Hybrid thermochromic material

Zhou, Yang

2015

Zhou, Y. (2015). Hybrid thermochromic material. Master's thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/62170>

<https://doi.org/10.32657/10356/62170>

NANYANG
TECHNOLOGICAL
UNIVERSITY

Hybrid Thermochromic Material

Zhou Yang

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2015

Hybrid Thermochromic Material

Zhou Yang

School of Materials Science and Engineering

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Master of Engineering

2015

I. Abstract

Vanadium dioxide (VO_2) is a key material for thermochromic applications, which has a great potential to respond to the environmental temperature changing due to metal-to-insulator (MIT) transition. Temperature response hydrogel is one of the organic thermochromic materials, which reversibly changes between a transparent and translucent state depending on temperature change. The application of PNIPAm hydrogel thin film for thermochromic smart windows has been investigated for the first time. With increasing thickness of hydrogel from 26 to 200 μm and increasing testing temperature from 20 $^{\circ}\text{C}$ to 60 $^{\circ}\text{C}$, the solar modulating ability (ΔT_{sol}) increases and the luminous transmittance (T_{lum}) decreases. Compared with the best reported result of the most studied inorganic VO_2 thermochromic coatings, an unprecedented good combination of near doubled averaged T_{lum} (**70.7%** v.s 42.8%), higher ΔT_{sol} (**25.5%** v.s 22.3%¹) and lower transition temperature (~ 32 $^{\circ}\text{C}$ v.s ~ 68 $^{\circ}\text{C}$) could be achieved by hydrogel with optimized thickness. Good durability and reversibility were established on proper sealing of the sandwich structure, thereby achieving a new milestone in the research for organic thermochromic materials.

Due to the great thermochromic performance of PNIPAm hydrogel, a new generation of composite thermochromic material which integrates hydrogel with VO_2 nanoparticles has been investigated and a dramatic enhancement of solar modulation has been observed. Our experimental data of VO_2 /hydrogel nanocomposite showed an unprecedented combination of thermochromic properties with solar modulation ability of **34.7%**, which is much higher than the best report data 22.3% and at the same time, a comparable high average T_{lum} of **61.1%**

can be achieved. The combination of vanadium dioxide nanoparticles and hydrogel could offer large transmission contrast both in luminous and infrared range resulting largely enhanced overall solar modulation and the hybrid system opens a new avenue of thermochromic materials.

II. Table of Contents

I. Abstract	i
II. Table of Contents	v
III. List of Figures	vi
IV. List of Tables	vii
1. Introduction	1
1.1. Background	1
1.2. Objective and scope	2
2. Literature review	3
2.1 Thermochromism	3
2.2 Inorganic thermochromic material	3
2.2.1 Metal-insulator transition	3
2.2.2 Vanadium dioxide (VO ₂)	4
2.3 Organic thermochromic material	10
2.3.1 Temperature-sensitive hydrogel	10
2.3.2 Thermotropic hydrogels	10
2.3.3 Thermochromic hydrogels	11
2.3.4 Chromogenic gel networks	13
2.3.5 Transition temperature (lower critical solution temperature) of hydrogel	14
3. Experimental Section	16
3.1 Preparation of the sandwiched pure hydrogel structure and Hydrogel with VO ₂ nanoparticles sample	16
3.2 Optical properties tests	19
4. Results and Discussion	20
4.1 Thermochromic properties for pure hydrogel in different thickness	20
4.2 UV-Vis-NIR spectra for hydrogel/ VO ₂ nanoparticles composite	27
5. Conclusion and Recommendation	35
5.1 Conclusion	35
5.2 Recommendation	35

6. References	36
---------------------	----

III. List of Figures

Figure 1. Structure of VO ₂ /hydrogel composite.....	2
Figure 2. Crystal structures of VO ₂ (M) (left) and VO ₂ (R) (right).....	4
Figure 3. Typical VO ₂ thermochromic performance below and above T _c	5
Figure 4. Process to make SiO ₂ /VO ₂ core shell composites	9
Figure 5. DSC curves of aqueous polyether samples with polyether water mixing ratios of 5:1, 4:1 and 3:1. ³¹	11
Figure 6. (a) Photograph of the gel between two glass plates (2 mm thickness) at 20°C. (b) Photograph of the gel at 70°C. ³⁹	12
Figure 7. Transparency and color behavior of a Bromothymol Blue (BB) doped gel network in respect for temperature at 750 nm wavelength of light. (Layer of thickness: 1 mm, [BB] = 1.9 x 10 ⁻⁴ mol/L). ³⁷	14
Figure 8 The process of samples preparation.....	18
Figure 9. Hydrogel with VO ₂ nanoparticles (left) sample and Pure Hydrogel reference (right)	19
Figure 10 Solar light transmitted at temperature lower than τ_c (left); Solar light partially blocked at temperature higher than τ_c (right).....	20
Figure 11 Temperature dependence of optical transparency of the sample (a) 200 μm thickness PNIPAAm; (c) 52 μm thickness; Trend of optical properties of the sample (b) 200 μm thickness; (d) 52 μm thickness.....	22
Figure 12 (a) Optical transmittance spectra of the three samples with different thickness between 20 °C and 40 °C; (b) Trend of ΔT_{sol} , ΔT_{lum} , ΔT_{IR} and T_{lum} at 40°C for different thickness.....	25
Figure 13 Smart hydrogel thin films at room temperature (left) and in sunshine environment at 35 °C (right) with thickness of (a) 26 μm ; (b) 52 μm ; (c) 78 μm and (d) 200 μm	26
Figure 14 Durability test of hydrogel with thickness of 36 μm between 20 °C and 40 °C.....	27
Figure 15 (a) Pure hydrogel thin film at room temperature (25 °C), (b) VO ₂ /hydrogel hybrid at room temperature, (c) VO ₂ /hydrogel hybrid at 35 °C, TEM image of VO ₂ nanoparticles at (d) 31500 $\times$ and (e) 50000 $\times$, (f) Angular frequency dependence of storage modulus and loss modulus for pure hydrogel and VO ₂ /hydrogel hybrid at 25 °C, (g) DSC of VO ₂ /hydrogel hybrid and commercial VO ₂ powder (inset).....	28

Figure 16 (a) Optical transmittance spectra of the three samples with different thickness between 20 °C and 80 °C; (b) Trend of ΔT_{sol} , ΔT_{lum} , ΔT_{IR} and T_{lum} at 80°C for different thickness.....	31
Figure 17 UV-Vis spectrums of pure hydrogel (black), pure VO ₂ (red) and VO ₂ /hydrogel hybrid (blue) at low and high temperature, the grey area indicates the normalized values of the visible (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 VO ₂ /hydrogel hybrid.	33

IV. List of Tables

Table 1. Different approaches to enhance both ΔT_{sol} and T_{lum}	6
Table 2 Thermochromic properties of PNIPAAm hydrogel thin film with 200 µm thickness.	23
Table 3 Thermochromic properties of PNIPAAm hydrogel thin film with 52 µm thickness ...	23
Table 4 The optical properties comparison between hydrogel thin film (52 µm) and VO ₂ thin film	25
Table 5 The comparison between different thickness of hybrid with DPM to monomer ratio 1:6.....	31
Table 6 The comparison of thermochromic properties of pure hydrogel, pure VO ₂ , VO ₂ /hydrogel hybrid structures and the best reported data in the reference. ¹	33

1. Introduction

1.1. Background

The rapidly growing world energy usage has raised alarm over exhaustion of energy resources and heavy environmental pollution (ozone layer depletion, global warming, climate change, etc.). The global contribution from buildings towards energy consumption, both residential and commercial, has steadily increased reaching figures between 20% and 40% in developed countries ² and has exceeded 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) ². The current world demand for flat glass is ~ 7 billion square meters with 7.1% annual increase ³.

