Broadband Light Management with Thermochromic Hydrogel Microparticles for Smart Windows

This article reports the intelligent control of solar gain through windows based on the tunable scattering behaviors of temperature-responsive hydrogel particles. High luminous transmittance and broadband solar transmittance modulation including unprecedented IR modulation are simultaneously achieved for the first time using co-polymerized pNIPA-AEMA microparticles with prescribed particle size and internal structure. The design strategy to maneuver the real part of refractive index is applicable for broader fields beyond energy-saving smart windows.

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HIGHLIGHTS
Full solar spectrum transmission modulation by pNIPAm-AEMA hydrogel microparticles
Methodical tuning of scattering with prescribed particle size and internal structure
Unprecedented IR transmission modulation by extending the scattering range
Outstanding stability and scalability of thermochromic hydrogel device

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**SUMMARY**

Control of solar transmission through windows promises to reduce building energy consumption. However, the ability of current chromogenic technologies to regulate solar gain with the tunable extinction of phase-change materials is still far from optimum. We report a strategy for optimizing the transmittance modulation range of temperature-responsive hydrogel particles by means of tuning the light-scattering behaviors through controlling particle size and internal structure. An emerging thermochromic material, poly(N-isopropylacrylamide)-2-aminoethylmethacrylate hydrochloride (pNIPAm-AEMA) microparticles, was synthesized to demonstrate this strategy. The average size of pNIPAm-AEMA microparticles varies from 1,388 nm at 25°C to 546 nm at 35°C, contributing to an unprecedented infrared transmittance modulation of 75.6%. A high luminous transmittance of 87.2% at 25°C had also been accomplished. An investigation of the tunable scattering behaviors of pNIPAm-AEMA particles provided mechanistic insight into light management by this class of materials, the application field of which is beyond energy-saving smart windows.

**INTRODUCTION**

Considerable endeavors have been devoted to light management for energy-efficient buildings to reduce energy use in heating, ventilation, and air conditioning systems, which account for 13% in 2006 and 10% in 2020 (projected) of the total energy consumption in the United States. Light management using advanced smart window technologies is promising as it can theoretically lead to annual energy savings of more than 1.055 \times 10^{15} \text{kJ/year} in the United States. Previous transmittance modulation processes mainly rely on the change of extinction in thermochromic metal oxides or electrochromic active materials. However, this reliance leads to challenges for concurrently achieving a large tuning contrast of refractive index, a broad modulation spectrum, and a near-room-temperature transition. In practical terms, we also need to address several critical claims for large-scale adoption in building technologies, such as luminous transparency, transmittance modulation efficiency, economics of manufacturing and operation, stability, and scalability.

Electrochromic devices achieve the dynamic modulation of transmittance over visible and infrared (IR) regions based on an electrochemical-cell structure. An operation power is usually required for electrochromic devices, such as in the majority of commercial electrochromic smart windows employing transition metal oxides (e.g., WO₃) as the active material, which switches between oxidized/reduced states during faradic charge injection/extraction, and some emerging...
electrochromic technologies based on reversible metal electrodeposition and plasmonic nanocrystals. In general, the fabrication of these functional thin films relies on costly physical vapor deposition and a high-temperature process. Up to now, concerns about the cost of production and durability limit the scalability of electrochromic devices. Alternatively, thermochromic devices are considered as autonomous systems with no net energy input because the facade change can be triggered by the temperature change of the environment. The simplicity of the single-component structure holds promise for industrial production and ease of implementation.

