sokolov, S Magdassi, and Y Long, "Electro-Thermochromic Devices Composed of Self-Assembled Transparent Electrodes and Hydrogels". *Advanced Materials Technologies*, 2016, 1, 1600069.
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3.1 Materials

3.1.1 Materials of HPCA microgel and their composites

Hydroxypropyl cellulose (HPC, 99% purification, Sigma-Aldrich), W-VO₂ (Sigma-Aldrich), Acrylic acid (AA) (Sigma-Aldrich), Disperbyk 180 (Sigma-Aldrich) and a multipurpose sealant (Selleys All Clear). AA was dried by MgSO₄ and then vacuum distilled before use. N, N'-Methylene bisacrylamide (MBA) (Fluka) was recrystallized from methanol. Cerium (IV) ammonium nitrate (CAN) (Sigma-Aldrich) was recrystallized from dilute nitric acid containing an appropriate amount of ammonium nitrate.

3.1.2 Materials of PNIPAm hydrogel and Si-Al gel

N-isopropylacrylamide (NIPAm, 98%, Wako Pure Chemical Industries Ltd), N, N – methylenebis (acrylamide) (99%, Sigma-Aldrich), N,N,N,N-tetramethylethylenediamine (TEMED, accelerator, 99%, Sigma-Aldrich), ammonium peroxydisulfate (98%, Alfa Aesar), (3-Glycidyloxypropyl)trimethoxysilane (GPTMS, 98%, Sigma-Aldrich); trimethoxymethylsilane (MTMS, 98%, Sigma-Aldrich), Aluminum-tri-sec-butoxide (ATSB, Sigma-Aldrich), Polyvinylpyrrolidone (PVP40, Sigma-Aldrich), Nitric acid (HNO₃, 70%, Sigma-Aldrich), Methanol (99.9%, Sigma-Aldrich), Verowhite (Stratasys), and Loctite 3414 were used without further purification. Deionized water (18.2 MU), Ethanol (99.8%, Sigma-Aldrich) was used throughout the experiments.

3.2 Samples preparation

3.2.1 Preparation of HPCA microgel thin film and W-doped VO₂/HPCA microgel composite films

An aqueous solution of 50 mg CAN in 2.5 mL of 0.1 mol/L nitric acid and 0.7 mL AA were successively added to 100 mL of 2% aqueous solution of HPC under gentle stirring and nitrogen bubbling. The reaction proceeded at 25 °C for 1 h, then 15 mL AA and 5 g

MBA were added, stirred more 4 h with keeping pH = 1-2, followed by adjusting the pH to 7.0 with 3 mol L⁻¹ NaOH. Excess precursors and side-products were removed over a 7 days dialysis using a membrane bag with a molecular weight cutoff of 14000. The resultant microgels were obtained by freeze-dried the remaining solvent in the membrane bag. 0.03 g HPCA sample was mixed in 2 mL deionized water to form HPCA microgel by ultrasonic for one hour to ensure it thoroughly dissolved and stranded for one day to form microgel. The dispersion of W-doped VO₂ (Jing Cheng PTE LTD) into hydrogel has been previously reported [1]. 0.05 g W-doped VO₂ nanoparticles was added into the 0.5 mL DPM solutions, after 30 minutes' ultrasonic dispersion, 5 μ L BYK 180 was added into the solution, then dispersed it in ultrasonic for 30 minutes more. The W-VO₂ solution was mixed with the HPCA solution with volume ratio at 1:10. Samples with 12.5 μ m, 25 μ m and 50 μ m films were made and the sealant was applied at the edges to prevent mass exchange with the outside environment.

3.2.2 Preparation of the transparent electrical grid

The fabrication of the transparent electrical grid was conducted directly on the polyethylene terphthalate substrate (PET 125 μ m, Jolybar Israel). Briefly, a 420 screen printing stainless steel mesh (Ponger 2000 Israel) was placed onto the PET. Next, droplets of the silver nanoparticles (NP) aqueous dispersion were placed on top of the mesh. During evaporation of the water, the silver NP self-assembled along the walls of the mesh. After 20 min, the mesh was removed, leaving a grid pattern composed of the silver NP. Once the transparent patterns were formed, it was sintered by exposure to HCl vapors for 30 seconds. This was achieved by placing it in a 10 mL glass petri dish, which was placed in a larger petri dish (100 mL) that contained 10 mL of conc. HCl (37 wt%, Aldrich)

3.2.3 Preparation of PNIPAm hydrogel electro-thermochromic devices

PNIPAm hydrogel was synthesized by in-situ polymerization of monomer in deionized (DI) water. In this case, 7.91 g (0.07 mol) N-Isopropylacrylamide (NIPAm), 1.32 g (0.03 mol) Polyvinyl alcohol (PVA), and 215.6 mg (0.0014 mol) N,N'-Methylenebis (acrylamide)

were dissolved in 70 °C DI water to make a homogenous 100 ml aqueous solution. After the homogeneous and transparent solution was obtained, the temperature was reduced to 25 °C and this solution was purged with N₂ for 30 minutes. 520.0 µL of this stock solution was pipetted into one 1 mL centrifuge tube, and then 7.0 µL N,N,N',N''-Tetramethylethylenediamine (TEMED, catalyst) and 16.0 µL ammonium persulfate (APS, initiator) were added in sequence to the centrifuge tube with vigorous vibration on vortex for 10 seconds. Then the solution was poured into the prepared 1 mm thickness PET plastic box and sealed. The hydrogel formed inside the plastic box in next 24 hours. Then contact the hydrogel box with prepared silver grids electrode [2].

3.2.4 Preparation of liquid PNIPAm-hydrogel

The synthesis of the liquid PNIPAm-hydrogel follows the synthesis of pure PNIPAm-hydrogel [3]. 3.164g (0.14 mol) of PNIPAm and 862.4mg (0.028 mol) of N,N'-methylenebis(acrylamide) were dissolved in D.I. water at 25 °C to make 400 mL homogenous aqueous solution. Then 6.15 mL of TEMED (catalyst) was added, followed by mixing at 600rpm for 30 mins. Finally, 12.3 mL of APS (initiator) was added into the solution. In order for the reaction to be completed, the solution was left stirring for at least 24 hours. The whole procedure (including completion of the reaction) was conducted at room temperature (25 °C). Then the homogenous liquid underwent pre-freezing-freeze-drying process by liquid nitrogen and dried by vacuum at -50 °C for 72 hours. After freeze drying, the PNIPAm powder was directly dispersed into 20 ml DI water by using vortex for 1 min, then the PNIPAm liquid hydrogel was made. This pure PNIPAm liquid hydrogel is transparent at room temperature and will turn to opaque, when the temperature is above LCST (**Figure 17a, b**).

Figure 17. a. PNIPAm liquid hydrogel at room temperature; b. PNIPAm liquid hydrogel at 60 °C

3.2.5 Preparation of Si-Al gel

The preparation method of Si-Al gel was reported [4]. To begin with, 1500 ml DI water was poured into a 2 L three-neck flask on heating mantle. Following process was to heat up DI water to 80 °C while stirring at 200 rpm, then turn off the heating. 400 ml ASB was poured in quickly, under stirring, for 4 minutes. Then, 10 ml HNO₃ was added to adjust pH to 3~4. Then the flask was heated up again to 80 °C under stirring at 200 rpm for about 2 hours to evaporate from 600 ml liquid in the flask. 30 g PVP was added into the flask under stirring, until all PVP dissolved, resulting in “solution A”. 755 ml GPTMS, 218 ml MTMS, 1472 ml ethanol and 512 ml methanol were mixed and agitated ultrasonically for 30 mins to obtain “solution B”. After cooling down solution A to room temperature, it was poured into solution B slowly to obtain “solution C”. Finally, 120 g PVP was dissolved in solution C under ultrasonic agitation for about one hour.

3.2.6 Preparation of PNIPAm Si-Al hybrid hydrogel

2 ml PNIPAm liquid hydrogel were mixed into 8ml Si-Al based gel by stirring at 600rpm, heated up to 70 °C in water bath until 2 ml of the PNIPAm-Si-Al gel was obtained.

3.3 Characterization

Cary 5000 UV-Vis-NIR Spectrometer was used to test the optical properties of all the samples. Direct optical transmittance (% T) tests were run between 20°C and 80°C with a variation of wavelengths ranging from 2500 nm to 250 nm for transmittance profiles for all the samples. The spectrophotometer is equipped with a heating and cooling stage (PE120, Linkam, UK).