Therefore, to reduce the air-conditioning usage is of prime importance in energy saving. Thermochromic materials are the most economical smart window materials. Optical properties of chromogenic materials will be changed due to some external stimulus, such as light irradiation, change in temperature, or an external electric field. Photochromic, thermochromic and electrochromic materials are the most common materials belonging to chromogenic materials. ⁴ For thermochromic materials, solar energy inflow is allowed as the temperature below the critical temperature T_c . However, as the temperature exceeds T_c , the thermochromic materials will reduce the energy inflow effectively. ⁵

Vanadium dioxide (VO_2) is an attractive thermochromic material, which has an excellent near-room temperature-responsive behavior at 341K (T_c), making itself a suitable candidate as smart applications material. ⁶

Intelligent hydrogels also belongs to chromogenic materials, which are sensitive to some external stimulus such as temperature. ⁷ They are applied in many areas, such as in thermally adjustable applications and temperature sensitive applications in medical technologies. ⁸

1.2. Objective and scope

This project aims to report hybrid thermochromic composite for solar energy control application and the structure is displayed in **Figure 1**.

Figure 1. Structure of VO_2 /hydrogel composite

In order to improve the thermochromic property of vanadium dioxide nanopowders, NIPAm/PVA hydrogel is applied to disperse the VO_2 nanoparticles and form a transparent solar energy control composite between two pieces of glass, which could glaze solar energy more effectively. This sandwich structure sample could offer larger transmission contrast both in luminous and infrared range which could enhance overall solar modulation.

2. Literature review

2.1 Thermochromism

Thermochromism is the change of the optical properties for a material under some external temperature stimulus. As reaching the critical temperature, the thermochromic material can modulate light transparency in terms of changing from a transparent state at low temperature to a less transmitting state at high temperature.⁹

Generally, there are two kinds of thermochromic materials. The first one is continuous thermochromic material, which demonstrates a gradual colour change within a range of temperatures. The other one is discontinuous thermochromic material. For discontinuous thermochromism, it involves a reversible or irreversible structure phase change at the transition temperature, governed by the thermodynamics of the system.⁴

Thermochromism has big potential in technological applications, such as temperature sensors for safety in thermometers or warning signals.

2.2 Inorganic thermochromic material

2.2.1 Metal-insulator transition

Metal-insulator transitions (MIT) are transitions from a metal to an insulator with abrupt changes in electrical conductivity, and the magnitude of changing can be very large. These transitions can be achieved by particular ambient parameters, such as pressure and temperature, etc.

For an insulator, its highest occupied electronic state is within a band gap. As external stimuli provides a 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 expose metallic behavior.¹⁰

2.2.2 Vanadium dioxide (VO_2)

Vanadium dioxide (VO_2) is one of most promising "smart materials" which are sensitive to temperature due to the thermochromic mechanism. Vanadium dioxide has two polymorphs, the monoclinic and rutile (VO_2 (M/R)) (**Figure 2**). These two compounds will undergo a first order metal-to-insulator transition (MIT) at nearly 68°C as temperature increasing and this transformation is sharp and reversible. As temperature increasing, the structure transforms from monoclinic VO_2 (M) (low temperature) to rutile VO_2 (R) (high temperature) accompanied with a dramatic change in near-infrared optical properties.¹¹

Figure 2. Crystal structures of VO_2 (M) (left) and VO_2 (R) (right)

During the process of converting VO₂ (M) to VO₂ (R), a decrease with magnitude of 10⁴ to 10⁵ in resistivity happened, and the transparency changed a lot in the infrared region.¹²

VO₂ behaves like a semiconductor at low temperature region, which allows large amount of solar light to be absorbed or transmitted through. As temperature exceeds the transition temperature of it, VO₂ will behave like metal, which will reflect the light at near-infrared region. Infrared region contains the nearly half heat energy carried by solar light.

Due to these characteristics, VO₂ becomes a promising material for a wide variety of technological applications, such as field-effect devices (transistors, switches, sensors) and smart windows.¹³ A typical VO₂ thermochromic performance is shown by **Figure 3**, and Table 1 summarize the best VO₂ optical properties by experimental and simulation.

Figure 3. Typical VO₂ thermochromic performance below and above T_c.

Table 1. Different approaches to enhance both ΔT_{sol} and T_{lum}

		ΔT_{sol}	T_{lum}	Remark
Doping	Experimental	6.7%	53.8%	Eu doping, T_c decrease to 47.5% ¹⁴
	Experimental	10.6%	54.2%	Mg doping, T_c decrease to 54% ¹⁵
Porosity	Experimental	14.1%	41.6%	Polymer-assisted deposition ¹⁶
	Experimental	14.7%	50%	Freeze Drying ¹⁷
	Simulation	20%	45%	155nm Thickness ¹⁶
Nanocomposite	Experimental	12%	59.1%	VO ₂ /Si-Al nanocomposite foils ¹⁸
	Experimental	11.7%	51.4%	Sb: SnO ₂ (ATO)/PU matrix ¹⁹
	Experimental	22.3%	42.8%	VO ₂ /PU nanocomposite foils ¹
	Simulation	20%	67%	Sphere nanoparticle ⁵
Anti-Reflective	Experimental	14%	22%	Si-Al gel AR coating ²⁰
	Experimental	43.5%	12%	Five-layered TiO ₂ /VO ₂ /TiO ₂ /VO ₂ /TiO ₂ films ²¹

Vanadium dioxide is the most intensively investigated solid-state thermochromic material, but according to **table 1**, it is still not ready for industrial or commercial application due to several problems. First of all, due to the high critical temperature, which is 68°C, is too high, it is difficult for VO₂ to be applied in daily life, such as smart windows application. Second, the VO₂'s luminous transmittance, which is 50% or less, is too low for daily use. The third one is the modulation of the solar energy throughput between the VO₂'s two states is modest.

⁵ There are also some other problems such as cost, even though VO₂ film has good effect on solar energy control, but the production cost is too high to be used in industrial applications, and at the same time, it is hard to be applied on large area. Vanadium dioxide nanoparticles are not thermodynamically stable when it is exposed to air for a long time or in high temperature environment.

