Spectrally Selective Smart Window with High Near-Infrared Light Shielding and Controllable Visible Light Transmittance

Mengchun Wu, Yusuf Shi, Renyuan Li, and Peng Wang

ACS Appl. Mater. Interfaces, **Just Accepted Manuscript** • DOI: 10.1021/acsami.8b15574 • Publication Date (Web): 26 Oct 2018

Downloaded from <http://pubs.acs.org> on October 31, 2018

Just Accepted

"Just Accepted" manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides "Just Accepted" as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. "Just Accepted" manuscripts appear in full in PDF format accompanied by an HTML abstract. "Just Accepted" manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). "Just Accepted" is an optional service offered to authors. Therefore, the "Just Accepted" Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the "Just Accepted" Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these "Just Accepted" manuscripts.

1
2
3
4
5
6
7 Spectrally Selective Smart Window with High Near-
8
9
10
11 Infrared Light Shielding and Controllable Visible
12
13
14
15 Light Transmittance
16
17
18
19

20 *Mengchun Wu, Yusuf Shi, Renyuan Li and Peng Wang**
21

22
23 Water Desalination and Reuse Center, Division of Biological and Environmental Science and
24 Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi
25
26
27
28 Arabia
29

30
31 KEYWORDS: NIR light shielding, photo-thermal effect, thermo-responsive hydrogel, smart
32
33 window, energy saving
34
35
36
37
38
39

40 **ABSTRACT**
41
42
43

44 Smart windows with high near-infrared (NIR) light shielding and controllable visible light
45 transmittance are highly sought after for cooling energy saving in buildings. Herein we present a
46 rationally designed spectrally selective smart window which is capable of shielding 96.2% of the
47 NIR irradiation from 800 nm to 2500 nm and at the same time permitting acceptable visible light
48 (78.2% before and 45.3% after its optical switching) for indoor daylighting. The smart window
49 synergistically integrates the highly selective and effective NIR absorption based photothermal
50
51
52
53
54
55
56
57
58
59
60

conversion of cesium tungsten bronze (Cs_xWO_3) with the transparent thermo-responsive poly(*N*-isopropyl acrylamide) microgel-polyacrylamide (PAM-PNIPAM) hydrogel. The optical switching of the smart window is a direct result of the phase transition of PAM-PNIPAM hydrogel which in turn is induced by the photothermal effect of Cs_xWO_3 under sunlight irradiation. The smart window exhibits fast optical switching, shows a long-term operational stability, and can be made highly flexible. Under the experimental conditions in this work, the indoor temperature with the smart window is $\sim 21^\circ\text{C}$ lower than that with regular single-layered glass window under one sun irradiation. The smart window design in this work is meaningful for further development of effective smart windows for energy saving in the build environment.

INTRODUCTION

Building energy-consumption, including air conditioning, ventilation, heating and lighting, etc., are responsible for about 30–45% of the global energy demand nowadays, and it is still growing fast due to the growing global population and rapid urbanization.¹⁻⁵ Among them, the energy demand by building cooling is increasing drastically. It is predicted that the global cooling energy consumption will increase from ~ 3000 PJ in 2018, to ~ 15000 PJ in 2050 and ~ 50000 PJ in 2100, mostly driven by the rapid income growth in emerging economy and global warming.^{1,3} According to the forecast by Isaac and co-workers, the cooling energy demand in China and India in 2100 would represent an dramatic increase by $\sim 11450\%$ and $\sim 49920\%$ from the year of 2000, respectively.¹ Various kinds of technologies have been developed in the past to reduce the energy consumption in building cooling, such as nighttime ventilation, ground cooling, solar reflective paint, thermal insulation wall, and sky cooling roof.³ Emerging nowadays is smart window which creates a weather adaptive shell to control the solar energy input into a building by modulating the light transmission properties of the windows.^{2,6}

The light transmission modulation of smart windows can be achieved by thermochromism,⁷⁻¹⁶ electrochromism¹⁷⁻²² and photochromism²³ processes and these modulation processes can be obtained either in an active mode involving external intervention (*e.g.*, voltage input) or by a passive response of the smart window itself to surrounding parameters (*e.g.*, sunlight intensity and the temperature).² In comparison to the active mode, the passive one is typically more suitable for building application since it is automated and its structures are usually simpler. One popular strategy in the passive mode smart window is utilizing photothermal effect to alter the light transmission via thermochromism.^{10-11,16} Photothermal material is a key component in these systems, without which the temperature change of the smart window has to rely on the temperature of indoor space and the outer space. Only a few thermochromism systems can work well in this condition. With photothermal materials, the heat *in situ* generated is proportional to the sunlight intensity and consequently the temperature can be modulated within a large range, typically from room temperature to even above 80 °C,²⁴⁻²⁹ which greatly enhances the sensitivity and expand the library of candidate materials for smart windows.^{10-11,16}

Lighting room is an important functionality of many windows, which, instead of the entire solar spectrum, only the visible light contributes to.³⁰⁻³¹ The solar spectrum crosses UV, visible and NIR range, and the NIR part possesses more than 50% proportion of solar energy.³²⁻³³ If a photothermal material absorbs too much visible light for heat generation to achieve the temperature threshold of the thermochromism material, it will affect the room lighting and artificial electric lighting may be needed in this case.

In this work, we fabricated a smart window by rationally selecting a cesium tungsten bronze (Cs_xWO_3 film) as photothermal component and thermo-responsive poly(*N*-isopropyl acrylamide) (PNIPAM) microgels embedded in highly transparent polyacrylamide (PAM) hydrogel matrix as

controllable optical switching component. The Cs_xWO_3 film possesses high shielding performance in NIR ($\sim 88.2\%$) and UV range ($\sim 93.6\%$), while allows for high visible light transmission ($\sim 78.3\%$). Thus, the photothermal material in our design is mainly heated by the NIR light and does not affect the lighting functionality of the window. The transmission of visible light by the smart window is highly reversibly modulated by the phase change of PNIPAM microgels. This $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window system can be heated up to $\sim 47^\circ\text{C}$ under non-concentrated one sun irradiation (1000 W m^{-2}). The phase transition of PNIPAM microgels can be achieved by sunlight with intensity as low as 400 W m^{-2} . Under one sun illumination, more than $\sim 96.2\%$ of the NIR irradiation was shielded while $\sim 45.3\%$ of visible light was transmitted by the smart window for daylighting. Under the experimental conditions in this work, the indoor temperature with the smart window was $\sim 21^\circ\text{C}$ lower than that with single-layer glass window under one sun irradiation. The fact that this type of spectrally selective smart window is able to cut off $>75\%$ solar energy but still allows $>40\%$ visible light through for day lighting makes it very suitable for torrid zone, where the space cooling is much more important than space heating.