The integral luminous transmittance T_{lum} (380–780 nm), IR transmittance T_{IR} (780–2500 nm) and solar transmittance T_{sol} (280–2500 nm) were calculated by equation 1:

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

where $T(\lambda)$ denotes spectral transmittance, $\phi_{\text{lum}}(\lambda)$ is the standard luminous efficiency function of photopic vision in the wavelength range of 380–780 nm, $\phi_{\text{IR}}(\lambda)$ and $\phi_{\text{sol}}(\lambda)$ is the IR/solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon)³⁹ Solar modulating ability (ΔT_{sol}), luminous modulating ability (ΔT_{lum}) and infrared modulating ability (ΔT_{IR}) were calculated based on the recorded spectra using the following expression:

$$\Delta T_{\text{lum/IR/sol}} = T_{\text{lum/IR/sol}}(20^\circ\text{C}) - T_{\text{lum/IR/sol}}(80^\circ\text{C})$$

TGA Q500 (TA instrument) was used to test the water content of PNIPAm Si-Al hybrid hydrogel (PSAHH) and pure PNIPAm hydrogel for 25 to 60 °C. The TGA analysis was performed for all the samples at 25 to 60 °C, while holding the temperature fixed at 25, 40 and 60 °C for 30 minutes at each temperature with ramping temperature of 20 °C per min. The viscosity and shear stress of NIPAm solution, PSAHH and pure PNIPAm hydrogel were tested by Anton Paar Physica MCR 501 Rheometer, with 1 to 0.1 1/s shear rate.

JSM-5310 and FESEM-6340F were used to capture the scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDX) images of the sample. Prior to the experiment, Samples were freeze-dried using liquid nitrogen (N₂) before drying

in a chamber for 72 hours. Thereafter, the freeze-dried powder was examined using SEM. The Fourier transform infrared spectroscopy (FTIR) data was collected by FTIR Perkin Elmer Spectrophotometer (Spectrum 400 FT-IR). All the samples were pre-freezed in liquid nitrogen and freeze dried at -50 °C in vacuum chamber. 0.01 gram of each sample was milled and mixed with 0.3 gram KBr powder, then pressed into appropriate tablets. All the data were collect by transmittance mode.

Raman spectra was recorded using a Witec alpha300 SR (WITec) Raman microscope configured with a charge-coupled device array detector with the excitation laser line of 488 nm.

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Chapter 4

Tungsten doped VO₂/microgels hybrid thermochromic material and its smart window application

In this chapter, the optical and thermochromic properties of W-VO₂/HPCA microgel are investigated. The concept of this composite is: Thermochromic microgel based on HPC is transparent at room temperature and will turn to opaque once temperature increased above its LCST, which was able to control solar light, especially visible light, while its IR regulating ability is negligible. In order to obtain both large luminous and IR modulating ability, tungsten doped VO₂ nanoparticles have been dispersed and embedded into a microgel gel matrix, which will provide IR modulation with temperature changing. Thermal sensitive microgels were synthesized directly from hydroxypropyl cellulose (HPC) and acrylic acid (AA) in pure water. The composite microgels were obtained by dispersing W doped VO₂ in HPCA microgels, this composite microgel had excellent T_{lum} (~ 80%) at room temperature. The excellent ΔT_{sol} (~ 36%) and high averaged T_{lum} (~56%) were reached with LCST lower than 50 °C, which is more suitable for smart windows application than pure VO₂ and previous reported thermochromic composite.

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4.1 Introduction

In order to reach the ZERO extra energy requirement and large solar energy blocking effect, thermochromic materials including VO₂ and hydrogels become candidates for cost-effective smart window applications. For an ideal thermochromic smart-window, a large ΔT_{sol} , a suitable τ_c , and relatively high T_{lum} are required [1]. VO₂ is the hottest thermochromic material addition in the materials concern energy-saving smart window applications [2, 3]. The phase transition critical temperature is around 68 °C, which means VO₂ can block infrared (IR) transmission (T_{IR}) at a temperature above τ_c and allows IR transmission below τ_c [4]. To attain good thermochromic properties, much efforts such as doping (such as Mg²⁺/W, rare earth doping such as Tb, La and Eu³⁺) [5-10], nanoporous structuring [11-13], antireflective coating [14, 15], nanoparticle-based composites [16-21], nano grinding [22] and biomimetic nanostructuring [23, 24] have been investigated. However, the intrinsic physical properties of VO₂ of high τ_c at 68 °C restricted it to be applied directly to smart windows applications. Doping by tungsten can significantly reduce τ_c of VO₂ nanoparticles. According to the strong IR modulating ability (ΔT_{IR}), VO₂ nanoparticles have been introduced to a new thermochromic Hydroxypropylcellulose-Poly acrylic acid (HPCA) microgel.

Hydroxypropylcellulose (HPC) is a water-soluble cellulose derivative [25], which have been developed into materials such as environmentally friendly and biocompatible requirement [26], biodegradable, non-toxic and solid polymer [27]. As a renewable resource, HPC also has a number of traditional applications including biological, medical and pharmaceutical fields [28-34].

A thermochromic material based on HPC has been reported in previous work [35]. In this paper, a facile way of preparing HPC derivative's (HPCA microgel) based thermochromic material, which provides both large luminous and IR modulating ability with relative high T_{lum} is provided, while its working temperature is more suitable, which extend its applications in smart windows.

4.2 Results and discussion

As temperature increased from 20 °C to 65 °C, the T_{lum} of pure HPCA microgel is dramatically decreased, while the IR transmittance change is negligible (**Figure 18a**). As shown in **Figure 18b**, pure HPCA microgel will turn to translucent from transparent, as temperature increased from 20 °C to 65 °C. Meanwhile, T_{lum} of the sample reduced from almost 85% to less than 40%. Once the temperature decreased to room temperature, the HPC microgel will return to transparent within 1 min.

Figure 18. a Optical transmittance spectra of the 25 μm HPCA microgel sample with temperature from 20 °C to 65 °C. b Pictures of 20 °C and 50 °C of HPCA microgel.

In order to analyze the micro-structures difference of HPCA microgel at both transparent and opaque state, HPCA microgel was pre-freezing in liquid nitrogen for 5 mins when it was at 20 and 80 °C. Then both of the frozen samples were put into vacuum freeze drier for sublimation drying. **Figure 19** shows the micro-structure of HPCA microgel at 20 and 80 °C. At 20 °C, the polymer fibers are thinner and longer compared with fibers at 80 °C (**Figure 19a**), which is due to the aggregation of polymer chains at 80 °C. Then more complicated polymeric web structure act as a scattering center to block the visible light and result in opaque status above the phase change temperature as shown in **Figure 19b**.

Figure 19. SEM image of freeze-dried HPCA microgel at (a) 20 °C and (b) 80 °C.

A hysteresis loop for pure HPCA, W-VO₂ HPCA composite microgels and W-VO₂ of 2500 nm were plotted to record transmittance in the temperature range from 20 to 65 °C as heating and cooling cycles (**Figure 20**). The size of W-VO₂ nanoparticles is around 50 nm, which is shown in the TEM image (inset of **Figure 20**). The LCST of pure HPCA microgel is around 52.5 °C while the average τ_c of W-VO₂ nanoparticles is 40 °C. Once W-VO₂ nanoparticles embedded into pure HPCA microgel, the LCST of HPCA microgel decreased 50 °C, which indicates that W-VO₂ nanoparticles could influence the phase change of HPCA microgel.

Figure 20. Hysteresis loop for the temperature-dependent transmittance of the HPCA and W-VO₂ HPCA composite microgels with 12.5 μm thickness at a wavelength 580 nm and W-VO₂ nanoparticles with 12.5 μm thickness at a wavelength 2500 nm with the corresponding derivative on the right. Inset (TEM picture of W-VO₂ nanoparticles).

Thickness is another character to influence the thermochromic properties of the composite microgel. **Figure 21a** shows the solar spectrum of HPCA microgel films with different thickness. As the thickness of pure HPCA microgel film samples increased from 12.5 to 50 μm , the T_{lum} of HPCA films decreased from 87.5% to 85.1% at room temperature; while, at 60 $^{\circ}\text{C}$, T_{lum} dramatically drops from 49.2% to 22.9%. As shown in **Figure 21b**, the luminous, ΔT_{IR} and ΔT_{sol} were all increased from 12.5 to 50 μm . Although the HPCA microgel film with 50 μm thickness exhibit highest ΔT_{sol} value of 44%, while the low T_{lum} less than 25% limited it for smart window applications.