Conventional thermochromic devices are generally based on the extinction of IR light by the phase-change medium that can be characterized by a change to the imaginary part of refractive index. For example, vanadium dioxide (VO₂) varies from an IR transparent state to an IR reflective metallic state at the critical temperature (Tc) of ~68°C. However, such mechanism of transmittance modulation has two intrinsic limitations. (1) A transparent heating unit is needed for VO₂ to be functionalized as a smart window coating, and the resulting elevated temperature of the window surface would diminish the heat-shielding ability. Some of the best-performing VO₂ devices in literature work at 90°C, showing a solar transmittance modulation (ΔT_solar) of 22.3% with a luminous transmittance (T_lum) of 45.6% before phase transition. Although dopants such as tungsten, niobium, and magnesium have been used to reduce T_c, the introduction of foreign ions will induce degradations in ΔT_solar and T_lum. (2) the strong inner-band and inter-band absorption of VO₂ lies in the visible region, leading to the reduced T_lum. Strategies such as elemental doping, antireflection coating, porosity tuning, and multilayered structure could improve the T_lum of VO₂ thin films to maximal 67.5% while the ΔT_solar was limited to 5.4%. Furthermore, doping and microscopic structure fabrications noticeably increase the complexity and cost of manufacturing. Current techniques to conquer the aforementioned obstacles in conventional thermochromic windows are still far from optimal.

In this work, we focus our study on a new group of thermochromic materials that achieve light management via tunable scattering behaviors. The light-blocking mechanism is elucidated with Mie scattering theory, which predicts efficient scattering in a broad solar spectrum with the aid of co-polymerized hydrogel microparticles of prescribed diameters. In particular, our aim is to achieve efficient transmittance modulation in the IR region (780–2,500 nm) where the thermal radiation contributes 53% of the total solar energy (UV 3%; visible 44%). As an example, we fabricated poly(N-isopropylacrylamide) (pNIPAm) and 2-aminoethylmethacrylate hydrochloride (AEMA) co-polymerized pNIPAm-AEMA hydrogel microparticles, whose crosslink uniformity and particle size are manipulated experimentally to attain ultra-high performance in both ΔT_solar and T_lum as compared with other thermochromic counterparts (Figure 1). Besides, pNIPAm-AEMA hydrogel microparticles can undergo phase transition under solar irradiance due to the low critical solution temperature (LCST) of ~32°C, making them preferable for smart windows. In contrast, an outdoor temperature higher than 50°C is required for the phase transition of VO₂ under natural convection, which is practically infeasible. Notably, heating-cooling cycles demonstrate the excellent stability of the device. Furthermore, the solution-phase synthesis described herein permits an industrial-scale and cost-effective production, whereby a 12 x 12 inch device is fabricated to display its scalability and the prospect of practical applications (Figure 2; see also Figure S1).
RESULTS AND DISCUSSION

The Synthesis of Co-polymerized pNIPAm-AEMA Microparticles

The uniqueness of temperature-responsive pNIPAm hydrogel particles for light management is that their scattering behaviors can be tuned profoundly regarding the particle size, internal structure, and volume fraction of water. A homogeneously low mismatch of refractive index between pNIPAm hydrogel particles and water at the “OFF” state is responsible for high $T_{\text{lum}}$ (Figure 3A), while the strong optical contrast between pNIPAm hydrogel particles and water is established when the polymer collapses above LCST. The light is scattered at the interface between the dense polymer and surrounding water, regarding the “ON” state. An effective light management for solar heat-shielding purposes requires that the light scattering covers the full solar spectrum, especially the IR region (53% of total solar energy). Problematically, heterogeneous internal structure of pNIPAm particles made by classical one-pot synthesis results in high turbidity of the hydrogel at the “OFF” state (Figure 3B1). Meanwhile, pNIPAm particles synthesized by radical emulsion polymerization reach the size limitation so that the size parameter ($2\pi r/\lambda$) is comparable with 1 only in the visible region, leading to inefficient scattering in the IR region at the “ON” state (Figure 3B2). To extend the transmittance modulation spectrum and guarantee...
the high $T_{\text{Lum}}$, the synthesis strategy is to enlarge the hydrogel particle size and maintain a homogeneous crosslink density.