RESULTS AND DISCUSSION

Scheme 1 presents the conceptual design of the Cs_xWO_3 -hydrogel composite smart window and its application principle. The Cs_xWO_3 component has a high NIR shielding, photothermal conversion and high visible light transmittance. The hydrogel complex is in a form of PNIPAM microgels embedded inside PAM hydrogel matrix. The cross-linked PAM hydrogel skeleton shows highly visible light transmittance, holds and keeps the PNIPAM microgels and water inside. The thermo-responsive PNIPAM microgels are responsible for modulating the visible light transmittance by their reversible phase transition. Under sunlight irradiation, most of the NIR light

is absorbed and converted to heat by Cs_xWO_3 to induce the phase transition of PNIPAM microgels. Therefore, this spectrally selective smart window blocks most solar heat to reduce the indoor temperature and at the same time permits visible light transmittance after the PNIPAM microgel phase transition to ensure an acceptable indoor brightness.

Scheme 1. The conceptual design of the Cs_xWO_3 /PAM-PNIPAM smart window.

Fabrication of Cs_xWO_3 /PAM-PNIPAM Windows. The process for fabricating the Cs_xWO_3 /PAM-PNIPAM window is schematically presented in **Figure 1a**. The free-radical precipitation polymerization was employed to synthesize the PNIPAM microgels.³⁴⁻³⁵ Thermosensitive PNIPAM microgels were chosen as the phase transition component due to their rapid phase transition property in response to external stimuli and the uniformly distributed scattering state owing to their narrow size distribution after phase transition.^{9,34-35} The PAM-PNIPAM window was then fabricated in the sealed double-layer glass by *in situ* polymerization of AM monomers in the aqueous dispersion of PNIPAM microgels (step 1-3 of **Figure 1a**). The PAM hydrogel was used as the skeleton of the hydrogel matrix because of its high transparency, hydrophilicity, stability, and facile solution-based polymerization.³⁶⁻³⁹ The Cs_xWO_3 /PAM-

PNIPAM window was finally obtained by pasting the Cs_xWO_3 film to the outside glass of PAM-PNIPAM window (step 4 of **Figure 1a**). Cs_xWO_3 film was chosen as the photo-thermal component because of its high NIR shielding, effective photothermal conversion, and high transmittance in the visible region.^{13,27,31,40}

Figure 1. (a) Schematic illustration of the fabrication of Cs_xWO_3 /PAM-PNIPAM window. (b) Dependence of the hydrodynamic diameters of the PNIPAM microgels on temperature. The insets

are photographs of the aqueous dispersion of the PNIPAM microgels at 22 °C (left) and 36 °C (right) with the concentration of 1.6×10^{-2} wt%. (c) Hydrodynamic diameter distribution curve of the PNIPAM microgels in the aqueous dispersion. The inset is the SEM image of the dried PNIPAM microgels.

The size distribution and phase transition of PNIPAM microgels were characterized by dynamic light scattering (DLS). As shown in **Figure 1b**, the hydrodynamic diameter (D_h) of PNIPAM microgels decreased from ~992 nm to ~329 nm by increasing the temperature from 22 °C to 36 °C. This is because that PNIPAM microgels are relatively hydrophilic and they are in a highly swollen state with water at 22 °C, while they become relatively hydrophobic and highly shrunken at 36 °C. The PNIPAM microgels shrunk sharply when the temperature increased to ~32 °C, indicating that the volume phase transition temperature (VPTT) for these PNIPAM microgels is ~32 °C, which agrees with the lower critical solution temperature (LCST) of PNIPAM polymer in literature.³⁵ The aqueous dispersion of PNIPAM microgels (1.6×10^{-2} wt%) is transparent at room temperature (22 °C), but looks opaque at 36 °C due to the greatly increased refractive index difference between the microgels and the solvent, which causes strong light scattering (inset of **Figure 1b**).^{34,41} The aqueous dispersion of PNIPAM microgels at 36 °C is stable without any aggregation (inset of **Figure 1b**). As shown in **Figure 1c**, the DLS curve of the aqueous dispersion of PNIPAM microgels at 36 °C exhibits a unimodal distribution with a D_h of ~329 nm. The scanning electron microscopy (SEM) image shows that the dried PNIPAM microgel particles are sphere-like with the uniform size of ~230 nm (inset of **Figure 1c**).

The PAM-PNIPAM hydrogel with a thickness of 1 mm was fabricated with the concentration of PNIPAM microgels aqueous dispersion of 1.6 wt%. The chemical composition of PAM-

PNIPAM hydrogel was verified by Fourier-transform infrared (FTIR) spectroscopy (**Figure 2a**). Compared to the spectrum of PAM, two bands at $\sim 1662\text{ cm}^{-1}$ and $\sim 1610\text{ cm}^{-1}$ in the spectrum of PAM-PNIPAM can be assigned to the amide I band (C=O stretching) and amide II band (N–H bending) of PAM, respectively. The absorptions at $\sim 3398\text{ cm}^{-1}$ and $\sim 3194\text{ cm}^{-1}$ correspond to the asymmetrical and symmetrical N–H stretching vibrations, respectively.⁴² Furthermore, the peak at $\sim 1419\text{ cm}^{-1}$ is attributed to the amide III band (C–N stretching) of PAM.⁴² The characteristic deformation vibration peaks of the C–H bond in the isopropyl group of PNIPAM are found at $\sim 1388\text{ cm}^{-1}$ and $\sim 1368\text{ cm}^{-1}$,⁴³ indicating a successful synthesis of PAM-PNIPAM composite hydrogel. The X-ray photoemission spectroscopy (XPS) was also used to confirm the composition of PAM-PNIPAM hydrogel. As shown in **Figure S1**, compared to the C 1s spectrum of PNIPAM microgel, the peak at $\sim 286.2\text{ eV}$ in the spectrum of PAM-PNIPAM is ascribed to C–N unit in the isopropyl group of PNIPAM,⁴⁴ and the enhanced peaks at $\sim 285.0\text{ eV}$ and $\sim 288.0\text{ eV}$ are due to the C–C/C–H units and O=C–N unit of PAM, respectively, indicating the PNIPAM and PAM components in the hydrogel.