For the first problem, Doping with other elements can modify the physical and chemical parameters of vanadium oxides, and different dopants may produce different doping effects. The most widely investigated dopant is tungsten, with which the VO₂'s T_c can be brought to the room temperature region ²², it can decrease the transition temperature at a range of 21 to 28°C per 1at%. ²³ and ²⁴ VO₂ films with T_c of 30.0°C and 38.5°C were reported in the reference ⁶ and ²⁵, respectively. Transition temperature is a critical parameter for VO₂, and it can be changed directly by doping other elements to replace V⁴⁺ and O²⁻ ions. ²⁶

Normally, doping cations with larger radius and valence than V⁴⁺, such as W⁶⁺, Mo⁶⁺, Nb⁵⁺, and Ta⁵⁺, can decrease the critical transition temperature of VO₂. For example, every 1 at% W⁶⁺ in VO₂ can decrease up to 23°C of the critical transition temperature theoretically. Another way to decrease the critical transition temperature is doping anions with respect to O²⁻, such as F⁻ and P³⁻.^{27, 28}

According to the mechanism of substitution, the above two types of doping are effective. Because of imbalance charge from dopants, extra electrons or holes are introduced into the crystal lattice. These electrons and holes combine with V⁴⁺ and exist in the form of V³⁺ and V⁵⁺. As a result, equilibrium charge carrier density is increased, which leads to a more rapid decrease of T_c . Many researchers have proven the doping effects of the above two types over the past several decades. As Tan, X. et al. reported, in atomic level, as tungsten doped, it will form an intrinsically symmetric tetragonal-like structure, driving the detwisting of the nearby asymmetric monoclinic VO₂ lattice towards rutile phase. ²²

For the second problem, multi-layer structure is adopted to improve the VO₂ coating's luminous transmittance ^{29, 30}. And the VO₂ film with improved solar energy modulation has been prepared ^{9, 31}, but it is not very effectively. Add new materials, which have novel effect in improving optical properties should be used. .

Both VO₂ films and VO₂ powders are two main potential products which can be used for smart windows. According to several studies such as UV-Vis-NIR test, VO₂ films have higher optical contrasting and larger switching sharpness during the MIT comparing with VO₂ powders. But except for the transition temperature, VO₂ film still has other problems which restrict its immediate use in solar control area. Firstly, when VO₂ film reaches considerable transition temperature, the luminous transmittance becomes low. Secondly, because of limited thermochromic reflectance modulation outside of the near infrared region, VO₂ film has a low throughput in solar energy management.

These two problems can be solved by making VO₂ nanopowders instead of thin film. Based on calculations, when nanoparticles dispersed in a dielectric host, they have advantages over what thin solid film can offer, both in luminous transmittance and solar energy transmittance modulation. ^{12, 32} Size effect of VO₂ can affect the phase transition behavior: the smaller the VO₂ particles, the wider hysteresis curve (loop) will be during the MIT, at the same time, the lower the transition temperature will be. Both benefit smart windows applications.

It can be easily incorporated into thin plastic thermochromic films and smart windows. At the same time VO_2 nanopowders have a lower 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, SiO_2/VO_2 composites with a core/shell structure can be put into solution to prepare transparent, stable and flexible VO_2 -based composite films. VO_2 powders are not very stable in dry air, for example, they may be reduced to V_2O_5 for long time storage or affecting by acid. As a result, making VO_2 powders into composite can expand their applications.³³

Figure 4 shows the process of making the SiO_2/VO_2 core shell composites and pigments.

Figure 4. Process to make SiO_2/VO_2 core shell composites

2.3 Organic thermochromic material

2.3.1 Temperature-sensitive hydrogel

Temperature-sensitive hydrogel belongs to chromogenic materials, which will change optical properties in response to external stimuli, such as temperature. Among the chromogenic materials, three types of hydrogel have the ability to control solar energies: thermotropic materials, thermochromic materials and some chromogenic materials that combine thermotropic and thermochromic properties in one.

2.3.2 Thermotropic hydrogels

Thermotropic hydrogels have reversible transparency control of the optical properties in respect with temperature. Thermotropic hydrogels are transparent in a colorless state below the critical transition temperature.^{34, 35} As the temperature increasing to and even higher than the critical transition temperature, transparent hydrogels will translate from the colorless state into a milky white reflective state.

The transition temperature of thermotropic hydrogels can be adjusted by modifying the concentration of polymers. **Figure 5** shows the difference of the transition temperature with respect to different of polymer concentrations.

A lot of polymer matrixes have reversible transparency control property, such as aqueous polyvinyl methyl and polyalkoxy derivative, aqueous LiCl-containing buffer solution. In

opaque state, thermotropic hydrogels can reflect most visible light. Thus the thermotropic hydrogels are very commonly used in solar control glazing.

Figure 5. DSC curves of aqueous polyether samples with polyether water mixing ratios of 5:1, 4:1 and 3:1. ³¹

2.3.3 Thermochromic hydrogels

Thermochromic hydrogels can change their color and transparency with a constant volume depending on temperature. There are several types of color changing methods.

Firstly, due to the light scattering effect, during the gel-sol-gel transition process^{8, 36}, thermochromic materials can exhibit reversible color changes.³⁷ A lot of hydrogel matrixes, such as gelled poly(1-butene) solved tetra-chloroethylene and 3 wt% isotactic polypropylene dissolved benzene non-aqueous gel belong to this group. ³⁸

Secondly, poly(phenylenevinylene) undergoes a red to yellow color change during gel-sol-gel process, but this thermochromic material cannot behave fully reversible.³⁷

Lastly, suitable pH-sensitive indicator dye was doped into some hydrogel matrix which has a reversible pH change from low temperature to high temperature. For example, phenolphthalein (with color transition from colorless to red at pH8.3-10.0) was embedded in the transparent polyvinyl alcohol (PVA)/borax/surfactant gel network. **Figure 6** 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.³⁹

Figure 6. (a) Photograph of the gel between two glass plates (2 mm thickness) at 20°C. (b) Photograph of the gel at 70°C.³⁹

2.3.4 Chromogenic gel networks

Chromogenic gel network is a matrix for hybrid transparency and color control with temperature, during the thermochromic process they are changed from a colored state into a reflective colored state. Such gel networks can change both their color and transparency due to a temperature change at a constant volume.^{40, 41}

This kind of hydrogel is a mixture of a polyalkoxy derivative, aqueous LiCl-containing buffer solution, which is mixed with a suitable pH-sensitive indicator dye, for example, Bromothymol Blue. The transparency and color behavior of the pH-sensitive indicator dye doped gel networks is shown in **Figure 7**.