The aforementioned requirements on the scattering behaviors of hydrogel particles were achieved by co-polymerizing pNIPAm and AEMA via a continuous feeding solution-phase synthesis (Figure 3B). The AEMA co-polymer modified the surface charge of particles with the positive terminal primary amine groups.\textsuperscript{41} The electrostatic repulsion of the hydrogel particles was diminished, which can be corroborated by the change of the zeta potential from $-23.9$ mV to $-9.0$ mV. Thus, the oligomers precipitated on primary particles and consequently increased the particle size. The hydrodynamic diameter ($D_h$) enlarges to 1,388 nm at $25^\circ$C and 546 nm at $35^\circ$C (Figure 3C), contributing to a size parameter ($2\pi r/\lambda$) comparable
with 1 in the IR region. Meanwhile, the continuous feeding method kept a constant monomer concentration and a reaction rate throughout the entire synthesis. The hydrogel particles were formed with a homogeneous internal structure, contributing to a very low scattering contrast to surrounding water at the swollen state. The temperature response of the pNIPAm-AEMA microparticles was evaluated by differential scanning calorimetry (DSC), revealing endothermic peak temperature
of 31.6°C and exothermic peak temperature of 30.9°C (see Figure S2). Additionally, the strong phase transition from swollen to deswollen state was observed by optical microscopy (see Figures S3A and S3B). In contrast, the average $D_h$ of pure pNIPAm particles is 548 nm at 25°C and shrinks to 282 nm at 35°C (Figure 3C), which reaches its size limitation despite carrying out the polymerization in a longer period of time and with a larger amount of monomer (see Figure S4). Our synthesis achieves the homogeneous crosslink density of particle and the controlled particle size from 200 to 2,000 nm (Figure S3C), which simultaneously fulfills the high $T_{lum}$ and the extending transmittance modulation in the IR region for the first time. In addition, compared with the thin-film manufacture of thermochromic VO$_2$, such a solution-phase synthesis of hydrogel particles suggests great potential for industrial-scale and cost-effective production.

Scattering Behavior of pNIPAm-AEMA Microparticles
Tunable scattering behaviors of pNIPAm-AEMA microparticles herein are elaborated in terms of the change of particle size parameter and optical density. Particularly, the scattering cross-section and refractive index were investigated based on Mie theory and Beer-Lambert law,$^{42,43}$ which show that the effective modulation of IR light by scattering could be delivered in response to the size parameter around 1 in the IR wavelength region and a strong enhancement of real part of refractive index above the LCST. Figures 3D1 and 3D2 show the complex refractive index of pNIPAm-AEMA microparticles, which was deduced from the attenuation coefficient ($\mu_a$) of the diluted suspension (see Figure S5). The $n$ of particles closes to the $n$ of water at the swollen state, which is attributed to the large volume fraction of water and a homogeneous crosslinked structure. The small scattering cross-section ($\sigma_s$) before phase transition is beneficial for a high $T_{lum}$ (Figure 3D3). Meanwhile, the small absorbing cross-section ($\sigma_a$) indicates a low absorption loss in the pNIPAm-AEMA (Figure 3D4), where two peaks near 1,450 nm and 1,930 nm are associated with the absorption of water molecules (see Figure S5). After the phase transition, the internal structure of pNIPAm-AEMA microparticles changes from a homogeneous water-rich state to the collapsed state. The $n$ approaches that of the bulk polymer with the reduction in the volume fraction of water. The $n$ of pNIPAm-AEMA at the deswollen state increases to approximately 1.45 in the visible region and to 1.40 in the IR region, which is in good accordance with the $n$ of hydrogel particles with similar chemical structures estimated by the effective medium approximation.$^{42,43}$ Figure 3D3 shows that the $\sigma_s$ of pNIPAm-AEMA appreciably increases in both the visible and IR regions after the phase transition. In contrast, the $\sigma_a$ of pure pNIPAm particles in the IR region is two orders lower due to the size limitation (see Figures S6 and S7), which narrows the transmittance modulation region. The dependence of $\sigma_s$ on different particle sizes was also investigated (Figure 3D4), indicating that the enlargement of particle size is responsible for delivering a stronger scattering in the broad solar spectrum. On the other hand, the $\sigma_a$ of pNIPAm-AEMA microparticles keeps a similar value (Figure 3D4), indicating that the transmittance is modulated via the enhancement of scattering, with respect to the increases in the real part of the refractive index, instead of absorbing.