SEM image of freeze-dried PAM-PNIPAM hydrogel shows that the hydrogel exhibits uniformly porous structures with the pore diameter of $\sim 1.15\text{ }\mu\text{m}$ (inset of **Figure 2a**), which supposedly provides enough free-space for the swelling and shrinking of PNIPAM microgels. The PAM-PNIPAM window is highly transparent in the visible region with a transmittance of $\sim 92.1\%$ at 550 nm at room temperature, which is almost exactly the same as the single-layer glass ($\sim 92.2\%$) and higher than the double-layer glass ($\sim 85.6\%$) (**Figure 2b**). Presumably, the high visible transmittance of PAM-PNIPAM window is due to the fact that glass and PAM-PNIPAM hydrogel show negligible visible light absorption (**Figure S2**) and that the refractive index of PAM-PNIPAM hydrogel (~ 1.35)^{38,41} lies between the glass (~ 1.50) and air (~ 1.0), which is beneficial to

suppress the light reflection at the interface.⁴⁵⁻⁴⁶ The lower visible light transmittance of the double-layer glass is because of the large refractive index difference between the glass and the trapped air in the interspace of the double glass layers, leading to a larger light reflection loss⁴⁵⁻⁴⁶ (Figure S2).

Figure 2. (a) FTIR spectra of PAM-PNIPAM hydrogel, PAM hydrogel, and PNIPAM microgel. The inset in (a) is the SEM image of freeze-dried PAM-PNIPAM hydrogel. (b) Visible light transmission spectra of PAM-PNIPAM window, single-layer glass window, double-layer glass window, Cs_xWO_3 film, and $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window. Transmittance of the (c) PAM-PNIPAM ($x\%$) window and (e) $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ ($x\%$) window as a function of temperature at the wavelength of 550 nm. Photographs of (d) PAM-PNIPAM ($x\%$) window and (f) $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ ($x\%$) window at 22 °C (top) and 36 °C (bottom), respectively. The x in PAM-PNIPAM ($x\%$) represents the concentration of PNIPAM microgel aqueous dispersion used in the fabrication of PAM-PNIPAM hydrogel.

The thermo-responsive optical switching property of PAM-PNIPAM hydrogel was demonstrated by measuring the temperature-dependent transmittance at the wavelength of 550 nm (**Figure 2c**). At 22 °C, the PAM-PNIPAM window is highly transparent with a transmittance of ~92.1% at 550 nm (**Figure 2c and d**). The transmittance of the PAM-PNIPAM window decreases sharply when the temperature increases to ~30 °C, indicating the LCST of PAM-PNIPAM hydrogel was ~30 °C (**Figure 2c**). The LCST of PAM-PNIPAM hydrogel was slightly lower than the PNIPAM microgels, which was presumably caused by the formation of intermolecular interaction, such as hydrogen bonding, between PAM and PNIPAM. The interaction protects PNIPAM from exposure to water and results in a hydrophobic contribution to decrease the LCST.³⁹ The PAM-PNIPAM window turned translucent after the phase transition process (**Figure 2c and d**). The light transmittance of PAM-PNIPAM window decreased after the phase transition when increasing the concentration of PNIPAM microgels aqueous dispersion ($x\%$). As shown in **Figure 2c**, after phase transition, the light transmittance of PAM-PNIPAM (0.4%), PAM-PNIPAM (0.8%)

and PAM-PNIPAM (1.6%) window was 78.4%, ~67.3%, and ~55.7%, respectively. The light transmittance after phase transition could be further decreased by increasing the thickness of PAM-PNIPAM hydrogel. When increasing the hydrogel thickness from 1 mm to 2 mm, the light transmittance of PAM-PNIPAM window decreased from ~55.7% to ~45.1% after phase transition (**Figure S3**). This is because that the content of PNIPAM microgels in the extended light path increased by increasing the hydrogel thickness, resulting in an increase in light scattering and decrease in light transmittance after the phase transition. Therefore, the PAM-PNIPAM (1.6%) window (thickness of the hydrogel was 1 mm) shows high optical transparency at room temperature, and acceptable visible light scattering and transparency after phase transition. Based on these results, this PAM-PNIPAM window was then combined with Cs_xWO_3 to make spectrally selective smart window.

Commercially available Cs_xWO_3 film is highly transparent in the visible region with a transmittance of ~78.3% at 550 nm (**Figure 2b**). After pasting the Cs_xWO_3 film on the outside of the previous PAM-PNIPAM window, the resulting Cs_xWO_3 /PAM-PNIPAM smart window still shows high transmittance in the visible region with a transmittance of ~78.2% at 550 nm at room temperature (**Figure 2b**). The patterns and words behind Cs_xWO_3 /PAM-PNIPAM window can clearly be seen (**Figure 2f**). The LCST of Cs_xWO_3 /PAM-PNIPAM window is also ~30 °C (**Figure 2e**). After phase transition, Cs_xWO_3 /PAM-PNIPAM window turned translucent with a light transmittance of ~45.3% at 550 nm. The light transmittance of Cs_xWO_3 /PAM-PNIPAM ($x\%$) windows turned to ~64.6% and ~54.2% after phase transition by decreasing the concentration of PNIPAM microgels aqueous dispersion ($x\%$) to 0.8% and 0.4%, respectively (**Figure 2e and f**). We observed that the transmittance of Cs_xWO_3 /PAM-PNIPAM window remained constant at the temperature beyond ~36 °C (**Figure 2e**), which is because that the dimension of the fully collapsed

PNIPAM microgel remains constant at temperature beyond ~ 36 °C.⁴⁷ The PNIPAM microgels further shrunk beyond the LCST (~ 31 °C), and reached their minimal dimension at ~ 36 °C (**Figure 1b**). Therefore, the optical properties of PAM-PNIPAM and $\text{Cs}_x\text{WO}_3/\text{PAM-PANIPAM}$ window after phase transition were measured at 36 °C. The $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ (1.6%) window has a high optical transparency ($\sim 78.2\%$) at room temperature, a relatively high visible light shielding effect and an acceptable visible light transmittance ($\sim 45.3\%$) after phase transition, altogether making it a desirable smart window.

The pure PNIPAM hydrogel was also fabricated for comparison and it showed a significant phase separation and volume shrinkage when heated to 50 °C due to the de-swelling of the water in the hydrogel (**Figure S4**, a-d). Fortunately, the PAM-PNIPAM hydrogel maintained its uniform shape without any shrinkage or deformation during the heating process (**Figure S4**, e-h) because that the water was retained within the hydrophilic PAM network during the phase transition process of PNIPAM microgels. On the other hand, embedding PNIPAM microgels in PAM hydrogel matrix can improve the stability of PNIPAM microgels during the repeated heating-cooling cycles because that the PAM hydrogel network is able to hold and lock the microgels in the matrix against aggregation.³⁵ As shown in **Figure S5**, after 100 cycles of heating-cooling process with heating at 50 °C for 5 min and cooling at 22 °C for 5 min, the $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window still maintained its reversible phase transition and optical switching properties with high optical transparency at room temperature ($\sim 78.0\%$) and optical translucency at 50 °C ($\sim 44.9\%$). The PAM-PNIPAM hydrogel was stable without any aggregation or volume change during the heating-cooling cycle, indicating that the PNIPAM microgels in PAM-PNIPAM hydrogel are stable during its shrinking-swelling process. The thermo-responsive optical switching of

$\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window was very rapid within ~ 30 s in the heating process and within ~ 5 min in the cooling process, indicating it is a quick thermo-response smart window.