As temperature increases, three color states of net gel can be shown in different temperature. According to **Figure 7**, the net gel is in green colorless state when the temperature is lower than 32°C. With temperature increasing, this gel system will change to yellow colorless state; and with further temperature increase, the color becomes opaque yellow in a reflective state. During the 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.³⁷

Figure 7. Transparency and color behavior of a Bromothymol Blue (BB) doped gel network in respect for temperature at 750 nm wavelength of light. (Layer of thickness: 1 mm, [BB] = 1.9×10^{-4} mol/L).³⁷

2.3.5 Transition temperature (lower critical solution temperature) of hydrogel

The hydrogel is essentially synthesized by in-situ polymerization of monomer in water. The lower critical solution temperature (LCST) of hydrogel can be tuned by selecting thermal sensitive monomers. Such as NIPAm with LCST of around 32°C, hydroxypropyl cellulose with LCST around 55°C and poly(N-vinylcaprolactam) with LCST of around 30°C. PNIPAm is most widely used since its transition temperature range is narrow. The LCST of PNIPAm hydrogel can be tuned by copolymerization with second component. The rule of thumb is that 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 noticed is that overdosing of ionic species would cause disappearance of LCST. For example, when the molar ratio of NIPAm to sodium acrylate is smaller than 4, the thermal sensitivity disappears.⁴²

The PVA introduced constructed hydrophilic tunnel for water release, especially when the hydrogel dimension is large. This is because when 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.⁴³ The PVA and PNIPAm form semi-IPN structure and the presence of PVA would not influence the LCST too much.

3. Experimental Section

Chemicals used in this study were N-isopropylacrylamine (NIPAAm, $\geq 98\%$, Wako Pure Chemical Industries Ltd), N, N' -methylenebis(acrylamide) ($\geq 99\%$, crosslinker, Sigma-Aldrich), polyvinyl alcohol (PVA, Mw = 61,000, Sigma-Aldrich) and N,N,N' ,N' -tetramethylethylenediamine (TEMED, accelerator, 99%, Sigma-Aldrich), ammonium peroxydisulfate (initiator, 98%, Alfa Aesar) and multipurpose sealant (Selleys All Clear). All were used as received without any further purification.

NIPAm is the monomer to be polymerized and imparts the thermosensitivity; PVA is the additive used to make the hydrophilic-hydrophobic transition complete; N,N'-methylenebis(acrylamide) is the crosslinker and overdose of it would make the hydrogel opaque; N,N,N',N''-Tetramethylethylenediamine is the catalyst which accelerates the polymerization at room temperature; ammonium persulfate is the initiator. The ratios can be changed to meet color requirement, for example, if the synthesized gel is opaque, reduce the concentration of monomer and proportionally other species would make it transparent.

3.1 Preparation of the sandwiched pure hydrogel structure and Hydrogel with VO₂ nanoparticles sample

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. The solution was dropped on the surface of clean glass slide and covered by another one to make a sandwich structure after the reaction completed at room temperature for 24 hours. Samples with thickness of 26 µm, 52 µm, 78 µm and 200 µm were successfully made and the sealant was applied at the edges to prevent mass exchange with outside environment.

It is nearly the same as preparation of pure hydrogel sample, after NIPAm, PVA and N,N'-Methylenebis homogeneous obtained, 260.0 µL of monomer solution was pipetted into a 1 mL centrifuge tubes. Then 43.3 µL of DPM (DPM:monomer = 1:6, vol%) with 23wt% VO₂ nanoparticles were added into the centrifuge tube with vibration. 3.0 µL N,N,N',N''-Tetramethylethylenediamine (TEMED, catalyst) and 7.0 µL ammonium persulfate (APS, initiator) were added in sequence to the centrifuge tube with vigorous vibration on vortex for 10 seconds. The solution was transferred in between 2 pieces of glass slides to make a sandwich structure after the reaction completed at room temperature for 24 hours. Samples with thickness of 13 µm, 26 µm and 52 µm were successfully made and the sealant was

applied at the edges to prevent mass exchange with outside environment. **Figure 8** shows the process of samples preparation and **figure 9** is the one of the samples.

Figure 8 The process of samples preparation

Figure 9. Hydrogel with VO₂ nanoparticles (left) sample and Pure Hydrogel reference (right)

3.2 Optical properties tests

Cary 5000 UV-Vis-NIR Spectrometer was used to test the optical properties of all the samples. Optical transmittance (%*T*) tests were run between 20°C and 80°C with variation of wavelengths ranging from 2500 nm to 250 nm for transmittance profiles for all the samples. The calculation for integrated solar/luminous transmittance can be found in a previous publication.²⁰ 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:

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

4. Results and Discussion

4.1 Thermochromic properties for pure hydrogel in different thickness

NIPAm/PVA hydrogel has a thermotropic feature, when there is a temperature change, the hydrogel exhibits absorption and desorption of its water content leading to a reversible change in its transparency. Compared with VO₂ thin films, one similarity between them is the exhibition of first-order transition that controls its light transmittance. The optical performance was shown by **Figure 10**.

Figure 10 Solar light transmitted at temperature lower than τ_c (left); Solar light partially blocked at temperature higher than τ_c (right)

Figure 11a and **11c** shows the solar light transmittance (250 nm-2500 nm) profiles of PNIPAm hydrogels with thickness of 200 μm and 52 μm under various temperatures. According to **Figure 11**, two transmittance reductions happened at around 1430 nm and 1930 nm wavelength for both thick and thin samples, which is due to the absorption of water

at these two wavelengths.⁴⁴ The absorption peak of water at around 1400nm is due to the O-H stretch in the water molecule, while at around 1900nm water has a unique peak due to a combination of O-H stretch and H-O-H bending.⁴⁵ At low temperature, more hydrogen bonds exist between water and PNIPAm polymer chains;⁴⁶ as temperature increases, these hydrogen bonds are gradually broken, which indicates a continuous phase separation. The oscillator strength of O-H bond is proportional to the hydrogen bond energy,⁴⁷ therefore, with fewer existing hydrogen bonds, the intensity of the transmittance valleys decreases.

For the thick PNIPAm hydrogel film with 200 μm thickness, it maintained transparency below the LCST with the calculated T_{lum} of 89.1% at 20 °C and slightly reduced T_{lum} of 75% at 30 °C (Table 2). However, it turns into milky white at 35 °C with dramatically diminished T_{lum} of 7.3% and only 0.6% at 60 °C (**Figure 11a**, Table 2). The sharp decline of T_{lum} suggested that the LCST occurred at between 30 °C and 35 °C. The blocking effect around LCST was not only observed for luminance range but for infrared, which can be seen in Table 2 that the T_{IR} reduced from 79.4 to 48.4% significantly at 35 °C with further steady decline to 19.3% when the temperature reaches 60 °C. Both largely reduced T_{IR} and T_{lum} resulted in continuously declined T_{sol} from 83.3 to 9.4 % (Table 2), thereby leading to soared ΔT_{IR} , ΔT_{lum} and ΔT_{sol} between 30 and 40 °C and reached plateau afterwards with temperature increase (**Figure 11b**). Therefore, the effective blocking of both IR and visible light at temperature above LCST makes the overall solar modulating ability of PNIPAm hydrogel with 200 μm thickness impressive ($\sim 70\%$ at 40 °C), but the severely paralyzed luminance transmittance (1.2% at 40 °C) excludes the hydrogel with 200 μm thickness from being applied in smart window.