Pure HPC microgel thin film with 25 μm thickness was selected for smart windows application. **Figure 21c** shows the optical spectrum of pure HPCA microgel, W-VO₂ thin film, and W-VO₂ HPC composite microgel thin films at both 20 °C and 60 °C. The T_{lum} of pure HPC microgel thin film is 87% at 20 °C, which shows the highest T_{lum} . Once temperature increased up to 60 °C, pure HPCA microgel thin film turned to opaque and T_{lum} reduced to 43%, while IR transmittance change is negligible. For pure W-VO₂ thin film, IR transmittance reduced with temperature increased, while ΔT_{IR} is 15% and T_{lum} change is negligible. Then W-VO₂ act as the smart dye of IR blocking embedded into HPC microgel matrix to fabricate composite microgel. As shown in **Figure 21d**, W-VO₂ nanoparticles enhanced the IR modulating ability compared with pure HPC microgel at 25 μm thickness (12 vs 24%). The ΔT_{sol} increased around 10% with 15% T_{lum} sacrificed.

Figure 21. a Optical transmittance spectra of 12.5, 25 and 50 μm thickness of HPCA microgel samples; b Thickness influence on ΔT_{sol} , ΔT_{lum} , ΔT_{IR} and T_{lum} (20 and 60 °C) of HPCA samples; c Optical transmittance spectra of 25 μm HPCA, W-VO₂, W-VO₂ with HPCA microgel samples. d ΔT_{sol} , ΔT_{lum} , ΔT_{IR} and T_{lum} (20 and 60 °C) of 25 μm HPCA, W-VO₂, W-VO₂ with HPCA microgel samples.

4.3 Conclusion

Temperature-sensitive HPCA thermochromic microgel was successively synthesized, which acts as a matrix for W-VO₂ nanoparticles. The microgel composite thin film with 25 μm thickness is totally transparent at room temperature, with a high T_{lum} of 80%. The luminous contrast contributed from HPCA combined with the IR transmission contrast due to the W-VO₂ give a high ΔT_{sol} of 36%. The SEM of the room temperature and high temperature samples indicated that the polymer fiber became more diminished and the pores became smaller, and this polymeric web structure acts as a scattering center to block the visible light and result in an opaque status at high temperature.

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Chapter 5

Electro-thermochromic devices composed of Self-Assembled Transparent electrode and Hydrogels

In this chapter, the new device for smart window application, which can be driven by both temperature and electricity change are investigated. The device consists of a transparent conductive grid and a thermochromic PNIPAm hydrogel. When the temperature is above LCST or apply enough current on the silver grid, the PNIPAm hydrogel will start to turn to translucent and finally become opaque, this process is reversible. For this device, a ΔT_{sol} above 58% with an optimal contrast of 75% and a response time of ≈ 1 min is obtained.

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5.1 Introduction

More than 50% of the world's population resides in urban area consuming approximately 70% of the global energy [1]. Energy consumption in the building sector is particularly alarming, as it consists of 40% of the world's energy usage [2]. This leads to the rise in the research and development of energy saving materials for the application in solar thermal control of buildings [3]. Chromogenic technologies, including a photochromic, electrochromic and thermochromic focus on reducing energy consumption and promote comfortness in buildings [4-6].

Thermochromic materials are typically in form of a glazing system [7-9], which are advantageous for smart windows, due to its passive and zero-energy input properties, as well as the large wavelength range transmission modulation [10-12]. For ideal thermochromic smart-windows materials, suitable phase transition temperature (τ_c), the large disparity in solar transmission at temperatures above and below τ_c (ΔT_{sol}), and high visible light (380 nm-780 nm) transmission (T_{lum}) [13] are the most important factors.

Vanadium dioxide (VO_2) are the most widely studied inorganic thermochromic materials as it regulates only infrared (IR) transmission [11, 14]. Hydrogel materials are the best-known candidate of organic thermochromic material, having a reversible transition behavior from a gel state (transparent) to a collapsed state (opaque/translucent) when the temperature is higher than the lower critical solution temperature (LCST) [15-18]. Numerous methods have been investigated to improve the thermochromic properties and **Figure 22** summarizes the best performance reported data in different approaches.

Figure 22. Thermochromic properties of different research area; porosity [19, 20], nanothermochromism [11, 21-23], moth-eyed nanostructure [24, 25], anti-reflective overcoat [26], doping [27-29], nanowire [13], organic hydrogel [30] and hybrid [31].

As shown in **Figure 22**, organic hydrogel has both outstanding ΔT_{sol} and T_{lum} , while some hydrogel, such as PNIPAm, has more suitable phase change temperature (32 °C) than VO₂ based materials (68 °C). Even though the τ_c of VO₂ based materials can be decreased by doping, the thermochromic properties are sacrificed [27, 29].

Electrochromic materials can be applied in windows glazing system, due to their color changing properties affected by electron transfer [32]. Various types of materials and structures can be used to construct electrochromic devices, which include metal oxides [33], viologens [34], conjugated conducting polymers [35], metal coordination complexes [36],

and metal hexacyanometallates [37]. However, the major disadvantages of conventional electrochromic materials are high cost and complicated setup [38].

The thermochromic window is passive. By integrating a transparent electrical heater, we report a new approach to activate the thermochromic hydrogel light transmission regulation via electrical heating to extend the usage of thermochromic films into the electrochromic field. PNIPAm hydrogel was chosen due to its outstanding thermochromic properties (**Figure 22**) as well as its ability to regulating light in the visible range. We expect that the electro-thermochromic concept will reduce the market penetration barrier and thus can provide an alternative solution for electrochromic market.

Previous reports have shown the use of transparent electrodes as electrical heaters by using typical ITO glass, CNT [39], graphene [40], and silver grids and NW films [41, 42]. Due to the brittle nature of metal oxide, such electrical heaters have a major disadvantage that they cannot be used with flexible substrates. Though, in order to obtain the conductive mesh layer onto the ITO, a polystyrene template is first formed onto the ITO followed by bar-coating of commercial silver ink. The process resulted in a small size electrode of 3x4 cm, which makes the multiple step process less industrially compatible. Even though graphene-based transparent heaters [40] showed very low sheet resistance of 43 Ohms/sq, the fabrication method is also considered a multi-step and expensive process where the graphene is first grown on copper foils by CVD and transferred onto a target substrate. Here we report a self-assembled grid composed of silver nanoparticles (NP), which is fabricated in simple steps at room temperature directly on a flexible substrate. The transparent electrode is comprised of silver NP which is self-assembled into a grid pattern having micrometer lines, transparent to the human eye. We have previously reported on the fabrication of self-assembled transparent conductive grid for electrochromic windows, where the grids were used as the bottom electrodes to form a bias of ~3V with the counter electrode. Here we used the grids as an electrical heater, which can be heated up to 80 °C, once an electrical current is applied through the two edges of the transparent grid. As elaborated in previous reports [39-42], the grid is formed by placing a droplet of silver NP dispersed in water on top of a screen printing mesh. The wetting properties of the mesh,

silver ink and substrate are tailored accordingly, causing the immediate spreading of the silver ink between the mesh and plastic substrates. Due to capillary forces and the wetting, the NP aligns according to the wires of the mesh, resulting in line widths smaller than 5 micrometers, thus, the resulting grid has high transparency.

Here we show for the first time, the fabrication of a honeycomb structure by using the same method and replacing the screen printing mesh with a tailored honeycomb plastic mesh. While applying a bias of 1-2 V, temperatures of 30-80 °C could be obtained. We compared the sheet resistance and obtained temperatures between the grid and honeycomb structure. The idea of electro-thermochromic device (ETD) simple, the general scheme of the ETD device is: a transparent electrode (either regular or honeycomb) is fabricated on PET. After sintering, a PNIPAm hydrogel sealed between two PET substrates is placed on the silver grid, followed by sealing of the two layers (**Figure 23**).

Figure 23. General scheme of the ETD device

5.2 Results and discussion

Figure 24a shows the PNIPAm hydrogels' solar light transmittance (250–2500 nm) spectrum with different thickness of 0.2 mm [30], 0.6 mm and 1 mm at various temperatures. At room temperature (below LCST) intermolecular hydrogen bonds exist between the PNIPAm polymer chains and water environment; as temperature increased above LCST, intermolecular hydrogen bonds are broken and intramolecular hydrogen bonds formed between C=O and N–H groups.[43].