Photothermal Property of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ Smart Window. The light absorption and transmission spectra of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window, Cs_xWO_3 film, PAM-PNIPAM window and single-layer glass window are shown in **Figure 3a** and b. As shown in **Figure 3a**, at 22°C , PAM-PNIPAM window and glass window exhibited relatively weak light absorption. Cs_xWO_3 film and $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window showed strong absorption in the NIR region (800-2500 nm) with an average absorption ($A_{800-2500}$) of $\sim 83.4\%$ and $\sim 89.7\%$ respectively, owing to the strong and broadband NIR absorption of the Cs_xWO_3 component. After optical switching at 36°C , the $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window showed a slightly increased NIR absorption with an average $A_{800-2500}$ of $\sim 91.6\%$ (**Figure 3a**).

As shown in **Figure 3b**, after phase transition, the $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window showed a decreased visible light transmittance with a T_{550} of $\sim 45.3\%$ (ΔT_{550} : $\sim 32.9\%$) due to the increased light scattering and a very low NIR light transmittance with the average $T_{800-2500}$ of $\sim 3.8\%$. This result shows that after phase transition, $\sim 96.2\%$ NIR light was shielded by $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window. The high NIR shielding performance is crucial for a good energy efficiency of a smart window,⁴⁸ because the NIR light carries more than 50% of the solar energy.^{13,31}

Figure 3. UV-vis-NIR absorption (a) and transmission (b) spectra of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window, Cs_xWO_3 film, PAM-PNIPAM window, and single-layer glass window, respectively. (c) Time-dependent top surface temperature changes of $\text{Cs}_x\text{WO}_3/\text{glass}$, $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$, PAM-PNIPAM, and glass windows in response to 1000 W m^{-2} light irradiation. Time-dependent top surface temperature changes of (d) PAM-PNIPAM and (e) $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ windows in response to different light intensity. (f) IR thermal images of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ under light irradiation with different light intensity.

The photothermal property of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window was investigated by using a simulated solar light as the light source. The windows were installed on a lab-made model house (Figure S6), and the measurements were carried out at ambient temperature (22 °C). Figure 3c presents the surface temperature of the window (recorded by an IR camera) as a function of light irradiation time (1000 W m^{-2}). The steady state surface temperatures of pure glass window and PAM-PNIPAM window were just ~26.3 °C and ~33.1 °C (Figure 3c), respectively, because of

their relatively weak light absorption. While, after irradiation for ~60 min, the steady state surface temperatures of $\text{Cs}_x\text{WO}_3/\text{glass}$ window and $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window were as high as ~48.8 °C and ~47.1 °C, respectively, owing to the effective photothermal conversion property of Cs_xWO_3 film. The surface temperature of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window rapidly increased to ~30 °C (the LCST of the window) after ~2.5 min sunlight irradiation, while it took ~16 min for PAM-PNIPAM window to reach the temperature of ~30 °C (**Figure 3c**). As shown in **Figure S7**, the light transmittance of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window and PAM-PNIPAM window decreased sharply after ~2.5 min and ~16 min light irradiation, respectively. After ~6.5 min light irradiation, the temperature of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window reached ~36 °C, meanwhile the transmittance of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window reached the steady state. The rapidly decreased transmittance of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window under light irradiation is beneficial to shield more solar heat. When the light intensity was less than 800 W m^{-2} , the surface temperature of PAM-PNIPAM window failed to reach above 30 °C under sunlight irradiation (**Figure 3d**) even after 90 min. When the light intensity decreased to 800 W m^{-2} , 600 W m^{-2} , and 400 W m^{-2} (**Figure 3e and f**), the steady state surface temperatures of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window could reach ~42.8 °C, ~38.1 °C, and ~33.0 °C, respectively. The fact that the surface temperature of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window is greater than 30 °C enough to induce optical switching of the smart window under sunlight irradiation with different and reduced light intensity allow us to explore the use of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window for the solar-assisted energy-saving smart window.

Energy-Saving Performance of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ Smart Window. In order to examine the feasibility of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window for reducing indoor temperature of the model house under solar irradiation, the windows were installed on the model house, and the

thermocouple thermometer was placed in the model house to monitor the changes of room temperature (**Figure S6**). The thermocouple sensor was wrapped with white paper to avoid the direct exposure to the sunlight irradiation. As shown in **Figure 4a**, after ~60 min sunlight irradiation (1000 W m^{-2}), the steady state room temperature with pure glass window was $\sim 46.0^\circ\text{C}$, which is due to the high light transmittance of the glass window. The steady state room temperatures with Cs_xWO_3 /glass window ($\sim 31.5^\circ\text{C}$) and PAM-PNIPAM window ($\sim 31.6^\circ\text{C}$) were lower, which was due to the NIR shielding property of Cs_xWO_3 component or the optical switching permanence of PAM-PNIPAM component, respectively. Meanwhile, the steady state room temperature with Cs_xWO_3 /PAM-PNIPAM window was as low as $\sim 24.5^\circ\text{C}$ after ~60 min light irradiation (1000 W m^{-2}), which is $\sim 21.5^\circ\text{C}$ lower than the pure glass window, $\sim 7.0^\circ\text{C}$ lower than the Cs_xWO_3 /glass window, and $\sim 7.1^\circ\text{C}$ lower than the PAM-PNIPAM window, respectively. The above results indicate that the synergistic effect of Cs_xWO_3 film and PAM-PNIPAM window plays a key role in the shielding performance for heat energy from solar irradiation. Cs_xWO_3 /PAM-PNIPAM window with high NIR shielding and reversible optical switching property has the abilities to reduce the room temperature under solar irradiation by effectively blocking the sunlight both in NIR region and visible region. It is reported that, in the highly developed cities, a cooling electricity of $35\text{--}90 \text{ W}/^\circ\text{C}/\text{capita}$ is required due to the usage of air conditioning as room temperature increases.⁵ Therefore, the usage of Cs_xWO_3 /PAM-PNIPAM window would effectively reduce the cooling energy consumption for air conditioning. For example, the solar transmittance of Cs_xWO_3 /PAM-PANIPAM window (25%) after phase transition is close to the reported window with sputtered solar film (21%),⁴⁹ which can reduce $\sim 29\%$ cooling energy demand per year in their test houses.