Figure 11 Temperature dependence of optical transparency of the sample (a) 200 μm thickness PNIPAAm; (c) 52 μm thickness; Trend of optical properties of the sample (b) 200 μm thickness; (d) 52 μm thickness

In order to enhance the luminance transmittance at temperatures above LCST, the thickness of hydrogel was reduced to 52 μm and the optical properties were shown in **Figure 11c** and **11d**. The T_{lum} maintained at high level of higher than 50% even at 60 $^{\circ}\text{C}$. Admittedly, the reduced thickness of hydrogels and consequently declined blocking abilities resulted in higher T_{IR} , T_{lum} and T_{sol} (Table 3) at temperatures above LCST compared with 200 μm hydrogel, however, the combined high luminance transmittance of >60% and compromised solar modulating ability of >20% (**Figure 11d**) at 40 $^{\circ}\text{C}$ are still higher than one of the best

performing VO₂ thin films ($T_{lum} \sim 54\%$ and $\Delta T_{sol} \sim 12\%$ at 90 °C). Moreover, ΔT_{IR} , ΔT_{lum} and ΔT_{sol} increased progressively with temperature as shown in **Figure 11d**, which is preferable to ensure a relatively stable indoor temperature. Meanwhile, the transmittance is still higher than 50% even at 60 °C that a good indoor luminance is provided.

Table 2 Thermochromic properties of PNIPAAm hydrogel thin film with 200 μm thickness

200 μm	20°C	30°C	35°C	40°C	50°C	60°C
T_{lum} (%)	89.1	75.0	7.3	1.2	0.7	0.6
T_{IR} (%)	79.4	77.3	48.4	30.2	23.6	19.3
T_{sol} (%)	83.3	73.6	57.3	14.2	10.8	9.4

Table 3 Thermochromic properties of PNIPAAm hydrogel thin film with 52 μm thickness

52 μm	20°C	30°C	35°C	40°C	50°C	60°C
T_{lum} (%)	87.9	63.3	62.6	59.9	56.5	53.6
T_{IR} (%)	80.0	72.6	72.7	70.5	68.4	66.1
T_{sol} (%)	83.0	65.5	65.0	62.3	59.8	57.5

According to the discussion above, the potential of PNIPAm hydrogel thin film to be used in smart window application is related to the hydrogel's thickness. The thickness effect of "thin" hydrogel was further studied within the thickness of less than 100 μm . As can be seen from **Figure 12a**, the water absorption intensity at both 1930 nm and 1430 nm increased when the thickness increases from 26 μm to 78 μm , and the temperature decreased from 40 °C to 20 °C which is similar to **Figure 11**. As shown in **Table 4**, the T_{lum} (20°C) remained nearly

unchanged for all 3 samples, while $T_{lum(40^{\circ}C)}$ underwent a monotonous reduction from $\sim 80\%$ ($26\ \mu m$) to less than 20% ($78\ \mu m$). Although the hydrogel with $78\ \mu m$ thickness showed impressive ΔT_{sol} of nearly 50% , its low $T_{lum(40^{\circ}C)}$ of less than 20% can be least satisfactory for ideal smart window. The compromise between T_{lum} at high temperature and ΔT_{sol} also applied for hydrogel with thickness of $26\ \mu m$. The extremely low thickness was accompanied by almost unchanged luminance transmittance as well as poor solar modulating ability at temperatures above LCST. The averaged $T_{lum(40^{\circ}C)}$ decreases with the thickness while ΔT_{lum} , ΔT_{IR} and ΔT_{sol} increases with thickness (**Figure 12b**).

The hydrogel with thickness of $52\ \mu m$ was picked to compare its thermochromic performance with that of the best reported VO_2 samples to date. As highlighted in **Table 4**, $52\ \mu m$ hydrogel sample has much higher T_{lum} at $20\ ^{\circ}C$ (87.9% v.s 63.7%) and slightly higher T_{lum} at high temperature ($59.9\%_{(40\ ^{\circ}C)}$ v.s $54.4\ \%_{(90\ ^{\circ}C)}$) which results in enhanced averaged T_{lum} (73.9% v.s 59.1%). In addition, hydrogel has much larger ΔT_{lum} compared with VO_2 (28.0% v.s. 9.3%) with slightly reduced ΔT_{IR} (9.5% v.s 17.2%). Since visible range has higher $\varphi_{sol}(\lambda)$ compared with infrared range, the greatly enhanced ΔT_{lum} resulted in nearly doubled solar modulating ability (ΔT_{sol} , 20.4% v.s 12%) compared with VO_2 , indicating a more effective modulation of solar radiation.

Figure 12 (a) Optical transmittance spectra of the three samples with different thickness between 20 °C and 40 °C; (b) Trend of ΔT_{sol} , ΔT_{lum} , ΔT_{IR} and T_{lum} at 40 °C for different thickness. Table 4 The optical properties comparison between hydrogel thin film (52 μm) and VO₂ thin film

	$T_{lum(20^{\circ}C)}$	$T_{lum(40^{\circ}C)}$	ΔT_{lum}	Ave T_{lum}	$T_{sol(20^{\circ}C)}$	$T_{sol(40^{\circ}C)}$	ΔT_{IR}	ΔT_{sol}
26 μm	88.9	79.9	9.0	84.4	84.2	77.7	2.1	6.5
52 μm	87.9	59.9	28.0	73.9	83.0	62.7	9.5	20.4
77 μm	85.8	19.9	65.9	52.8	81.0	31.6	31.7	49.6
VO₂ thin film¹⁸	63.7	$T_{lum(90^{\circ}C)}$ 54.4	9.3	59.1	61.9	$T_{lum(90^{\circ}C)}$ 49.9	17.2	12

The actual outdoor test of hydrogels with various thicknesses was done in Singapore at atmospheric temperature of 35 °C in a sunny day. As shown in **Figure 12**, except the hydrogel with thickness of 26 μm that was proved with poor solar modulating, all other thicker hydrogels would become translucent or totally opaque within one minute outdoors and recover its transparency within one minute indoors. The outdoor translucency of hydrogels with thicknesses of 78 μm and 200 μm is too poor for windows, while the thickness of 52 μm shows acceptable outdoor transparency at high temperature.

Figure 13 Smart hydrogel thin films at room temperature (left) and in sunshine environment at 35 °C (right) with thickness of (a) 26 μm ; (b) 52 μm ; (c) 78 μm and (d) 200 μm .

Importantly, the good performance can be maintained in the durability test as shown in **Figure 13**, with consistent T_{lum} at both high and low temperature and relatively unchanged ΔT_{sol} after 20 cycles of measurement, indicating that the performance stability should be reliable in actual smart window application as long as good sealing to prevent water evaporation is achieved. Considering the hydrogel's more suitable and easily tunable transition temperature, the temperature responsive hydrogels surpassed the best reported VO_2 films and should be one of the best candidates for thermochromic smart window application.

Figure 14 Durability test of hydrogel with thickness of 36 μm between 20 $^{\circ}\text{C}$ and 40 $^{\circ}\text{C}$.

4.2 UV-Vis-NIR spectra for hydrogel/ VO_2 nanoparticles composite

According to the discussion above, pure hydrogel thin film can provide a high solar modulation ability $\sim 20.4\%$, in order to get even higher ΔT_{sol} , VO_2 nanoparticles were added into hydrogel.