Transmittance Modulation by pNIPAm-AEMA Hydrogel Devices
To fulfill efficient light management for energy-saving purposes, the ideal thermochromic smart window requires a near-room-temperature transition and a sharp gradient of transmittance.$^{45}$ The transmittance spectra of a pNIPAm-AEMA hydrogel device (250–2500 nm) at the layer thickness of 240 μm are reported in Figure 4A. At temperatures below LCST (22°C or 25°C), the $T_{lum}$, $T_{IR}$, and $T_{solar}$ are as high as 87.2%, 81.6%, and 84.1%, respectively (Figure 4B). Figure 4B shows luminous ($\Delta T_{lum}$), IR
(ΔT_{IR}), and solar (ΔT_{solar}) transmittance modulations at different temperatures. The phase transition started at 31°C along with a ΔT_{solar} of 26.2%, implying the strong temperature-responsive nature of pNIPAm-AEMA microparticles. Notably, at 34°C, the T_{IR} was significantly reduced from 81.6% to 6.0%, indicating an unprecedentedly high ΔT_{IR} of 75.6%. As a result, the ΔT_{solar} was boosted to 81.3%. Such a dramatic transition is desired for promptly blocking a large amount of solar irradiance.44 In contrast, pure pNIPAm particles with small size (Dh = 548 nm at 25°C and 282 nm at 35°C) barely afforded transmittance modulation in the IR region (see Figure S8). The pNIPAm hydrogel layer with the same thickness (240 μm) only showed a low ΔT_{IR} of 32.1%, leading to a limited ΔT_{solar} of 59.1% (see Figure S8). Although a hybrid of hydrogel with VO₂ or antimony-tin oxide nanoparticles has been attempted to improve ΔT_{IR},28,33 the operating temperature of metal oxide nanoparticle/hydrogel composite is as high as 80°C. Also, the complicated fabrication procedures for both nanoparticle doping and composite preparation cause difficulties for practical application. Furthermore, the performance of the pNIPAm-AEMA hydrogel device regarding transmittance modulations is superior to all known VO₂-based thermochromatic materials and thermochromic films made by hydrogels, hydrogel/VO₂ composites, ionogels, and ligand exchange of thermochromic films.9,12,22–34

Figure 4. Characterization of the pNIPAm-AEMA Hydrogel Film

(A) Transmittance spectra of pNIPAm-AEMA hydrogel with a layer thickness of 240 μm at different temperatures. The inset is the solar irradiance spectrum (gray area).

(B) The luminous (T_{lum}), IR (T_{IR}), and solar (T_{solar}) transmittances (solid lines) and corresponding transmittance modulations (ΔT_{lum}, ΔT_{IR}, and ΔT_{solar}) (dashed lines) in response to the temperature.

The excellent light blocking by the pNIPAm-AEMA hydrogel device in the IR spectrum results from microparticles whose dimensionless size parameter (2πr/λ) reaches unity in the IR region. The IR light is effectively scattered by microparticles in the device with the layer thickness from thin (40 μm) to thick (380 μm) (Figure S9A). By contrast, the transmittance modulation of pNIPAm particles is confined in the visible spectrum and is hardly improved by increasing the layer thickness (see Figure S9B). A Monte Carlo simulation of multiple scattering process based on Mie theory was applied to investigate the dependence of ΔT_{solar} on the layer thickness.45 The experimental results of transmittance modulation at different layer thicknesses were well reproduced, in which the estimated n and k of hydrogel particles were adopted (see Note S1; Figures S9 and S10). Owing to the broadband transmittance modulation, ΔT_{solar} of pNIPAm-AEMA hydrogel is higher than ΔT_{solar} of pNIPAm hydrogel for any given layer thickness (see Figure S11A). Meanwhile, the simulation shows the potential of pNIPAm-AEMA hydrogel of achieving a high T_{lum}, and
maintaining a decent $\Delta T_{\text{solar}}$ after phase transition by further reducing the layer thickness (see Figure S11B).