Figure 4. (a) Time-dependent room temperature changes of Cs_xWO₃/glass, Cs_xWO₃/PAM-PNIPAM, PAM-PNIPAM, and glass windows in response to 1000 W m⁻² light irradiation. (b) Room temperature changes of Cs_xWO₃/glass, Cs_xWO₃/PAM-PNIPAM, PAM-PNIPAM, and glass windows in response to different light intensity. Time-dependent room temperature changes of (c) Cs_xWO₃/PAM-PNIPAM window and (d) PAM-PNIPAM window in response to light intensity. (e) Room temperature changes of Cs_xWO₃/PAM-PNIPAM (x%) windows in response to different light intensity. (f) The flexible Cs_xWO₃/PAM-PNIPAM window before bending and after bending at room temperature (f1, f2), and after phase transition (f3, f4).

Under sunlight irradiation (1000 W m⁻²), the room temperature with Cs_xWO₃/PAM-PNIPAM smart window rapidly increased to ~26 °C in the first 2 min (**Figure 4a**). This is because, in the first 2 min, the surface temperature of Cs_xWO₃/PAM-PNIPAM smart window was less than 30 °C, lower than its LCST value. Therefore, certain amount of sunlight irradiated into the room interior through the transparent window (**Figure S7**), resulting in the initial room temperature

increase. Afterwards, the room temperature decreased to ~ 23.6 °C at the end of ~ 7 min sunlight irradiation and gradually reached the steady state temperature of ~ 24.5 °C after ~ 60 min. This is because the surface temperature of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ smart window increased to 30 °C after ~ 2.5 min sunlight irradiation (**Figure 3c**), which successfully induced the phase transition of the smart window. After the phase transition, the $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ smart window turned from a transparent to translucent state with the light transmittance decreased to $\sim 45.3\%$ in the visible region and to $\sim 3.8\%$ in the NIR region. Therefore, almost all the NIR light and most visible light were shielded by the phase transitioned $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window. Owing to the photothermal conversion of Cs_xWO_3 and rapid phase transition of PAM-PNIPAM, the room temperature could rapidly decrease to ~ 23.6 °C after ~ 7 min sunlight irradiation, which is very desirable for energy saving purpose as a rapid shielding leads to more required cooling energy saving. Compared with the $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window, PAM-PNIPAM window shows a similar room temperature-time dependent behavior due to its similar transparent-translucent phase transition, but it has a much longer cooling time (~ 35 min) and a higher steady state temperature of ~ 31.6 °C (**Figure 4a**), because of its poor photothermal performance and poor NIR shielding ability.

Figure 4b shows the room temperature changes with pure glass window, $\text{Cs}_x\text{WO}_3/\text{glass}$ window, PAM-PNIPAM window, and $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window under sunlight irradiation with different light intensity. The indoor temperatures with pure glass window and $\text{Cs}_x\text{WO}_3/\text{glass}$ window increased when increasing the light intensity. When the light intensity was increased from 400 to 1000 W m^{-2} , the room temperatures with $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ windows were all lower than ~ 25 °C, indicating the feasibility of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window for reducing the room temperature under sunlight irradiation with varying light intensity (**Figure 4b**). Under light

irradiation (400 to 1000 W m⁻²), the room temperatures with Cs_xWO₃/PAM-PNIPAM window all rapidly increased first, and then decreased to a lower steady state temperature (**Figure 4c**) due to the surface temperatures of Cs_xWO₃/PAM-PNIPAM window being all higher than 30 °C (**Figure 3e**). For the PAM-PNIPAM window, the room temperature increased from ~31.5 to ~34.2 °C by increasing the light intensity from 400 to 600 W m⁻². Interestingly, when the light intensity was increased from 600 to 1000 W m⁻², the room temperature decreased from ~34.2 °C to ~31.6 °C. This is because, when the light intensity was 400 and 600 W m⁻², the surface temperature of PAM-PNIPAM window was only ~26.3 °C and ~28.4 °C, respectively, both incapable of inducing phase transition of PAM-PNIPAM hydrogel, and the room temperature increased with increased light intensity (**Figure 4b and d**). However, when the light intensity was 800 W m⁻², the surface temperature of PAM-PNIPAM window was enough to induce the phase transition (**Figure 3d**) and therefore, light was partially blocked by the phase transitioned PAM-PNIPAM window at 800 and 1000 W m⁻² intensity, resulting in a decreased room temperature (**Figure 4b and d**).

The light transmittance of Cs_xWO₃/PAM-PNIPAM window after phase transition could be tailored by changing the content of PNIPAM (**Figure 2e**), which in turn would affect room temperature under light irradiation. As shown in **Figure 4e**, the room temperature with Cs_xWO₃/PAM-PNIPAM window decreased when increasing the content of PNIPAM under light irradiation. Under 1000 W m⁻² light irradiation, the room temperature decreased from ~26.7 °C to ~24.5 °C when increasing the content of PNIPAM from 0.4% to 1.6% due to the decreased light transmittance. It is believed that Cs_xWO₃/PAM-PNIPAM window with adjustable light transmittance and room temperature could expand its potential applications.

In addition, flexible Cs_xWO₃/PAM-PNIPAM windows can be fabricated on flexible substrates instead of glass substrates, such as polyethylene terephthalate (PET) substrates. As shown in

Figure 4f, the flexible windows were transparent at room temperature ($\sim 78.8\%$), and turned translucent after phase transition ($\sim 51.2\%$).

Figure 5. Time-dependent top window temperature and room temperature changes of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window in response to 1000 W m^{-2} light irradiation for 10 cycles.

In order to verify the temperature stability of the $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window for long-time operation in the model house, repeated solar irradiation and cooling tests were carried out. At each solar irradiation/cooling cycle, the model house with $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window was first exposed to the 1000 W m^{-2} light irradiation for 90 min, then air cooled at ambient temperature for 30 min without light irradiation. As shown in **Figure 5**, the surface temperature of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window and the room temperature were stable at each cycle. After 10 cycles, the steady state surface temperature of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window remained at $\sim 47^\circ\text{C}$ and the steady state room temperature was stable at $\sim 24.7^\circ\text{C}$, indicating the phase transition process and the light blocking properties of $\text{Cs}_x\text{WO}_3/\text{PAM-PNIPAM}$ window is highly repeatable and stable.