Figure 15 (a) Pure hydrogel thin film at room temperature (25 °C), (b) VO₂/hydrogel hybrid at room temperature, (c) VO₂/hydrogel hybrid at 35 °C, TEM image of VO₂ nanoparticles at (d) 31500× and (e) 50000×, (f) Angular frequency dependence of storage modulus and loss modulus for pure hydrogel and VO₂/hydrogel hybrid at 25 °C, (g) DSC of VO₂/hydrogel hybrid and commercial VO₂ powder (inset).

At room temperature, pure PNIPAm hydrogel was colorless transparent (Fig. 15a) while VO₂/hydrogel hybrid was brownish transparent due to the presence of VO₂ nanoparticles (Fig. 15b) and started to appear translucent when temperature increased above LCST at

35 °C. The TEM images at different magnification (Fig. 15d, e) show that the milled nanoparticles are irregular and non-spherical which are well dispersed within matrix. Agglomeration is sparsely observed and the particle size ranges approximately from 20 to 100 nm. Both the storage and loss modulus of hybrid are lower than those of pure hydrogel (Fig. 15f), indicating that the effective crosslinking density is reduced in the hybrid. The role of VO₂ nanoparticle in reducing crosslinking density can also be proven in swelling ratio tests that pure PNIPAm hydrogel has an equilibrium swelling ratio of 6.12 g/g while VO₂/hydrogel hybrid assumes a larger swelling ratio of 13.58 g/g. However, the storage modulus of hybrid hydrogel is still higher than loss modulus over the observed frequency range and this is a confirmative indication of crosslinked hydrogel.⁴⁸ The critical transition temperatures of both hydrogel matrix (~ 32 °C) and VO₂ (~ 68 °C) have been preserved in the hybrid as shown in Fig. 15g. It worth well to mention that the phase transition specific enthalpy of hybrid at ~ 68°C is only ~ 0.154 J/g and the nanoparticle concentration in hydrogel is ~ 0.372% as calculated from TGA result, which gives the VO₂ nanoparticles in hydrogel 41.39 J/g (0.154/0.372%) phase transition enthalpy. This is very close to the phase transition enthalpy of commercial VO₂ micro-sized powders (41.87 J/g) (Fig. 15g inset) and it proves that the hydrogel matrix does not affect the VO₂ nanoparticle phase transition at 68°C.

For VO₂/hydrogel hybrid, two transmittance reductions happened at ~1430 nm and 1930 nm wavelength (Fig. 3a), which are typical absorption peaks of water at these two wavelengths. The 1400 nm peak is due to the O-H stretch in the water molecule, while 1900

nm peak is a combination of O-H stretch and H-O-H bending. At low temperature, more hydrogen bonds exist between water and crosslinked chains; these hydrogen bonds are gradually broken with increasing temperature, which indicates a continuous phase separation.⁴⁹

When the thickness of hydrogel is higher than 52 μm , the luminous transmittance was too low to apply on smart windows applications, so three different thickness of hybrid was selected (13 μm , 26 μm and 52 μm). According to **Figure 14** and **Table 5**, at the 20 °C, as VO₂ nanoparticles introduced into pure hydrogel, T_{lum} still remained nearly unchanged and stayed at a high level for all the samples. While temperature increased to 80 °C, T_{lum} decreased to an accepted level from 61.8% to 43.2% with thickness increasing. At the same time, ΔT_{IR} was increased dramatically from 10.5% to 29.9% with thickness increasing. Thus, both of the large ΔT_{IR} and ΔT_{lum} led to sharp increasing for ΔT_{sol} from 18.5% to 34.7%. So the 52 μm thickness sample is most suitable for smart windows application due to its highest $\Delta T_{\text{sol}} \sim 34.7\%$ and an acceptable average $T_{\text{lum}} \sim 62.6\%$, which is much higher than both of organic and inorganic reported results (34.7% vs. 20.4% and 22.3%).

Figure 16 (a) Optical transmittance spectra of the three samples with different thickness between 20 °C and 80 °C; (b) Trend of ΔT_{sol} , ΔT_{lum} , ΔT_{IR} and T_{lum} at 80 °C for different thickness.

Table 5 The comparison between different thickness of hybrid with DPM to monomer ratio 1:6.

DPM:Monomer 1:6								
Thickness	$T_{lum}(20)$	$T_{lum}(80)$	ΔT_{lum}	Ave T_{lum}	$T_{sol}(20)$	$T_{sol}(80)$	ΔT_{IR}	ΔT_{sol}
13μm	86.8	61.8	25	74.3	84	56.5	10.5	18.5
26 μm	84	52.3	31.7	68	80.7	51.5	26.3	29.2
52 μm	82.1	43.2	38.9	62.6	78.9	44.2	29.9	34.7

Compared with pure hydrogel, the 52 μm composite sample has a slightly lower T_{lum} at 20 °C (82.1% v.s 87.9%) and a lower T_{lum} at high temperature (43.2%(80 °C) v.s 59.9 %(90 °C)), because of the introduction of pure VO₂ nanoparticles, which gives an sacrificed average luminous transmittance (62.6% v.s 73.9%). VO₂ nanoparticles' introduction reduced the luminous transmittance, on the other hand, it greatly increased infrared modulation ability ($\Delta T_{IR} \sim 29.9\%$ v.s 9.5%) of the composite. Since both visible and infrared range of the composite have higher $\varphi_{sol}(\lambda)$ compared with pure hydrogel, the greatly enhanced ΔT_{lum} and ΔT_{IR} resulted in much higher solar modulating ability (ΔT_{sol} , 34.7% v.s 20.4%), and at the same

time, the composite has an acceptable luminous transmittance. Hydrogel and VO₂ nanoparticle composite achieved an unprecedented largest solar modulation with the compromised T_{lum} at high temperature, which is of great significance in the energy saving.

According to the discussion above, hydrogel can act as a suitable smart matrix for VO₂. The UV-Vis spectra for pure hydrogel, VO₂ nanoparticles and hydrogel/VO₂ nanoparticles hybrid are shown in **Figure 15**.

For the pure hydrogel (black lines), there is a large contrast in visible range (380-780 nm wavelength) while pure VO₂ (red lines) only provides the contrast in the near infra-red (IR) range (780-2500 nm). The large contrast in the hybrid structure (blue lines) occurs in both visible and IR range gives an improved solar modulation ΔT_{sol} while maintaining moderate T_{lum} as shown in **Table 6**.

Figure 17 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 visible (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.