**Solar Energy Shielding and Device Stability**

Practical applications of smart windows raise the claims of reducing the solar gain and maintaining stability. A direct solar energy modulation was introduced to characterize the reduction of the heat flux from solar irradiance due to the phase transition of the window device (see Note S2). The irradiance from a solar simulator was slashed by 69.5% after passing through a pNIPAm-AEMA device, which is significantly higher than all existing smart window products on the market (see Figure S12).\(^{46}\) The pNIPAm-AEMA device was also installed on a chamber, and the temperature change inside the chamber was recorded under 1 sun, air mass 1.5 illumination (Figure 5A). The window made by double-glass slides was used as a control experiment, wherein the initial temperature of 25.0°C rapidly increased to 39.1°C after 20 min and reached a plateau at 30 min (14.1°C increments); whereas the phase transition of the pNIPAm-AEMA device was spontaneously triggered and completed after 5 min of illumination and the inner temperature only increased by...
Notably, the inner chamber temperature rose merely 1.3°C once the phase transition of the pNIPAm-AEMA hydrogel was completed. A slight decline in temperature after the phase transition indicates a net negative heat gain inside the chamber induced by a sudden opacity change whereby the heat dissipation was more significant than the heat input from illumination. After 10 min of illumination, the outside temperature reached 40.9°C and the inside temperature increased gradually due to heat conduction and convection. A smaller temperature rising rate of 0.10°C/min was delivered, compared with the rising rate of 0.26°C/min in the control experiment.

Figure 5B1 demonstrates visible transparency of the pNIPAm-AEMA device before and after phase transition, and Figure 5B2 shows the corresponding thermal IR images. The pNIPAm-AEMA device became opaque when the temperature rose to 35°C. In particular, the outstanding IR modulation of pNIPAm-AEMA device was proved by the IR images (Figure 5B3). At 25°C, the near-IR (NIR) light (850–2,200 nm) passed through an “MIT” logo and was captured by the IR camera, whose intensity was significantly slashed once the phase transition was triggered, indicating an excellent ΔTIR, which is barely obtained by VO2 thin films and other kinds of thermochromic thin films.1,9,27,30

A heating-cooling test of 1,000 cycles was conducted on the pNIPAm-AEMA device to test its stability for long-term operation, which shows less than a 4% decrease in ΔTIR (Figures 5C and 5D). Besides, no shrinkage of the hydrogel film was observed during heating-cooling cycles (see Figure S13 and Video S1). Such high stability regarding the number of testing cycles has not yet been reported, as most smart windows made by hydrogels suffer severe and non-reversible deformation after cycling tests.27,30 Additionally, the pNIPAm-AEMA device maintained its transparency at −2.1°C, and the phase transition was reserved when the sample was heated to 32.1°C (Figure S14).

Conclusions
In summary, a new type of light-management device based on thermochromic pNIPAm-AEMA microparticles has been demonstrated. The large and broadband transmittance modulation makes the device ideal for energy-saving applications. Especially by tailoring the particle size and internal structure, the pNIPAm-AEMA hydrogel effectively extends light rejection into the IR region, contributing to a significantly enhanced ΔTIR of 75.6% and an ultra-high ΔTsol of 81.3%. Meanwhile, the superiorities of hydrogel over conventional VO2-based thermochromic materials are maintained, exhibiting a high Tsum of 87.2% and a low phase-transition temperature of ~32°C. A decline of indoor temperature of ~5°C can be expected by using the pNIPAm-AEMA thermochromic windows, whose excellent stability and scalability also display its prospect of practical applications. Building upon the advancement of light management in the use of pNIPAm-AEMA microparticles over counterpart thermochromic materials, future progress in dynamic transmittance modulation is enabled by pursuing the optimal mechanism that leads to the change in the refractive index. The tunable scattering behaviors of hydrogel particles not only pave a way to revamp energy-saving smart windows but will also be broadly applicable to optical modulators, displays, and invisibility cloaking.47,48

EXPERIMENTAL PROCEDURES
Materials
The N-isopropylacrylamide monomer (NIPAm, 98%), N,N’-methylenebis(acrylamide) (BIS, 99%) crosslinker, ammonium persulfate (APS, ≥ 98%) initiator, and
SDS (≥98.5%) surfactant were purchased from Sigma-Aldrich. 2-Aminoethylmethacrylate hydrochloride monomer (AEMA, 95%) was purchased from Polysciences.