CONCLUSION

In summary, we have designed and produced a spectrally selective smart window by judiciously combining NIR based photothermal material and thermo-responsive hydrogel. The smart window is capable of shielding ~96.2% of the NIR solar irradiation from 800 nm to 2500 nm. The smart window is able to effectively keep the room temperature below 25 °C under sunlight irradiation with different light intensity, while maintaining acceptable visible light transmittance for day lighting, making it promising for highly energy-saving smart window. In addition, the smart window can be facilely fabricated, exhibits long-term operational stability, and can even be made flexible. The smart window in this work provides a new insight into developing multi-functional and highly energy efficient smart windows.

EXPERIMENTAL SECTION

Materials. *N*-Isopropyl acrylamide (NIPAM), *N,N'*-Methylenebisacrylamide (BIS), potassium persulfate (KPS), acrylamide (AM), *N,N,N',N'*-Tetramethylethylenediamine (TEMED) were purchased from Sigma-Aldrich. Self-adhesive Cs_xWO₃ film was purchased from Hangzhou Nanosemi Nanomaterials, Ltd. All the chemicals were used as received without further purification. Deionized water (18.2 MΩ cm) was used for all of the experiments.

Fabrication of PNIPAM microgels. PNIPAM microgels were fabricated by precipitation polymerization of NIPAM monomer, which was initiated by KPS in the presence of BIS as cross-linking agent.³⁴ Firstly, 2.5 g NIPAM and 2.5 mg BIS were added into 150 mL of pure water in a round-bottom flask and mixed by a magnetic bar until total solution. Then, the mixture solution was bubbled with N₂ gas for 10 min to remove the dissolved oxygen. Next, 0.05 g KPS (5 mL aqueous solution) was injected into the mixture solution with N₂ gas blowing into the flask above the liquid level. The polymerization was performed for 4 h at 60 °C with stirring at 300 rpm under

the N₂ gas atmosphere. The PNIPAM microgel dispersion was obtained with PNIPAM concentration of 1.6 wt%.

Fabrication of PAM-PNIPAM hybrid hydrogel. The PAM-PNIPAM hydrogel was fabricated by *in situ* polymerization of AM monomer in the aqueous dispersion of PNIPAM microgels. Briefly, 2.0 g AM monomer, 1 mg BIS, and 10 mg KPS were added into a 10 mL PNIPAM microgel dispersion with designated concentration (0.4 wt%, 0.8 wt%, and 1.6 wt%). Then, the mixture dispersion was treated by ultrasonic treatment in an ice–water bath to dissolve the AM monomer and then treated with nitrogen for 10 min to remove the most of oxygen. Finally, 50 μ L of TEMED was added under ultrasonic treatment. Then, the mixture dispersion was rapidly injected into a sandwiched glass mold (length and width: 7 $\times$ 4.5 cm²) which was sealed with 1 mm-thick sealant. The polymerization was conducted at 22 $^{\circ}$ C for 12 h to produce the PAM-PNIPAM hydrogel. The resulting hydrogel-glass system was noted as PAM-PNIPAM window.

Fabrication of Cs_xWO₃/PAM-PNIPAM windows. The self-adhesive Cs_xWO₃ film was pasted on the outside glass of the PAM-PNIPAM window to fabricate the Cs_xWO₃/PAM-PNIPAM window.

Material Characterization. Scanning electron microscopy (SEM) images were obtained on a Zeiss Merlin FE-SEM. Fourier-transform infrared (FTIR) spectra were measured on a Nicolet iS10 FTIR spectrometer. The spectra of X-ray photoemission spectroscopy (XPS) were measured on a Kratos AXIS Supra XPS spectrometer. UV-vis-NIR spectra were measured on an Agilent Cary 5000 UV-vis-NIR spectrophotometer. Temperature curves and thermal images of the samples were recorded by an FLIR A655 infrared camera. The simulated solar irradiation was provided by a 150 W Oriel Solar Simulator. An Oakton thermocouple thermometer with a 0.5 mm K-type thermocouple sensor was used to monitor simulate indoor temperatures. The hydrodynamic

diameter as a function of temperature was measured using dynamic light scattering (DLS) on a Malvern Zetasizer Nano-ZS. For DLS measurement, the concentration of the PNIPAM microgels dispersion is 8×10^{-3} wt%.

ASSOCIATED CONTENT

Supporting Information

XPS C 1s spectra of PNIPAM microgels, PAM hydrogel and PAM-PNIPAM hydrogel; visible light absorption and reflection spectra of single-layer glass window, PAM-PNIPAM window and double-layer glass window; optical switching property of PAM-PNIPAM (2 mm-thick) window; phase transition of pure PNIPAM hydrogels and PAM-PNIPAM hydrogels; 100 heating-cooling cycles of Cs_xWO_3 /PAM-PNIPAM window; schematic illustration of the lab-made model house; time-dependent transmittance of Cs_xWO_3 /PAM-PNIPAM window and PAM-PNIPAM window in response to light irradiation (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: peng.wang@kaust.edu.sa

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the King Abdullah University of Science and Technology (KAUST) Center Competitive Fund (CCF) awarded to Water Desalination and Reuse Center (WDRC).

REFERENCES

- (1) Isaac, M.; van Vuuren, D. P. Modeling Global Residential Sector Energy Demand for Heating and Air Conditioning in the Context of Climate Change. *Energy Policy* **2009**, *37*, 507–521.
- (2) Ke, Y.; Zhou, C.; Zhou, Y.; Wang, S.; Chan, S. H.; Long, Y. Emerging Thermal-Responsive Materials and Integrated Techniques Targeting the Energy-Efficient Smart Window Application. *Adv. Funct. Mater.* **2018**, *28*, 1800113.
- (3) Cao, X.; Dai, X.; Liu, J. Building Energy-Consumption Status Worldwide and the State-of-the-Art Technologies for Zero-Energy Buildings during the Past Decade. *Energy Build.* **2016**, *128*, 198–213.
- (4) Santamouris, M. Cooling the Buildings—Past, Present and Future. *Energy Build.* **2016**, *128*, 617–638.
- (5) Waite, M.; Cohen, E.; Torbey, H.; Piccirilli, M.; Tian, Y.; Modi, V. Global Trends in Urban Electricity Demands for Cooling and Heating. *Energy* **2017**, *127*, 786–802.
- (6) Khandelwal, H.; Schenning, A. P. H. J.; Debije, M. G. Infrared Regulating Smart Window Based on Organic Materials. *Adv. Energy Mater.* **2017**, *7*, 1602209.
- (7) Kim, D.; Lee, E.; Yoon, J. Optically Bistable Switching Glazing Achieved by Memory Function of Grafted Hydrogels *ACS Appl. Mater. Interfaces* **2018**, *10*, 22711–22717.