Table 6 The comparison of thermochromic properties of pure hydrogel, pure VO₂, VO₂/hydrogel hybrid structures and the best reported data in the reference.¹

Sample	T_{lum} (20 °C) (%)	T_{lum} (80 °C) (%)	T_{lum} (average) (%)	ΔT_{sol} (%)
Pure hydrogel	87.9	59.9(40 °C)	73.9	20.4
Pure VO ₂	43.7	41.3	42.5	11.2
VO ₂ /hydrogel Hybrid	82.1	43.2	62.6	34.7
Best reported data in references	45.6	40.0	42.8	22.3

The composite with thickness of 52 μm was picked to compare its thermochromic performance with that of the best reported VO₂ samples and pure hydrogel to date. As

highlighted in **Table 6**, compared with best reported VO₂ sample, 52 μm composite sample has a high T_{lum} at 20 °C (82.1% v.s 45.6%) and slightly higher T_{lum} at high temperature (43.2%_(80 °C) v.s 40.0 %_(90 °C)) which results in enhanced averaged T_{lum} (62.6% v.s 42.8%). In addition, composite has a 7 times larger ΔT_{lum} compared with VO₂ (38.9% v.s. 5.6%). Since visible range spectrum has higher (solar spectral irradiance distribution) compared with infrared range as shown in grey shaded area (Fig. 16), the large transmission difference in the visible range of the hybrid (light cyan) gives rise to largely enhanced ΔT_{sol} . It is of interest to observe that the two water absorption peaks at ~ 1430 and 1930 nm wavelength is coincident with two valley of the solar spectral irradiance (Fig. 16), which indicated that the water absorption gives the negligible effects on the T_{sol} and ΔT_{sol} . The dramatically enhanced ΔT_{sol} (34.7% vs. 22.3%) arises from large ΔT_{lum} mainly contributed by hydrogel and the large ΔT_{IR} by VO₂. This gives $\sim 56\%$ enhancement in ΔT_{sol} compared with best reported VO₂.

Most researchers focused on nanothermochromic VO₂⁵⁰ as it gave the best performance compared with other approaches (Table 1) and it predicted that the highest possible ΔT_{sol} is $\sim 20\%$ with $\sim 48\%$ T_{lum} . However, none of the matrix used are solar modulating and it is the first time that thermal responsive hydrogel matrix was adopted and such hybrid overcomes the physical limitation of nanothermochromism as shown in the simulation. Ultra large ΔT_{sol} contributed from both ΔT_{lum} and ΔT_{IR} could be achieved while high T_{lum} could be maintained. This opens a new avenue for the hybrid nanothermochromic materials.

5. Conclusion and Recommendation

5.1 Conclusion

The hybrid of temperature responsive hydrogel delegated by the PNIPAm and VO₂ nanoparticles was investigated as potential novel alternative thermochromic composite for smart window application. For pure hydrogel with properly tuned thickness, hydrogel can be totally transparent at room temperature with high T_{lum} of 87.9% and translucent at 40 °C, with acceptable T_{lum} of 59.9%. Also, it can provide both high modulation in visible range and moderate modulation ability in IR range, which lead to a largely overall enhanced ΔT_{sol} (20-40 °C) of 20.4% or 25.5% for ΔT_{sol} (20-60 °C) compared with the best reported VO₂ thermochromic film (ΔT_{sol} (20-90 °C) $\sim$ 22.3%, $T_{lum}(20^{\circ}C)$ 45.6% and $T_{lum}(90^{\circ}C) \sim$ 40.0%). This hydrogel demonstrated a combination of high T_{lum} , improved ΔT_{sol} and lowered transition temperature with good durability and reversibility, which is almost unlikely to be achieved by any modifications on current VO₂ based materials. When hydrogel combined with VO₂ nanoparticles, an unprecedented ΔT_{sol} (20-80 °C) of 34.5% can be achieved, which is more than doubled of the best reported VO₂ thermochromic film ΔT_{sol} (20-90 °C) $\sim$ 22.3%. At the same time, the average T_{lum} of the hybrid is also much higher than the best report VO₂ thermochromic film (62.6% v.s 42.8%). The outperforming temperature responsive hydrogel and VO₂ hybrid would pave the road to the development of thermochromic smart windows.

5.2 Recommendation

Tungsten can be introduced into VO₂ nanoparticles as a dopant to decrease the critical

temperature. The ultimate aim of this project is to commercialize this technology towards smart windows, which should exhibit a fully reversible phase transition around room temperature. This property will be governed by VO₂ nanoparticles in the hybrid structure. According to literature, W is the most effective dopant in reducing phase transition temperature of VO₂ to our best knowledge.⁵¹⁻⁵⁶ Hence, W would be selected to be the potential dopant in the near future.

The combination of hydrogel and VO₂ nanoparticles produced an unprecedented solar modulating ability, which is much higher than both of pure hydrogel and pure VO₂ nanoparticles. So the mechanism of the interaction between hydrogel and VO₂ nanoparticles should be further studied.

6. References

1. Z. Chen, Y. Gao, L. Kang, C. Cao, S. Chen and H. Luo, *Journal of Materials Chemistry A*, 2014, **2**, 2718-2727.
2. L. Perez-Lombard, J. Ortiz and C. Pout, *Energy Build.*, 2008, **40**, 394-398.
3. <http://www.freedoniagroup.com/World-Flat-Glass.html>.
4. P. Kiri, G. Hyett and R. Binions, *Advanced Materials Letters*, 2010, **1**, 86-105.
5. S.-Y. Li, G. A. Niklasson and C. G. Granqvist, *Journal of Applied Physics*, 2010, **108**, -.
6. M. Saeli, C. Piccirillo, I. P. Parkin, R. Binions and I. Ridley, *Energy and Buildings*, 2010, **42**, 1666-1673.
7. A. Seeboth, J. Kriwanek, D. Löttsch and A. Patzak, *Polymers for Advanced Technologies*, 2002, **13**, 507-512.
8. W. Y. Chung, S. M. Lee, S. M. Koo and D. H. Suh, *Journal of Applied Polymer Science*, 2004, **91**, 890-893.
9. Y. Gao, S. Wang, H. Luo, L. Dai, C. Cao, Y. Liu, Z. Chen and M. Kanehira, *Energy & Environmental Science*, 2012, **5**, 6104-6110.