**Synthesis of pNIPAm-AEMA Microparticles**

The pNIPAm-AEMA particles were synthesized by the continuous feeding of NIPAm and AEMA co-monomers into the reaction vessel. NIPAm (6.00 g), BIS (0.15 g), and AEMA (25.8 mg) were dissolved in 150 mL of deionized (DI) water and purged with N2 for 20 min. The one-fifth as-prepared solution was mixed with 60 mL of DI water and heated to 80°C, and 6 mL of 22.8 mM APS was added to initiate the polymerization. The remaining solution was continuously fed into the reaction vessel at a rate of 1 mL/min, and the solution was stirred intensively during the entire polymerization. The reaction was stopped after 75 min, and the colloidal suspension was quenched rapidly in a freezer. To improve the stability of colloid suspensions, we dissolved 0.87 mM SDS surfactant in the colloid suspension by ultrasonication after synthesis, keeping the temperature of the suspension below 30°C. The size of co-polymerized pNIPAm-AEMA particles was controlled by continuously feeding a constant concentration of co-monomers and predictably stopping the reaction at different feeding times (Figure S3C). The pure pNIPAm hydrogel particles were synthesized similarly (see Note S3). The effects of applying AEMA co-monomer and SDS surfactant in synthesis are elaborated in Figure S15.

**Device Fabrication**

The hydrogel particles suspension was centrifuged at 13,000 rpm for 1.5 hr (MiniSpin plus, Eppendorf, Germany). The hydrogel thin-film devices were fabricated by injecting close-packed pNIPAm-AEMA or pNIPAm hydrogel particles in between double-glass slides, where the thickness of the layer was controlled by using thermoplastic sealing films (Meltonix 1170, DuPont Surlyn).

**Characterization**

Dynamic light scattering measurements were performed on a Dynamic Nanostar (Wyatt Technology, USA) with a laser at the wavelength of 658 nm. The hydrogel suspensions were diluted to 50 ppm and injected into UV-vis cuvettes (Eppendorf International). The diffusion coefficient ($D$) was obtained from the measured autocorrelation function, by which the hydrodynamic diameter ($D_h$) of a diffusion sphere was determined via the Stokes-Einstein Equation 1:

$$D_h = \frac{kT}{3\pi\eta D}$$

where $k$ is Boltzmann’s constant, $T$ is the absolute temperature, and $\eta$ is the viscosity of the solvent. The temperature was controlled by a thermostat with an accuracy of ±0.1°C.

DSC analysis was conducted on Discovery DSC (TA Instruments) over the temperature between 20°C and 45°C with a heating/cooling rate of 2°C/min under nitrogen flow. The closely packed hydrogel particles after centrifugation were applied to the DSC measurement without further treatment.

The transmittance spectra were collected using a Lambda 1050 UV-Vis-NIR spectrophotometer (PerkinElmer, USA) at normal incidence. The calculations of integral luminous transmittance $T_{lum}$ (380–780 nm), IR transmittance $T_{IR}$ (780–2,500 nm),
solar transmittance $T_{\text{solar}}$ (280–2,500 nm), and corresponding transmittance modulations can be found in Equations 2 and 3, respectively:13

$$T_{\text{lum}} = \int \frac{\phi_{\text{lum}}(\lambda)}{\phi_{\text{solar}}(\lambda)} T(\lambda) d\lambda,$$  \hspace{1cm} (Equation 2)

$$\Delta T_{\text{lum}}/\text{solar} = T_{\text{lum}}/\text{solar} (\text{at low temperature } \leq 25^\circ \text{C}) - T_{\text{lum}}/\text{solar} (\text{at high temperature } \geq 31^\circ \text{C}),$$  \hspace{1cm} (Equation 3)

where $T(\lambda)$ denotes the recorded transmittance at a particular wavelength, $\phi_{\text{lum}}$ is the standard luminous efficiency function for the photopic vision of human eyes,50 and $\phi_{\text{IR/solar}}$ is the IR/solar irradiance spectrum for air mass 1.5.21