At room temperature, all the PNIPAm hydrogel films with different thickness are colorless and transparent with the same T_{lum} (~84%) at all thickness, from 0.2 to 1 mm (**Figure 24a**) [30]. As temperature increased above LCST, the solar transmittance decreased obviously, and the thermochromic properties of the 3 samples showed big differences. The coloration contrast at 600 nm wavelength of PNIPAm hydrogel films are increased with thickness increasing, the sample of 1mm thickness has an extremely high coloration contrast of 84% versus 63.4% of 0.2 mm sample (**Figure 24b**). At the same time, the sample of 1mm thickness also provided the highest ΔT_{sol} , which can reach 75.7% between 20 and 50 °C and this is 50% higher than that of the 0.2mm sample. It should be noted that ΔT_{sol} values higher than 60%, the solar modulation is clearly observed and the film becomes milky and opaque. For the 1mm thickness film, thermochromic properties changing process with temperature increasing is similar to the 0.6mm sample, and 3 important parameters (T_{lum} , coloration contrast, and ΔT_{sol}) are nearly the same (**Figure 24b**). As shown in **Figure 24**, the 1mm thickness film shows lower T_{IR} at both 20 °C and 50 °C (75.71% vs. 83.71, 7.16% vs. 20.39%), while provides a higher IR light modulating ability, which can be calculated ~ 68.55% vs. 63.32%. Thus, the 1mm thickness sample can block more IR energy at both low and high temperature, while has a higher IR energy control range. 1 mm thickness PNIPAm hydrogel film is a better choice for this electro-thermochromic device.

Figure 24 a Solar light transmittance (wavelength range 250 nm – 2500 nm) of 0.2mm, 0.6mm and 1mm thickness PNIPAm hydrogel films with different temperature; b Thermochromic properties (coloration contrast, ΔT_{sol} , T_{lum} and T_{IR}) of three PNIPAm hydrogel films. The best performing results are circled in red.

In order to test the grids as electrical heaters, both the regular grid and honeycomb electrodes were measured while applying different voltages and currents. The main goal while fabricating transparent electrical heater is to obtain the highest heating efficiency with high transparency. In order to investigate the transparent pattern, a grid pattern and a honeycomb pattern structure with a similar open area (~80%) were compared (**Figure 25**). As can be seen in **Figure 25b**, the width of the line comprising the honeycomb (HC) structure has a higher line width, resulting in lower measured resistances while compared to the transparent grids. As can be seen in **Figure 25c, d**, the general trend for both HC and grid patterns, that the higher the resistance, the higher maximum temperature, this phenomenon follows the **Joule heating law** $Q=I^2R$. Furthermore, increasing the current/voltage results in an increment of the obtained temperature. The temperature can be controlled between ~ 30-80 °C.

The heating efficiency of both regular and HC structure grids has been tested. **Figure 25e** showed the energy consumption (J/s) of the different grids, the value is calculated by applied current times detected voltage. The two samples with different structure and same electrical resistance (3.7 Ω) consumed the same energy with same applied current (blue and red solid line). The HC structure sample (3.7 Ω) showed a much higher heating efficiency than the regular grid, and the temperature difference reached 16 °C with 0.6 A applied current (**Figure 25f**). HC structure has a better charge collection due to the wider grid lines, which can be reflected by the temperature increasing efficiency, as more electrical energy was transformed into heating energy. It should be noted that the experiment was limited to currents below 0.6 A, since at higher currents, short circuits of both honeycomb and regular grid pattern electrodes were observed.

Figure 25. a, c Microscope images of the obtained regular square grid at $\times 5$ and $\times 10$ magnification, b, d Microscope images of the honeycomb at $\times 5$ and $\times 10$ magnification, e Energy consumption of different grids with different applied current, f Temperature of different grids with different applied current

PNIPAm hydrogel film with 1mm thickness is adopted for this electro-thermochromic device application, both HC structure grids and regular grids experimented. **Figure 26** shows the light transmittance of both regular and honeycomb electro-thermochromic films with different applied voltages. As shown in **Figure 26a**, both regular and HC structure electro-thermochromic devices showed solar transmittance change under electrical control,

the T_{lum} of both samples are a variety with different applied voltage, but the solar transmittance of the two samples are quite different. HC structure grids showed higher heating efficiency (**Figure 25e, f**), but the light transmittance is more important, and as shown in **Figure 26b**, regular grids have a much higher solar transmittance than the HC grids. The solar transmittance of regular grids is nearly 80% versus 50% of the HC grids, which makes it more preferable for smart windows applications. Thus, the solar transmittance, especially T_{lum} of regular grid/hydrogel film is higher than the HC structure sample, which reached 75%. According to **Figure 26a**, the coloration contrast change at 600 nm wavelength is ~48% with 1.5V voltage and ~68% with a 2V voltage applied, which is within the range of best reported electrochromic devices [33, 44, 45].

Figure 26. a Solar light transmittance of regular and honey comb electro-thermochromic films; b Solar transmittance of regular and honey comb electro-heater; c Coloration speed (response time) of regular electro-thermochromic film with different applied voltages (2V, 4V, and 6V); d Comparison of transmittance contrast and coloration speed between electro-thermochromic film and other published electrochromic materials; A: PEDOT [46], B: PEDOT:PSS [47], C: Poly((2,2-bis(2-ethylhexyloxymethyl)-propylene-1,3-dioxy)-3,4-thiophene-2,5-diyl) and poly(N-octadecyl-(propylene-1,3-dioxy)-3,4-pyrrole-2,5-diyl) [48], D: Poly(3,4-(2,2'-diethyl propylenedioxy) thio-

phene and FL dye¹, Br⁻ / Br³⁻ [49], E: Poly(aniline-N-butyl-sulfonate) and PEDOT and poly(3-hexylthiophene) [50], F: Vanadium pentoxide-polymer hybrids [51], G: Inkjet printed tungsten trioxide nanoparticles [52], and H Electrodeposition of tungsten trioxide crystalline nanoparticles [53].

Both response time and switching time are key parameters to characterize electrochromic devices. Since a typical electrochromic device, such as in WO₃-based devices, the active material is undergoing an oxidation-reduction reaction, therefore it is custom to differentiate between switching time and response time (one cycle of oxidation switching time and reduction switching time). According to **Figure 26c**, the switching time of this ETD is about 120s with 2V applied voltage, and once the applied voltage increased to 4V, the response time dramatically decreased to nearly 70s. At the same time, both of response and switching time can be decreased to 40s at an applied voltage of 6V. When the power was turned off, the transmittance switching back speed is also different, the sample with 2V applied is the fastest, which just take 125s, due to the relatively lower temperature. According to the discussion above, 6V was applied at the beginning 50s and then decrease to 2V will make this device more energy efficient. According to the high transmittance contrast, and switching time, this electro-thermochromic device is competitive with other electrochromic devices. As shown in **Figure 26d**, the electro-thermochromic material showed higher transmittance contrast and response time than the other organic material based electrochromic devices, compared with typical electrochromic materials, the electro-thermochromic material provided a comparable transmittance contrast and response time, while with a much lower cost.

Figure 27a, b show how an integration of the electrical heater and the hydrogel can result in an actual electrochromic window. After a few seconds of applying a steady current of 0.6 A, the window turns into opaque. It should be noted that the device shown in **Figure 27**, returns quickly to its transparent state. This is attributed to the fact that the heating is initiated within the upper part of the transparent electrode, and it takes time for the heat to propagate through the whole gel.

In previous reports using the transparent electrical heater, the largest size of a heater was smaller than 5×5 cm, except silver NW-based which are difficult to pattern [41]. Here, we show that the simplicity of the fabrication method, enables the simple and fast formation of large scale transparent electrical heaters as can be seen in **Figure 27c, d**.

Figure 27. (a, b) picture of the electro-thermochromic device before and after applying 0.6. Amp, c picture of 10x10 cm transparent grid, d the same electrode after applying 0.6 Amp (FLIR image),

e durability test at 600 nm for 100 cycles of electrothermochromic device at room temperature and at 60 °C (2 V voltages applied)

Importantly, the good performance was maintained in the durability test, as shown in **Figure 27e**. The transmittance of 600 nm at both 20 and 60 °C (2 V applied) were relatively stable and almost unchanged after 100 cycles of measurement, indicating that the performance stability should be reliable in actual smart window applications as long as good sealing prevents water evaporation.

5.3 Conclusion

In conclusion, we have shown a new approach how to fabricate low-cost and simple electro-thermochromic devices. The transparent electrical heater is composed of metallic NP which self-assemble into a grid or honeycomb structures, which were compared and the grid heater was shown to be more effective. The ΔT_{sol} of ETD is 58.2%, which is higher than most reported thermochromic materials, the coloration contrast and response time is comparable to the best performing electrochromic material. The PNIPAm hydrogel films used enable fabrication of devices with up to 75% coloration contrast, depending on the film thickness and the applied voltage. The facile fabrication method and the low cost of materials make this approach favorable for the lower end of the EC market. It can be used as a privacy window inside buildings and as external façade windows, while the high ΔT_{sol} ensures significant energy savings with the added functionality of active control.