10. V. Dobrosavljević, N. Trivedi and J. M. Valles, *Conductor-insulator quantum phase transitions / edited by Vladimir Dobrosavljevic, Nandini Trivedi, James M. Valles, Jr*, Oxford : Oxford University Press, 1st ed. , 2012.
11. J.-H. Son, J. Wei, D. Cobden, G. Cao and Y. Xia, *Chemistry of Materials*, 2010, **22**, 3043-3050.
12. Z. Lu, C. Li and Y. Yin, *Journal of Materials Chemistry*, 2011, **21**, 14776-14782.
13. S. Kittaka, H. Hamaguchi, T. Shinno and T. Takenaka, *Langmuir*, 1996, **12**, 1078-1083.
14. M. Becker, S. Bruckner, E. Lindner, M. Leich, M. Rothhardt, S. Unger and H. Bartelt, *Photonics North 2011*, 2011, **8007**.
15. N. R. Mlyuka, G. A. Niklasson and C. G. Granqvist, *Applied Physics Letters*, 2009, **95**, -.
16. L. Kang, Y. Gao, H. Luo, Z. Chen, J. Du and Z. Zhang, *ACS Applied Materials & Interfaces*, 2011, **3**, 135-138.
17. M. Balden, *Thin Solid Films*, 2011, **519**, 4032-4036.
18. C. Liu, X. Cao, A. Kamyshny, J. Y. Law, S. Magdassi and Y. Long, *Journal of Colloid and Interface Science*.
19. Y. Gao, S. Wang, L. Kang, Z. Chen, J. Du, X. Liu, H. Luo and M. Kanehira, *Energy & Environmental Science*, 2012, **5**, 8234-8237.
20. C. Liu, N. Wang and Y. Long, *Applied Surface Science*, 2013, **283**, 222-226.
21. N. R. Mlyuka, G. A. Niklasson and C. G. Granqvist, *physica status solidi (a)*, 2009, **206**, 2155-2160.
22. T. Xiaogang, Y. Tao, L. Ran, S. Zhihu, F. Yajuan, C. Hao, Y. Xun, Z. Wenqing, L. Qinghua, W. Changzheng, X. Yi and W. Shiqiang, *Scientific Reports*, 2012, **2**.
23. R. Binions, C. Piccirillo and I. P. Parkin, *Surface and Coatings Technology*, 2007, **201**, 9369-9372.
24. C. Batista, R. Ribeiro, J. Carneiro and V. Teixeira, *Journal of Nanoscience and Nanotechnology*, 2009, **9**, 4220-4226.
25. Z. Huang, S. Chen, B. Wang, Y. Huang, N. Liu, J. Xu and J. Lai, *Thin Solid Films*, 2011, **519**, 4246-4248.
26. Z. Luo, Z. Wu, X. Xu, M. Du, T. Wang and Y. Jiang, *Materials Science and Engineering: B*, 2011, **176**, 762-766.
27. G.V. JORGENSEN and J. C. LEE, *Solar Energy Materials* 1986, **14**, 205-214.
28. K.-D. UFERT, *phys. stat. sol. (a)*, 1977, **42**, 187-190.
29. N. R. Mlyuka, G. A. Niklasson and C. G. Granqvist, *Solar Energy Materials and Solar Cells*, 2009, **93**, 1685-1687.
30. C. G. Granqvist, P. C. Lansåker, N. R. Mlyuka, G. A. Niklasson and E. Avendaño, *Solar Energy Materials and Solar Cells*, 2009, **93**, 2032-2039.
31. Z. Chen, Y. Gao, L. Kang, J. Du, Z. Zhang, H. Luo, H. Miao and G. Tan, *Sol Energ Mat Sol C*, 2011, **95**, 2677-2684.
32. S. Y. Li, G. A. Niklasson and C. G. Granqvist, *Journal of Applied Physics*, 2011, **109**, 113515.
33. Y. F. Gao, S. B. Wang, H. J. Luo, L. Dai, C. X. Cao, Y. L. Liu, Z. Chen and M. Kanehira, *Enhanced chemical stability of VO₂ nanoparticles by the formation of SiO₂/VO₂ core/shell structures and the application to transparent and flexible VO₂-based composite foils with excellent thermochromic properties for solar heat control*.
34. T. Fischer, H. R. Holzbauer and A. Seeboth, *Influence of inorganic salts on optical transmission behaviour of thermotropic hydrogels*.
35. F. A. Aouada, M. R. de Moura, P. R. G. Fernandes, A. F. Rubira and E. C. Muniz, *Optical and morphological characterization of polyacrylamide hydrogel and liquid crystal systems*.
36. K. Ueno, K. Matsubara, M. Watanabe and Y. Takeoka, *Adv Mater*, 2007, **19**, 2807-+.

37. A. Seeboth, J. Kriwanek, D. Lotzsch and A. Patzak, *Chromogenic polymer gels for reversible transparency and color control with temperature at a constant volume*.
38. H. Fujimatsu, S. Ogasawara, H. Ihara, T. Takashima, K. Toyaba and S. Kuroiwa, *Colloid & Polymer Science*, 1988, **266**, 688.
39. W. Y. Chung, S. M. Lee, S. M. Koo and D. H. Suh, *Surfactant-free thermochromic hydrogel system: PVA/borax gel networks containing pH-sensitive dyes*.
40. J. Kriwanek, D. Lotzsch, R. Vetter and A. Seeboth, *Influence of a Zwitterionic surfactant on the chromogenic behavior of a dye-containing aqueous PVA-polyether gel network*.
41. A. Seeboth, J. Kriwanek and R. Vetter, *Novel chromogenic polymer gel networks for hybrid transparency and color control with temperature*.
42. S. Hirotsu, Y. Hirokawa and T. Tanaka, *Journal of Chemical Physics*, 1987, **87**, 1392.
43. J. T. Zhang, S. X. Cheng and R. X. Zhuo, *Poly(vinyl alcohol)/poly(N-isopropyl-acrylamide) semi-interpenetrating polymer network hydrogels with rapid response to temperature changes*.
44. B. Stenberg, R. A. Viscarra Rossel, A. M. Mouazen and J. Wetterlind, in *Advances in Agronomy*, ed. L. S. Donald, Academic Press, 2010, vol. Volume 107, pp. 163-215.
45. C. Ager and N. Milton, *GEOPHYSICS*, 1987, **52**, 898-906.
46. P. M. Reddy, M. Taha, P. Venkatesu, A. Kumar and M.-J. Lee, *The Journal of Chemical Physics*, 2012, **136**, -.
47. G. Ewing, M. Foster, W. Cantrell and V. Sadtschenko, in *Water in Confining Geometries*, eds. V. Buch and J. P. Devlin, Springer Berlin Heidelberg, 2003, ch. 9, pp. 179-211.
48. L. Xiong, X. Hu, X. Liu and Z. Tong, *Polymer*, 2008, **49**, 5064-5071.
49. Y. Zhou, Y. Cai, X. Hu and Y. Long, *Journal of Materials Chemistry A*, 2014, **2**, 13550-13555.
50. S.-Y. Li, G. A. Niklasson and C. G. Granqvist, *Journal of Applied Physics*, 2010, **108**, 063525.
51. G. X. Tong, Y. Li, F. Wang, Y. Z. Huang, B. Y. Fang, X. H. Wang, H. Q. Zhu, Q. Liang, M. Yan, Y. Qin, J. Ding, S. J. Chen, J. K. Chen, H. Z. Zheng and W. R. Yuan, *Acta Phys Sin-Ch Ed*, 2013, **62**.
52. A. H. Bi and J. H. Zhu, *J Exp Nanosci*, 2013, **8**, 46-53.
53. Y. F. Zhang, W. Li, M. J. Fan, F. F. Zhang, J. C. Zhang, X. H. Liu, H. N. Zhang, C. Huang and H. B. Li, *J Alloy Compd*, 2012, **544**, 30-36.
54. S. Chen, C. Z. Dong, L. F. Zhang and Z. M. Yu, *Materials Processing Technology li, Pts 1-4*, 2012, **538-541**, 101-104.
55. J. Z. Yan, Y. Zhang, Y. S. Liu, Y. B. Zhang, W. X. Huang and M. J. Tu, *Rare Metal Mat Eng*, 2008, **37**, 1648-1651.
56. W. Burkhardt, T. Christmann, B. K. Meyer, W. Niessner, D. Schalch and A. Scharmann, *Thin Solid Films*, 1999, **345**, 229-235.