The solar energy shielding test was conducted on a model chamber with a dimension of 0.15 $\times$ 0.10 $\times$ 0.08 m$^3$, which was covered by rigid melamine insulation sheets. The 0.04 $\times$ 0.05-m$^2$ window devices made by bare double-glass slides or the hydrogel device with a layer thickness of 380 $\mu$m were assembled upon the model chamber. The illumination intensity of a standard solar simulator (Peccell PEC-L01, Japan) was calibrated to air mass 1.5 illumination (100 mWcm$^{-2}$) on the top side of the window. The temperatures inside and outside of the chamber were measured simultaneously by a thermometer. The IR thermal images were recorded via a thermal imaging camera (FLIR Systems, USA). The IR images were captured by an IR camera (IR camera 85400, FJW Optical Systems, USA) with sensitivity from 400 to 1,800 nm. An NIR bulb incorporated with a long-pass filter (850–2,200 nm, Throlab FEL0850) was utilized as the irradiation light source for the demonstration of IR modulation.

### Evaluation of Optical Properties of Hydrogel Particles

The scattering cross-sections of the hydrogel particles were evaluated with an inverse method based on Mie theory.42 On the basis of Beer-Lambert law,43 the attenuation coefficient ($\mu_t$) of a low-concentration particle suspension could be obtained by determining the linear dependence of $\ln(T)$ on the thickness of suspension ($d$),43

$$\mu_t(\lambda) = -\frac{\Delta \ln|T(\lambda)|}{\Delta d}.$$  \hspace{1cm} (Equation 4)

The attenuation coefficient is determined by scattering and absorbing,43

$$\mu_t(\lambda) = \mu_s(\lambda) + \mu_a(\lambda),$$  \hspace{1cm} (Equation 5)

$$\mu_s = c \sigma_s,$$  \hspace{1cm} (Equation 6)

$$\mu_a = c \sigma_a + \frac{4\pi k_w}{\lambda},$$  \hspace{1cm} (Equation 7)

where $\mu_s$ and $\mu_a$ are the scattering and absorbing coefficient, respectively, and $\sigma_s$ and $\sigma_a$ denote the scattering and absorbing cross-section, respectively. $c$ is the concentration of particles and $k_w$ is the imaginary refractive index of water.51 The transmittance of 10 wt% as-synthesized suspensions with thickness from 130 to 670 $\mu$m was measured to determine the attenuation coefficient. We made the assumption that the particles at swollen state are incompressible. The concentration of the hydrogel particles was estimated by measuring the volume of particles after removing the surrounding water by centrifuging and dividing by $1/6 \pi D_h^3$. The scattering and absorption cross-sections of hydrogel particles were calculated based on a modified Mie scattering code.32,52 Here the fitted refractive index was chosen to keep the continuity of the real part ($n$) through both the visible and IR regions and
to achieve a relative error less than 1% between the fitted and measured attenuation coefficients. Step sizes of $10^{-4}$ in $n$ and $10^{-6}$ in the imaginary refractive index ($k$) for the visible region and $10^{-5}$ for the IR region were used in the fitting.

SUPPLEMENTAL INFORMATION
Supplemental Information includes Supplemental Experimental Procedures, 15 figures, 3 notes, and 1 video and can be found with this article online at https://doi.org/10.1016/j.joule.2018.10.019.

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AUTHOR CONTRIBUTIONS
X.-H.L., C.L., and N.X.F. developed the concept and designed and conducted the experiments. S.-P.F. contributed to the device preparation and solar simulator experiments. N.X.F., C.L., and X.-H.L. prepared the manuscript and contributed to the interpretation of the results. X.-H.L. and C.L. contributed equally to this work.

DECLARATION OF INTERESTS
N.X.F., C.L., and X.-H.L. are inventors on an invention disclosure at MIT (case no. 20597; created June 1, 2018) related to this work.

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