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Chapter 6

Fully Printed Flexible Smart Hybrid Hydrogel

In this chapter, a printable hybrid hydrogel is fabricated by embedding PNIPAm microparticles into a water-rich Silica-Alumina (Si-Al)-based gel matrix. The hybrid hydrogel holds a water content of up to 70 wt%, due to the unique Si-Al matrix, which will not shrinkage during heating process cross τ_c and the water holding ability is much better compared with pure PNIPAm hydrogel. The hybrid hydrogel can respond to both heat and electrical stimuli and can be directly printed layer-by-layer using a commercial 3-dimensional printer without requiring any curing. The hybrid ink is printed onto a transparent flexible conductive electrode, and it sustains bending angles of up to 180° , which enables patterning of various flexible devices such as smart windows and a 3D optical waveguide valve.

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6.1 Introduction

Hydrogels are formed through cross-linking of hydrophilic polymeric chains dissolved within an aqueous solution, which renders broadly tunable chemical and physical properties [1], particularly the intriguingly smart functionalities which can be activated by various external stimuli [2]. The versatility of hydrogels has gained popularity in applications such as tissue engineering [3], drug delivery [4], soft electronics [5, 6], smart devices [7, 8] and sensors [9]; in which the smart functionality of the hydrogel is a must. For example, poly(N-isopropylacrylamide) (PNIPAm) is a widely explored hydrogel, having a lower critical solution temperature (LCST) around 32 °C and is often used as an active matrix, responsive to temperature, pH and light irradiation [10, 11], in applications such as drug delivery [12, 13] and smart windows [7, 12, 13]. However, due to limitations of mechanical [14] and visco-elastic properties [15] during coil-to-globule transition, the processing and deposition methods of PNIPAm hydrogel are limited, especially for fabrication of complex structure patterning on flexible substrate.

Printing of hydrogels enables freedom-of-design, for fabrication of various patterns which are responsive to external stimuli, such as heat, that can yield a thermochromic response. Much effort has been devoted to developing printable hydrogel applications, including electrochemical devices [16-18] and biomaterials [19-22]. One of the most well-known classes of printable hydrogels is based on photopolymers such as Polyethyleneglycoldiacrylate (PEGDA) which requires a photopolymerization processes [23]. If the printing is performed by a layer-by-layer approach, it enables forming 3D objects with high aspect ratio, a process known as 3D or additive manufacturing (AM). To enable 3D printing, maintain the smart functionality and reduce the water evaporation, a new and facile route is presented here, by embedding PNIPAm micro-sized particles within a printable Si-Al based gel matrix. The water-rich microenvironment is essential for the functionality of the hydrogel as well as to activate tunable viscosity that is required for printing.

The traditional 3D printing technologies for hydrogels include stereolithography and nozzle-based printing [24, 25]. As introduced by Zhang *et al* [26], and other reports [27-29] for 3D printing of hydrogels, cross-linking processes (physical, chemical or photo cross-linking) were required to achieve their designed functions during and/or the deposition process. Unlike previous reports of hydrogels 3D printing, here we show the printing of PNIPAm particles which are used as a functional additive and are dispersed within a printable Si-Al-based gel to form a PNIPAm Si-Al hybrid hydrogel (PSAHH). This hybrid can be printed directly on a flexible substrate to achieve the designed functions, such as thermochromism, without any further crossing-linking process [26].

By either passive heating or electrical heating of the printed device, the water molecules which are trapped in the PNIPAm particles are excreted to the Si-Al sol gel matrix. This results in an optical change from a transparent to opaque state due to the dehydrated PNIPAm particles that act as light scattering centers. For electrically triggered heating, the hybrid ink is directly printed onto a flexible transparent conductive grid, which is composed of self-assembled silver nanoparticles (**Figure 28**) [30]. During the heating process, the Si-Al gel matrix retains the 3D structure and does not show any shrinkage, contrary to what is observed in pure PNIPAm hydrogels. As shown schematically in **Figure 28**, the new hybrid hydrogel can be deposited in various patterns by using a direct-write dispenser without the need for a further curing process.

Figure 28. Mechanism and structure of flexible electro-thermochromic device (FETD). Top images represent the printing of the hybrid hydrogel at room temperature (left) and high temperature or applied voltage on the grid (right). At low temperature, the visible light wavelength can pass through the hybrid hydrogel (middle left), and when it is heated the light is scattered (middle right) by the PNIPAm particles without any shrinkage of the hybrid hydrogel. The mechanism is shown in the two bottom schemes. At room temperature, the water molecules are within the PNIPAm particles. Once heated (bottom right), the water molecules will be released from the PNIPAm and the shrinkage particles will cause scattering of the light.

6.2 Results and discussion

Figure 29a shows the predesigned printing structure, while printhead describe the deposition mechanism of the PSAHH (PNIPAm-Si-Al hybrid hydrogel) gel onto a transparent PET plastic film with silver grid coated. The printhead will move along the X-Y axis during printing, and after each layer is finished, the platform go down along Z axis

for the next layer's printing work. As shown in **Figure 29b, c**, one 2mm thickness pattern was successfully printed through layer-by-layer printing. As the viscosity of PSAHH is suitable, the gel can be successfully printed while its shape can be kept after printing. As PSAHH gel contains PNIPAm as thermochromic dye, this printed pattern was able to turn to translucent after heating to 35 °C (**Figure 29d**).

Figure 29. a Schematic 3D printing; b Side view of printing process; c Printed hydrogel onto the transparent electrode at low temperature; d Printed hydrogel onto the transparent electrode at 35 °C.

Another geometry is presented in **Figure 30a, b** which shows the different optical response before and after heating.

Figure 30. a Unique printed geometry of PNIPAm Si-Al hybrid gel at room temperature, b 1.8 amp steady current applied on Unique printed geometry of PNIPAm Si-Al hybrid gel film.

Unlike the pure PNIPAm hydrogel which has a significant disadvantage of volume shrinkage while heating due to the deswelling of the water in the hydrogel (**Figure 31a, b**), the hybrid PSAHH did not show any shrinkage and deformation during heating (**Figure 31c, d**). The main reason for this is that the water is retained within the Si-Al gel matrix (**Figure 28**)

Figure 31. a Pure PNIPAm hydrogel at room temperature, b Pure PNIPAm hydrogel heated up to 70 °C for 10 mins (shrinkage and phase separation), c PNIPAm Si-Al hybrid hydrogel at room temperature, c PNIPAm Si-Al hybrid hydrogel heated up to 70 °C for 10 mins (no visible shape change).

In order to enable the gel through 3D printing print-head, the gel must flow with force applied, but at the same time, the gel must maintain its shape after printed on substrate (high viscosity at low shear rate). Typical viscosities range from 50 to 100 PaS enable such pseudoplastic behavior, while the PSAHH gel matched the viscosity range (**Figure 32a**

black). It should be noted that a slight increase in the viscosity in low shear rate is observed, probably due the release of water in the initial pressure on the disk. The viscosity of the pure NIPAm liquid before polymerization (blue), is low, (about 10^{-3} PaS), whereas the solid PNIPAm hydrogel (red) is in the range of hundreds of PaS. Furthermore, as can be seen from **Figure 32a** (dashed line), the dependence of the shear stress on the shear rate of the hybrid gel is distinctly less steep than for the cured PNIPAm gel and the liquid PNIPAm.

TGA analysis of pure PNIPAm, PSAHH and Si-Al matrix (without PNIPAm) from 25 to 60 °C was performed, during the test, temperature was hold and fixed at 25, 40 and 60 °C for 30 minutes. As shown in **Figure 32b**, there is a dramatic weight loss of 30% at 25°C and a total weight loss of 90 wt% at 60 °C of due to the evaporation of water for the pure PNIPAm sample, while for the hybrid gel only 31% total weight loss is observed up 60 °C (total water conternt was 67.5 wt%). It can be seen that the similar weight loss in the matrix without PNIPAm (blue line) and for PSAHH is observed, showing that the water holding is mainly contributed from Si-Al matrix.

Figure 32. a Viscosity vs. shear rate of NIPAm liquid, Solid PNIPAm hydrogel and PSAHH, b Weight loss of both pure PNIPAm hydrogel and PSAHH in heating process, c UV-Vis-Nir

spectrum of both both pure PNIPAm hydrogel and PSAHH, d Hypotheses loop and derivative of both pure PNIPAm hydrogel and PSAHH.