- (8) Zhou, Y.; Cai, Y.; Hu, X.; Long, Y. VO₂/Hydrogel Hybrid Nanothermochromic Material with Ultra-High Solar Modulation and Luminous Transmission. *J. Mater. Chem. A* **2015**, *3*, 1121–1126.
- (9) Owusu-Nkwantabisah, S.; Gillmor, J.; Switalski, S.; Mis, M. R.; Bennett, G.; Moody, R.; Antalek, B.; Gutierrez, R.; Slater, G. Synergistic Thermoresponsive Optical Properties of a Composite Self-Healing Hydrogel. *Macromolecules* **2017**, *50*, 3671–3679.
- (10) Lee, H. Y.; Cai, Y.; Bi, S.; Liang, Y. N.; Song, Y.; Hu, X. M. A Dual-Responsive Nanocomposite toward Climate-Adaptable Solar Modulation for Energy-Saving Smart Windows. *ACS Appl. Mater. Interfaces* **2017**, *9*, 6054–6063.
- (11) Chou, H.-T.; Chen, Y.-C.; Lee, C.-Y.; Chang, H.-Y.; Tai, N.-H. Switchable Transparency of Dual-Controlled Smart Glass Prepared with Hydrogel-Containing Graphene Oxide for Energy Efficiency. *Sol. Energy Mater. Sol. Cells* **2017**, *166*, 45–51.
- (12) Zhou, Y.; Layani, M.; Wang, S.; Hu, P.; Ke, Y.; Magdassi, S.; Long, Y. Fully Printed Flexible Smart Hybrid Hydrogels. *Adv. Funct. Mater.* **2018**, *28*, 1705365.
- (13) Liang, X.; Guo, C.; Chen, M.; Guo, S.; Zhang, L.; Li, F.; Guo, S.; Yang, H. A Roll-to-Roll Process for Multi-Responsive Soft-Matter Composite Films Containing Cs_xWO₃ Nanorods for Energy-Efficient Smart Window Applications. *Nanoscale Horiz.* **2017**, *2*, 319–325.
- (14) Wang, S.; Xu, Z.; Wang, T.; Xiao, T.; Hu, X. Y.; Shen, Y. Z.; Wang, L. Warm/Cool-Tone Switchable Thermochromic Material for Smart Windows by Orthogonally Integrating Properties of Pillar[6]arene and Ferrocene. *Nat. Commun.* **2018**, *9*, 1737.

- (15) Hao, Q.; Li, W.; Xu, H.; Wang, J.; Yin, Y.; Wang, H.; Ma, L.; Ma, F.; Jiang, X.; Schmidt, O. G.; Chu, P. K. VO₂/TiN Plasmonic Thermochromic Smart Coatings for Room-Temperature Applications. *Adv. Mater.* **2018**, *30*, 1705421.
- (16) Cao, D.; Xu, C.; Lu, W.; Qin, C.; Cheng, S. Sunlight-Driven Photo-Thermochromic Smart Windows. *Sol. RRL* **2018**, *2*, 1700219.
- (17) Liang, X.; Chen, M.; Guo, S.; Zhang, L.; Li, F.; Yang, H. Dual-Band Modulation of Visible and Near-Infrared Light Transmittance in an All-Solution-Processed Hybrid Micro–Nano Composite Film. *ACS Appl. Mater. Interfaces* **2017**, *9*, 40810–40819.
- (18) Wang, J. L.; Lu, Y. R.; Li, H. H.; Liu, J. W.; Yu, S. H. Large Area Co-Assembly of Nanowires for Flexible Transparent Smart Windows. *J. Am. Chem. Soc.* **2017**, *139*, 9921–9926.
- (19) Zhong, Y.; Chai, Z.; Liang, Z.; Sun, P.; Xie, W.; Zhao, C.; Mai, W. Electrochromic Asymmetric Supercapacitor Windows Enable Direct Determination of Energy Status by the Naked Eye. *ACS Appl. Mater. Interfaces* **2017**, *9*, 34085–34092.
- (20) Kim, Y.; Shin, H.; Han, M.; Seo, S.; Lee, W.; Na, J.; Park, C.; Kim, E. Energy Saving Electrochromic Polymer Windows with a Highly Transparent Charge-Balancing Layer. *Adv. Funct. Mater.* **2017**, *27*, 1701192.
- (21) Zhang, S.; Cao, S.; Zhang, T.; Fisher, A.; Lee, J. Y. Al³⁺ Intercalation/De-Intercalation-Enabled Dual-Band Electrochromic Smart Windows with a High Optical Modulation, Quick Response and Long Cycle Life. *Energy Environ. Sci.* **2018**, DOI: 10.1039/c8ee01718b.

- (22) Xu, J.; Zhang, Y.; Zhai, T.-T.; Kuang, Z.; Li, J.; Wang, Y.; Gao, Z.; Song, Y.-Y.; Xia, X.-H. Electrochromic-Tuned Plasmonics for Photothermal Sterile Window. *ACS Nano* **2018**, *12*, 6895–6903.
- (23) Yamazaki, S.; Ishida, H.; Shimizu, D.; Adachi, K. Photochromic Properties of Tungsten Oxide/Methylcellulose Composite Film Containing Dispersing Agents. *ACS Appl. Mater. Interfaces* **2015**, *7*, 26326–26332.
- (24) Wang, P. Emerging Investigator Series: the Rise of Nano-Enabled Photothermal Materials for Water Evaporation and Clean Water Production by Sunlight. *Environ. Sci.: Nano* **2018**, *5*, 1078–1089.
- (25) Li, R.; Zhang, L.; Shi, L.; Wang, P. MXene Ti_3C_2 : An Effective 2D Light-to-Heat Conversion Material. *ACS Nano* **2017**, *11*, 3752–3759.
- (26) Li, T.; Liu, H.; Zhao, X.; Chen, G.; Dai, J.; Pastel, G.; Jia, C.; Chen, C.; Hitz, E.; Siddhartha, D.; Yang, R.; Hu, L. Scalable and Highly Efficient Mesoporous Wood-Based Solar Steam Generation Device: Localized Heat, Rapid Water Transport. *Adv. Funct. Mater.* **2018**, *28*, 1707134.
- (27) Guo, W.; Guo, C.; Zheng, N.; Sun, T.; Liu, S. Cs_xWO_3 Nanorods Coated with Polyelectrolyte Multilayers as a Multifunctional Nanomaterial for Bimodal Imaging-Guided Photothermal/Photodynamic Cancer Treatment. *Adv. Mater.* **2017**, *29*, 1604157.
- (28) Zhang, L.; Tang, B.; Wu, J.; Li, R.; Wang, P. Hydrophobic Light-to-Heat Conversion Membranes with Self-Healing Ability for Interfacial Solar Heating. *Adv. Mater.* **2015**, *27*, 4889–4894.