UV-Vis-NIR measurement was performed on 400 μm thickness film samples. As seen in **Figure 32c**, two distinct valleys can be seen in the transmittance spectrum at 1400 and 1900 nm for both pure PNIPAm hydrogel and hybrid PSAHH; these valleys can be attributed to the IR light absorption of O-H stretching and bending of water molecules at these wavelengths [31, 32]. The solar transmittance spectra of pure PNIPAm and PSAHH samples are nearly the same at both room temperature and 60 $^{\circ}\text{C}$. This implies that the optical response of both hybrid and pure PNIPAm hydrogel are the same and the heat stimulated smart function is maintained. Furthermore, the coloration contrast of PSAHH is more than 80% at 600 nm, with an extremely high ΔT_{sol} , $\sim 72.7\%$, showing similar transmittance and ΔT_{sol} of pure PNIPAm.

The transmittance hysteresis loop at of 600 nm was recorded during a heating and cooling cycle within temperature range of 20 $^{\circ}\text{C}$ to 60 $^{\circ}\text{C}$ for the 400 μm thick sample. The inset of **Figure 32d** shows the derivative graph of the LCST of PSAHH compared to that of pure PNIPAm which was used to calculate the average LCST. Interestingly, the average LCST of PSAHH was 32.5 $^{\circ}\text{C}$, which is higher than that of the pure PNIPAm hydrogel at 28 $^{\circ}\text{C}$. This is probably due to the poor thermal conductivity of the inorganic Si-Al matrix as opposed to that of the pure PNIPAm hydrogel. Overall it can be concluded that after embedding the PNIPAm particles within the Si-Al matrix, the heat response of the hydrogel is maintained, and the rheology of the gel enables its printability.

All the samples were dried followed by SEM, EDX, FTIR and Raman spectrum characterization. As can be seen in the SEM image in **Figure 33a** and **34a**, the PNIPAm is present as small irregular particles in the size range of dozens of micrometers. EDX chemical mapping (**Figure 33b**) confirm that these particles are PNIPAm, since they do not contain any Si. As can be seen in **Figure 33c**, the microstructure of the surface of the PNIPAm micro piece does not change after embedded into the Si-Al gel matrix compared

with freeze-dried PNIPAm micro pieces in DI water matrix (**Figure 33c** inset) as the rough porous structure on the surface remains.

Figure 33. a SEM image of individuals PNIPAm particles, b EDX mapping of Si in Si-Al matrix, c SEM image of PNIPAm microparticles embedded in the Si\Al gel matrix after freeze-drying. Inset image shows pure PNIPAm micro pieces after freeze-drying in the same scale.

Figure 34b shows the porous structure of pure Si-Al matrix after freeze-drying, where the pores were formed due to the evaporation of water from the Si-Al gel.

Figure 34. a Freeze-dried PNIPAm liquid hydrogel micro pieces, b Porous structure of Si-Al matrix after freeze-drying

Figure 35 shows the FTIR spectrum of Si-Al matrix (blue), PSAHH (black) and the pure PNIPAm hydrogel (red). The three large absorption peaks at 1540 cm^{-1} (amide II group), 1650 cm^{-1} (amide I group) and 1460 cm^{-1} (-C=O bond) can be observed in pure PNIPAm sample, which are the three characteristic peak [33] to distinguish PNIPAm. Another absorption peak at 3300 cm^{-1} is due to -NH bond stretching, is partially merged by another peak at 3440 cm^{-1} , which is a significant peak of -OH [34]. For PSAHH sample (black) the amide II, amide I and -C=O peaks were clear. This is due to the unevaporated water left in PSAHH sample, and the existence of strong intramolecular hydrogen bonding formed between -C=O groups or -NH groups of PNIPAm and -OH groups of Si-Al matrix [35].

Figure 35. FTIR spectrum of freeze-dried pure PNIPAm hydrogel, pure Si-Al gel matrix and PSAHH.

Figure 36 shows the Raman spectra of the Si-Al matrix (blue), PSAHH (black) and the pure PNIPAm hydrogel (red). As can be seen for the Si-Al matrix, the Si-(OR)₄ stretching peak is at around 400 cm⁻¹ and a typical Al-(OH)₃ stretching is ~3600 cm⁻¹. [36-38] It is interesting to note that the Si-OR peak can be well observed after the addition of the PNIPAm particles, however the Al-OH stretching peak is merged by the PNIPAm organic large stretching peak around 3300-3600 cm⁻¹. This distinct peak can also be observed for the pure PNIPAm, which is due to stretching of -OH in water [39] and has extremely large intensity than other significant peaks in PNIPAm. The Raman spectra shows that the PSAHH is a combination of the pure PNIPAm embedded in a Si-Al matrix without any additional covalent bond.

Figure 36. Raman spectrum of pure PNIPAm hydrogel, pure Si-Al gel matrix and PSAHH.

The effect of the gel thickness in FETD on the optical and thermochromic properties were studied. **Figure 37a, b** showed optical spectrums and thermochromic properties of FETD composed of thickness of 100 μm , 200 μm , 400 μm and 800 μm (sample A, B, C, and D in sequence) of PSAHH film with/without applied current. It should be noted, that another advantage of printing the hydrogel is that the layer thickness can be tailored in a controlled manner.

As shown in **Figure 37b**, T_{lum} is decreasing as thickness increases at both 20 $^{\circ}\text{C}$ and 60 $^{\circ}\text{C}$, which is different from pure PNIPAm hydrogel. As temperature increasing, for pure PNIPAm hydrogel, there is negligible T_{lum} decrease below LCST [8]. As can be seen in **Figure 37b**, 400 μm films obtained the highest ΔT_{lum} of 80.1% and ΔT_{IR} of 66.15% between 20 $^{\circ}\text{C}$ and 60 $^{\circ}\text{C}$, which leads to an extremely high ΔT_{sol} of 73.5%, while at the same time, T_{lum} of 400 μm film is still higher than 80% at 20 $^{\circ}\text{C}$, which is just slightly lower than 100 and 200 μm films. Correspondingly, 400 μm films showed the largest contrast in transmittance at 600 nm wavelength, which is around 80%.

Figure 37. a Transmittance of 4 samples with and without applied current; b Optical properties of 4 samples

One interesting phenomenon was observed in **Figure 38a**, T_{lum} of pure silver grid is just 73.7%, which is lower than FETD samples A, B, C, but higher than sample D. The extremely high T_{lum} of sample A, B and C at room temperature without applied voltage, can be explained due to direct contact of PNIPAm-Si-Al gel and grid electrode. The difference in T_{lum} of various thicknesses can be derived from the correlation between height of the grids and thickness of the PNIPAm-Si-Al hydrogel layer. The height of silver grid lines is about 1 micrometers (**Figure 38b**), while the space between the lines is 50 μm (**Figure 38c**), thus grids on the surface of electrode performs like frosted glass, which is a bit translucent due to the light scattering of the packaging grids (**Figure 38d**). As shown in Figure 18e, once PSAHH covered on the grids directly, the space between grids will be fully filled, and the thickness of gel is much larger than the grids thickness (400 μm VS. 1 μm), there was a thick, transparent and homogenous layer of gel formed, which could increase transmittance.

Figure 38. a Luminous transmittance of 4 samples and pure silver grid at 20 °C; b Schematic of PSAHH cover on grids c, d SEM of silver regular grid, e, f Mechanism of high luminous transmittance of FETD.

As seen in **Figure 39a** (i) (ii), while applying a current of 1.8 amp on the two edges of the transparent grid the PSAHH heats up and the contrast of the device changes from

transparent to opaque. At room temperature, the FETD is colorless and transparent, and starts to appear translucent or opaque within several seconds after applying a steady current from 0.6 amp ($\sim 2V$) to 1.8 amp ($\sim 6V$). This is due to the heat causing PNIPAm passing the LCST. It should be noted that the time required for the device to return to its transparent state is just a few seconds.

The direct contact of hybrid with the grid enables high flexibility of the full FETD device, as can be seen in **Figure 39b**, 400 μm thickness sample at various bending angles (from 0 to 180 $^\circ$) were tested and no short-circuit of the transparent grids were observed with applied voltages up to 8 V. Even in bending angles of over 180 $^\circ$, the transparent electrode kept heating. The device was tested for 100 cycles of 90 degrees bending and no change in the heating temperature or applied current. This high flexibility is attributed due to the direct contact between gel and transparent electrode, which makes the gel adapting to the same geometry of the transparent electrode.

Figure 39. a FETD without applied voltage at room temperature and b with 1.8 A steady current applied; c FETD with 1.8 A steady current applied 180 $^\circ$ bending.

On the other hand, the actual response time (**Figure 40a**) of the FETD is mainly attributed to the observation that heating starts within the upper part of the transparent electrode, and propagates downwards. Due to the direct contact of hybrid gel on grids, the response time significantly decreased compared with previous report [8]. The actual starting response

time is directly depending on the applied current, which decreased from 35 to 17 s, while current increased from 0.6 to 1.8 amps (2 ~ 6 V).

As shown in **Figure 40b**, compared without other reported ETDs [8, 40, 41], this new FETD has a faster response time with relatively low energy consumption. As seen in **Figure 40c**, the T_{lum} is also dependent on the applied current, while after applying 0.6 amp on FETD, the device will turn from transparent to translucent, only when the current is increased to 1.8 amp, the FETD will turn to completely opaque. This was observed as well for the reverse state to transparent.

Figure 40. a Response time of FETD with different applied current, b reported ETDs response time and applied voltage, c pictures show the FETD at transparent state ~ 0 amp, translucent state ~ 0.6 amp, and opaque state ~ 1.8 amp.

The good performance was maintained in durability test, as shown in **Figure 41**, 400 μm thickness sample was tested, the transmittance of 600 nm at around 60 $^{\circ}\text{C}$ (1.8 amp applied) were relatively stable after 100 cycles of measurements, while T_{lum} at 20 $^{\circ}\text{C}$ (no current applied) was slightly decreased from 88% to 72%. Meanwhile the contrast at 600 nm was also decreasing as measurement cycles running, but it still has more than 64% remaining.

Figure 41 Thermo-durability of FETD

This smart hybrid hydrogel also can act as an optical valve in a printed waveguide. We printed different shapes waveguide composed of three segments: pure Si-Al gel-PSAHH-pure Si-Al gel. As can be seen in **Figure 42a, b** during the illumination of green laser the light passes through the whole waveguide (**Figure 42a (i)** and **42b (i)**). Whereas, after heating printed waveguide to 60 $^{\circ}\text{C}$, the green laser light stops and scattered at the PSAHH segment (**Figure 42a (ii)** and **42b (ii)**). This is due to the fact that during heating, the PNIPAm particles in PSAHH creates scattering centers of the light. Since the hybrid hydrogel is flexible, we further demonstrated the printed flexible waveguide on transparent

electrical heater while bending (**Figure 42c**) and twisting (**Figure 42**) with laser illumination.

Figure 42. a Pictures of straight line composed of a segmented Si-Al matrix and PSAHH (marked in dashed yellow line) printed on glass substrate at room temperature a(i) and 60 °C a(ii) with green laser illumination, g Pictures of s-shaped line composed of a segmented Si-Al matrix and PSAHH (marked in dashed yellow line) printed on glass substrate at room temperature b (i) and at 60°C b(ii) with green laser illumination. Pictures of straight line of a segmented Si-Al matrix and PSAHH printed on a transparent flexible electrode at room temperature while bending (c) and twisting (d) during laser illumination.

6.3 Conclusion

A new hybrid hydrogel ink was fabricated and printed layer-by-layer directly onto a flexible substrate and a transparent electrode. The new and simple approach involves a printable Si-based gel matrix with embedded smart hydrogel polymeric particles. The hybrid ink printed structures sustained bending angles of up to 180° and enabled patterning

of various flexible electro-thermochromic (FETD) devices such as a flexible smart window and an optical waveguide sawitch. We expect that this new approach will pave the way for fabrication of new smart optical devices by additive manufacturing processes, and for other materials with high water-loading hydrogel systems.

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Chapter 7

Implications/Impact/Outstanding Questions

This chapter firstly summarized the results: 1. The W-VO₂/HPCA microgel and its composite were fabricated, which will not shrink during temperature increasing process cross τ_c and able to regulate both luminous and IR light; 2. The electro-thermochromic device was firstly fabricated by a combination of PNIPAm hydrogel and silver grid electrolyte, which was unable to both temperature and electrical input; 3. A new generation of PNIPAm-Si-Al hybrid hydrogel was successfully fabricated, which shows extremely large ΔT_{sol} and T_{lum} , at the same time, this hybrid hydrogel shows much better water holding ability, negligible shrinkage cross τ_c , and also able to be printed printability achieve the complex design. The main findings are discussed with reflection in the original design target, which is thus verified.

7.1 Results summary

7.1.1 W-VO₂/HPCA microgel composite

Temperature-responsive W-VO₂/HPCA microgel composite was synthesized and the 25 μm thickness composite microgel thin film could be transparent at room temperature, with a high T_{lum} of 80%, and translucent at 60 °C, with an acceptable T_{lum} of 33%. For pure HPCA microgel, the LCST is 52.5 °C, once W-VO₂ nanoparticles added to the microgel, LCST decreased to 50 °C.

The SEM of the room temperature and high-temperature samples indicated that the polymer fiber became more diminished and the pores became smaller, and this polymeric web structure acts as a scattering center to block the visible light and result in an opaque status at high temperature.

7.1.2 Electro-thermochromic device

Electrochromic materials have color changing properties effected by electron transfer [1], which can be applied in a windows glazing system. Various types of materials and structures have been used to construct electrochromic smart windows. The major disadvantages of electrochromic materials based energy saving devices include cost, and difficult to fabricate into sophisticated display [2].

Compared with electrochromic smart windows, the thermochromic smart window is passive and more cost-effective. By combining with a transparent heater, we report a new approach to activate the passive thermochromic hydrogel to change solar transmission via joule heating, which is able to extend the usage of thermochromic films into the electrochromic field. We expect that the electro-thermochromic concept will reduce the market penetration barrier and thus can provide an alternative solution for electrochromic market, especially low-cost market due to the simple setup and cheap raw materials.

The transparent electrical heater is composed of metallic NPs self-assembled into a grid or honeycomb patterns and the former was shown to be more effective. The ΔT_{sol} is 58.2%, which is higher than the best reported thermochromic materials (before this paper published), the coloration contrast and the response time is comparable to the best performing electrochromic material (**Figure 24d**). The used PNIPAm hydrogel film enable fabrication of devices with up to 75% contrast, depending on the film thickness and the applied voltage.

For this device, at room temperature or without current, it is totally transparent, once temperature increased above the LCST of thermochromic material or apply enough current, the thermochromic hydrogel will turn to opaque within 1 min, as shown in **Figure 43**. It can be used as a privacy window inside buildings and as external façade windows, while the high ΔT_{sol} ensures significant energy savings with the added functionality of active control.

Figure 43 Schematic design and digital photos of the electro-thermochromic device without (left) and with applied current (right).

7.1.3 Fully Printed Flexible Smart Hybrid Hydrogel

The new and simple approach involves a printable Si-Al based gel matrix with embedded smart hydrogel polymeric particles. This PSAHH has thermochromic properties and can be easily printed through the 3D printing machine, and finally has been fabricated to flexible electro-thermochromic devices and smart thermochromic waveguide switch (Figure 44).

Figure 43. Hybrid hydrogel composed of embedded PNIPAm particles within a silicon-based matrix and printing of various functional devices onto flexible transparent electrical heaters. This approach enables fabrication of optoelectronic devices such as smart windows and optical waveguide valve.

This new hybrid hydrogel (PSAHH) nearly solved and improved all intrinsic problems of pure thermochromic hydrogel: shrinkage, ease to lose water, and poor mechanical strength. This PSAHH has negligible shrinkage during temperature increasing from 20 to 70 °C (Figure 29); during TGA test, pure PNIPAm hydrogel will lose 90% of water content, while PSAHH just loses 20%. Moreover, pure thermochromic hydrogel was hard to achieve complex structure, while PSAHH is printable and able to achieve complex design (Figure 27, 28).

The traditional 3D printing technologies for hydrogels include stereolithography and nozzle-based printing [3, 4]. For 3D printing of hydrogels, cross-linking processes (physical, chemical or photo cross-linking) were required to achieve their designed functions during and/or the deposition process. This PSAHH ink is able to print layer-by-layer directly onto a flexible substrate and a transparent electrode without cross-linking process. The printed structures sustained bending angles of up to 180° and enabled patterning of various flexible electro-thermochromic (FETD) devices such as a flexible smart window and an optical waveguide switch. We expect that this new approach will pave the way for the fabrication of new smart optical devices by additive manufacturing processes, and for other materials with high water-loading hydrogel systems.

7.2 Conclusion

In conclusion, the projects in the thesis aim to improve the hydrogel-based thermochromic smart window, which can mainly be concluded as to improve the intrinsic shrinkage problems, mechanical properties, water holding ability and to promote the thermochromic performance, the combination of T_{lum} and ΔT_{sol} . At the same time, dual response thermochromic smart window was fabricated.