- (29) Hong, S.; Shi, Y.; Li, R.; Zhang, C.; Jin, Y.; Wang, P. Nature-Inspired, 3D Origami Solar Steam Generator toward Near Full Utilization of Solar Energy. *ACS Appl. Mater. Interfaces* **2018**, *10*, 28517–28524.
- (30) Li, T.; Zhu, M.; Yang, Z.; Song, J.; Dai, J.; Yao, Y.; Luo, W.; Pastel, G.; Yang, B.; Hu, L. Wood Composite as an Energy Efficient Building Material: Guided Sunlight Transmittance and Effective Thermal Insulation. *Adv. Energy Mater.* **2016**, *6*, 1601122.
- (31) Yu, Z.; Yao, Y.; Yao, J.; Zhang, L.; Chen, Z.; Gao, Y.; Luo, H. Transparent Wood Containing Cs_xWO_3 Nanoparticles for Heat-Shielding Window Applications. *J. Mater. Chem. A* **2017**, *5*, 6019–6024.
- (32) Sang, Y.; Zhao, Z.; Zhao, M.; Hao, P.; Leng, Y.; Liu, H. From UV to Near-Infrared, WS_2 Nanosheet: A Novel Photocatalyst for Full Solar Light Spectrum Photodegradation. *Adv. Mater.* **2015**, *27*, 363–369.
- (33) Li, D.; Yu, S.-H.; Jiang, H.-L. From UV to Near-Infrared Light-Responsive Metal-Organic Framework Composites: Plasmon and Upconversion Enhanced Photocatalysis. *Adv. Mater.* **2018**, *30*, 1707377.
- (34) Pelton, R. H.; Chibante, P. Preparation of Aqueous Latices with *N*-Isopropylacrylamide. *Colloids Surf.* **1986**, *20*, 247–256.
- (35) Guan, Y.; Zhang, Y. PNIPAM Microgels for Biomedical Applications: from Dispersed Particles to 3D Assemblies. *Soft Matter* **2011**, *7*, 6375–6384.

- (36) Jing, Xin.; Mi, H.-Y.; Lin, Y.-J.; Enriquez, E.; Peng, X.-F.; Turng, L.-S. Highly Stretchable and Biocompatible Strain Sensors Based on Mussel-Inspired Super-Adhesive Self-Healing Hydrogels for Human Motion Monitoring. *ACS Appl. Mater. Interfaces* **2018**, *10*, 20897–20909.
- (37) Zhu, X.; Zhang, F.; Zhang, L.; Zhang, L.; Song, Y.; Jiang, T.; Sayed, S.; Lu, C.; Wang, X.; Sun, J.; Liu, Z. A Highly Stretchable Cross-Linked Polyacrylamide Hydrogel as an Effective Binder for Silicon and Sulfur Electrodes toward Durable Lithium-Ion Storage. *Adv. Funct. Mater.* **2018**, *28*, 1705015.
- (38) Wang, L.; Zhong, C.; Ke, D.; Ye, F.; Tu, J.; Wang, L.; Lu, Y. Ultrasoft and Highly Stretchable Hydrogel Optical Fibers for In Vivo Optogenetic Modulations. *Adv. Optical Mater.* **2018**, 1800427.
- (39) Djonlagi, J.; Petrovi, Z. S. Semi-Interpenetrating Polymer Networks Composed of Poly(*N*-isopropyl acrylamide) and Polyacrylamide Hydrogels. *J. Polym. Sci. Pol. Phys.* **2004**, *42*, 3987–3999.
- (40) Xu, W.; Meng, Z.; Yu, N.; Chen, Z.; Sun, B.; Jiang, X.; Zhu, M. PEGylated Cs_xWO₃ Nanorods as an Efficient and Stable 915 nm-Laser-Driven Photothermal Agent against Cancer Cells. *RSC Adv.* **2015**, *5*, 7074–7082.
- (41) Reufer, M.; Diaz-Leyva, P.; Lynch, I.; Scheffold, F. Temperature-Sensitive Poly(*N*-isopropylacrylamide) Microgel Particles: A Light Scattering Study. *Eur. Phys. J. E* **2009**, *28*, 165–171.
- (42) Kumar, P.; Choonara, Y. E.; du Toit, L. C.; Modi, G.; Naidoo, D.; Pillay, V. Novel High-Viscosity Polyacrylamidated Chitosan for Neural Tissue Engineering: Fabrication of Anisotropic

Neurodurable Scaffold via Molecular Disposition of Persulfate-Mediated Polymer Slicing and Complexation. *Int. J. Mol. Sci.* **2012**, *13*, 13966–13984.

(43) Futscher, M. H.; Philipp, M.; Muller-Buschbaum, P.; Schulte, A. The Role of Backbone Hydration of Poly(*N*-isopropyl acrylamide) Across the Volume Phase Transition Compared to its Monomer. *Sci. Rep.* **2017**, *7*, 17012.

(44) Dong, Y.; Zhu, X.; Shi, F.; Nie, J. Surface Photo-Anchored PNIPAM Crosslinked Membrane on Glass substrate by Covalent Bonds. *Appl. Surf. Sci.* **2014**, *307*, 7–12.

(45) Tadepalli, S.; Slocik, J. M.; Gupta, M. K.; Naik, R. R.; Singamaneni, S. Bio-Optics and Bio-Inspired Optical Materials. *Chem. Rev.* **2017**, *117*, 12705–12763.

(46) Lee, G. J.; Choi, C.; Kim, D.-H.; Song, Y. M. Bioinspired Artificial Eyes: Optic Components, Digital Cameras, and Visual Prostheses. *Adv. Funct. Mater.* **2018**, *28*, 1705202.

(47) Bischofberger, I.; Trappe, V. New Aspects in the Phase Behaviour of Poly-*N*-isopropyl acrylamide: Systematic Temperature Dependent Shrinking of PNiPAM Assemblies Well beyond the LCST. *Sci. Rep.* **2015**, *5*, 15520.

(48) Zhong, W.; Yu, N.; Zhang, L.; Liu, Z.; Wang, Z.; Hu, J.; Chen, Z. Synthesis of CuS Nanoplate-Containing PDMS Film with Excellent Near-Infrared Shielding Properties. *RSC Adv.* **2016**, *6*, 18881–18890.

(49) Moretti, E.; Belloni, E. Evaluation of Energy, Thermal, and Daylighting Performance of Solar Control Films for a Case Study in Moderate Climate. *Build. Environ.* **2015**, *94*, 183–195.

Table of Contents Graphic