The background is introduced, covering the building energy consumption, the energy-saving thermochromic smart windows, and the advances of hydrogel-based thermochromic smart windows. The advantages and disadvantages of hydrogel-based thermochromic smart windows are summarized, compared to other reported thermochromic materials, especially VO_2 -based thermochromic materials.

Methods are applied by compositing hydrogel based thermochromic materials with different functional materials and devices. In the first project (Chapter 4), the introduction of W- VO_2 nanoparticles is able to enhance the ΔT_{IR} of HPCA microgel from 12% to 24%, which results in dramatically high ΔT_{sol} of 36.4%. In the second project (Chapter 5), combining the transparent silver grids with the thermochromic hydrogel is demonstrated to fabricate an electro-thermochromic dual responsive device. This concept provides an active control to passive thermochromic materials. The highest $\Delta T_{sol} \sim 58.2\%$ is reported, while an extremely high coloration contrast $\sim 75\%$ at 600 nm is achieved, at the same time,

the response time of this ETD is competitive with other organic based electrochromic materials. In the last project (Chapter 6), the introduction of Si-Al gel transparent matrix is demonstrated to be an effective way to solve the intrinsic problems of the pure hydrogel. This concept is demonstrated on a transparent Si-Al based water-rich gel containing thermochromic PNIPAm hydrogel micro-pieces. For this Si-Al-PNIPAm hybrid hydrogel (PSAHH), the thermochromic properties of PNIPAm hydrogel were kept, at the same time, due to the Si-Al matrix, the water keeping ability was dramatically improved and this hybrid hydrogel won't shrinkage during the heating process. Moreover, the pure thermochromic hydrogel was hard to achieve complex structure, while this PSAHH is printable and able to achieve the complex design. We further demonstrate this PSAHH as smart window exhibits an unprecedented solar energy modulation ($\Delta T_{\text{sol}} = 72.7\%$). A new design of thermochromic waveguide switch was also achieved.

To our knowledge, these findings are original and reported for the first time by us in our related publications. To the published date of these works, recorded performance is achieved: (1) ΔT_{sol} of 36.4% in the W-VO₂/microgel was firstly achieved (2) the flexible electro-thermal dual response device was firstly fabricated with fast response time of the 40s and high coloration contrast of 75%, the extremely high ΔT_{sol} of 58.2% was achieved (3) shrinkage problem of thermochromic hydrogel was solved, as shrinkage of PNIPAm Si-Al hybrid hydrogel is negligible, while the water holding ability and durability was also improved, highest reported ΔT_{sol} of 72.7% was achieved (4) New flexible PSAHH electro-thermochromic device was fabricated with faster response time of 17s.

Though these progress made, the problems remain and there still much work needed to fulfill the practical application of the hydrogel based thermochromic smart windows in architects. Considering the energy-efficient smart windows hold much promise for contributing to a future, it is hoped that these projects can contribute to the development to some extent and may inspire further works targeting the performance promotion smart windows, which includes but not limited to that of the hydrogel based thermochromism.

7.3 Validation of the hypothesis

For problem 1 *“Pure thermochromic hydrogel will shrink during temperature increasing process”* As shrinkage of traditional thermochromic hydrogel after being heated above the LCST resulting in the damage of the hydrogel structure, which will lead to bad reproducibility and durability for the prepared smart windows. Both W-VO₂/HPCA microgel composite and PSAHH will no more shrinkage when temperature increase cross τ_c . Especially for PSAHH, once temperature increased above LCST of PNIPAm micro-hydrogel inside Si-Al matrix, hydrogen bond between PNIPAm micro-hydrogel and water will break, and water molecular will be released to Si-Al matrix. Once temperature decreased below LCST, PNIPAm micro-hydrogel will generate hydrogen bond with surrounding water molecules. During this process, Si-Al won't change shape.

For problem 2 *“Thermochromic material is passive, initiative control methods are required for new generation of thermochromic smart windows.”* The transparent electronic heater was introduced to fabricate electro-thermochromic devices with pure PNIPAm hydrogel and PSAHH, which provide active control of passive thermochromic smart window. The dual response smart window has much simpler structure compared with standard 5 layers electrochromic smart window, which expect to provide an alternative solution for the electrochromic market, especially the lower end of the market.

For problem 3 *“The durability of the thermochromic hydrogel is highly dependent on the water evaporation”* PSAHH shows much better water holding ability compared with pure hydrogel, after heat treatment from 25 to 60 °C, PSAHH just lost 20 wt%, while pure PNIPAm hydrogel lost 90 wt% water contents. The good water holding ability of PSAHH was provided by Si-Al gel matrix, which will lead to better reproducibility and durability for the prepared smart windows compared with traditional thermochromic hydrogel based smart windows.

For problem 4 *“The poor mechanical properties of normal thermochromic hydrogels limit them to fabricate complex structure design”* PNIPAm-Si-Al hybrid hydrogel has a suitable viscosity, which was able to be printed through the 3D printer to achieve the complex design, and the shape was kept during heating and cooling process. This new approach will pave the way for the production of smart optical devices by additive manufacturing processes, and for printing other materials with high water-loading.

For problem 5 “*The thermochromic properties should be further improved*” This PNIPAm-Si-Al hybrid hydrogel showed largest ΔT_{sol} at 73.5% compared with other reported data, at the same time, the T_{lum} is more than 80% at room temperature. Our project provided a solution of smart window that closer to the daily energy saving applications, due to the large ΔT_{sol} and T_{lum} , suitable τ_c , and better durability.

7.4 Future Work

7.4.1 “Sandwich” solar cell smart window

Integrating energy conservation and generation into one device is a highly attractive scientific and industry undertaking to achieve energy saving and optimal solar energy utilization in buildings which benefits the sustainable development of the human race. Thus, the device with both energy saving and harvesting functions is designed as:

The dual function device has extremely large ΔT_{sol} , and high power conversion efficiency (PCE). Conventional thermochromic material such as organic hydrogel can respond to the environmental temperature (close to room temperature) to intelligently regulate solar transmittance. Those materials work synergistically with semitransparent solar cells to provide dual functionality.

Figure 44 illustrates the design of “Sandwich” solar cell smart window with three main functional layers. The overcoat serves as an anti-reflection coating to enhance the solar transmission to maximize the PCE. The sandwiched parts between the glass substrate and overcoat is a newly designed bifacial semi-transparent solar cell. The bottom part is a layer of organic thermochromic smart coating, which is transparent at room temperature, and become opaque/translucent when temperature increasing above the critical temperature.

Figure 44. a design of “sandwich” solar cell smart window, b working mechanism of this device at low temperature (left) and high temperature (right).

In this design, for the first time, organic thermochromic smart window with semi-transparent solar cell sandwich structure is proposed. **Figure 44b** demonstrates its working mechanism. The anti-reflection coating will allow more solar light go through to solar cell part, and at the same time, provide protection of solar cell. Subsequently, the transmitted solar energy will be absorbed by the solar cell stack and converted into electricity and the rest will go through to smart thermochromic window part to regulate the solar energy inside the house. At room temperature (**Figure 44b** left), the organic smart window will be totally transparent, which will allow all the solar light transmit from solar cell to room. At a temperature above LCST, all those things need to be unified in the whole thesis. τ_c or LCST, which ever, (**Figure 44b** right), an organic thermochromic smart window will turn translucent or even opaque, which will reflect and scatter the light back to the bifacial solar cell, which may even further enhance the PCE.

7.4.2 3D printed mechanical-chromic smart windows

Traditional smart windows can control solar transmission under the application of a voltage (electrochromism), light (photochromism) or heat (thermochromism). In the future work, we would like to develop a thermomechanical micro-shades to function as a smart window. Using 3D printing technology, we are able to print the functional material as the micro shades. For this smart window, micro-shades made by shape memory and/ or responsive

actuators and are printed on a transparent substrate vertically (**Figure 45a**). At the relaxed state, the smart window will allow light to go through (**Figure 45b**) the micro-shades. Once increase the temperature, the shape memory or responsive actuator wall will bend to suitable angles which will block solar light to go through the smart window (**Figure 45c**). This process can be reversible by applying either the magnetic field or electricity (you need double confirm this). The research will be focused on investigating different materials and actuation mechanism as well as geometries of the shades. It should be noted that in order to tailor the specific wavelength filtered by the shades, different structure design are needed.

Figure 45. a Geometry design of micro-shades on the smart window; mechanical-chromic smart window at room temperature (b) and high temperature (c).

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