Supporting Information

A smart material built upon the photo-thermochromic effect and its use for managing the indoor temperature

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Methods

Preparation of the sandwiched photo-thermochromic film. Firstly, the photo-thermochromic DDF-BPA-TA mixture was prepared by mixing 0.01 g DDF (98.0%, TCI), 0.05 g of BPA (Sigma Aldrich), and 1 g of TA (97%, Sigma Aldrich) at 50 °C. PVA solution was prepared by dissolving 3.5 g of PVA (Mw≈130, 000, Sigma Aldrich) in 20 mL of DI water at 80 °C under magnetic stirring. For the PVA film containing 38.7 wt.% of DDF-BPA-TA, 0.8 mL of the as-prepared photo-thermochromic mixture was added into 6 mL of PVA solution. After stirring at a speed of 2000 rpm for 5 min, we obtained the photo-thermochromic film by casting the above mixture in a glass mold, followed by drying at 60 °C for 2 h. To prepare PVA films containing 13.6, 24.0, and 32.2 wt.% of DDF-BPA-TA, respectively, 0.2, 0.4, and 0.6 mL of the photo-thermochromic mixture was added into 6 mL of PVA solution. PE film was prepared by melting the PE (low density, Sigma Aldrich) in a glass mold at 150 °C and then cooling down to room temperature. The sandwiched photo-thermochromic films were prepared by separately covering the PVA film containing DDF-BPA-TA mixture at different concentrations with the PE films and heating at 150 °C for 5 min to form a sandwiched structure. For the measurements related to irradiation using a 660-nm diode laser coupled to a 100-μm-core fiber (Power Technology Inc.), the photo-thermochromic PVA film was prepared with a thickness of 50 μm, while that around 300 μm in thickness was used for the investigation under natural sunlight, allowing for a better absorption to the visible light. In both cases, the thickness of covered PE film was fixed as 150 μm.

Preparation of the sandwiched non-thermochromic film. A non-thermochromic film was used as a control group. The protocol for fabricating the sandwiched non-thermochromic film was essentially the same as the procedures used for the fabrication of sandwiched photo-thermochromic film except that TA was replaced with LA (97%, Spectrum Chemical).

Material characterizations. The surface morphology of the film was analyzed using a scanning electron microscope (SU8230, Hitachi). UV-vis extinction spectra were acquired using a Cary 60 spectrometer (Agilent Technologies, Santa Clara, CA). The 660-nm diode laser was used to irradiate the film for all indoor experiments. A K-type thermocouple (Omega Inc.) with a wire diameter of 250 μm and an IR-camera (FLIR E60) were used to measure and image the temperature during laser irradiation.

Thermochromic properties of the DDF-BPA-TA mixture and the sandwiched photo-thermochromic film. The photographs of the DDF-BPA-TA mixture and the sandwiched photo-thermochromic film were separately recorded by a digital camera during the heating process from 24 to 36 °C. The corresponding UV-vis spectra were acquired by the spectrometer. The UV-vis spectrum of the sandwiched photo-thermochromic film before and after operation to the measurements of ten rounds was separately recorded.

Photothermal effects of the DDF-BPA-TA mixture and the sandwiched photo-thermochromic film. The photothermal effects of the DDF-BPA-TA and DDF-BPA-LA mixtures under laser irradiation were separately evaluated by exposing the mixture (0.5 mL) to the 660-nm laser at an irradiance of 0.4 W/cm^2. To evaluate the photothermal effects of the sandwiched photo-thermochromic and non-thermochromic films, they were irradiated by the 660-nm laser at an irradiance of 0.2 W/cm^2, respectively. The temperatures of the mixture suspensions and sandwiched films were separately monitored with thermocouple and IR camera during the process.

Heating and cooling effects of the smart coating under natural sunlight. The building model was constructed with white cardboard of 4 mm in thickness. The size of the model is shown in Figure S8 (Supporting Information). The roof and the front wall were covered with the smart coating (*i.e.*, sandwiched photo-thermochromic film supported on aluminum foil). With this home-made building model, we measured the heating and cooling effect of the smart coating at a climate temperature of 12.3 °C (cold weather) and 24.3 °C (warm weather), respectively, in Atlanta, Georgia, USA (33°46'47.42"N, 84°23'48.09"W, 280 m altitude). As a control, building models with the same sizes, but covered with aluminum foil only or a sandwiched non-thermochromic film, were also evaluated. Room temperature rise profiles within the different building models were measured by a thermometer. IR images showing the surfaces of different building models were taken using the IR camera.

Tab. S1 Smart materials for building temperature management.

	Smart window	Smart film
Mechanism	The smart window is dark at high temperature to block the solar irradiation and is transparent at low temperature to let the light in.	In cold weather, the film takes a dark green color and can generate heat through the photothermal effect. In warm weather, the film is heated to colorless, while the transmitted sunlight will be reflected by the aluminum foil in the back.
Devices	Window.	Roof and wall.
Stimuli	Heat, electricity, light, humidity.	Heat and light.
Characteristics	Relatively low. 1. In warm weather, high temperature dark window will inevitably increase the energy consumption for cooling. 2. In cold weather, although the light is transmitted, the heating effect is limited due to the low photothermal conversion efficiency.	High. 1. Large area. 2. In warm weather, the sunlight can be completely reflected and the roof can be controlled at a relatively low temperature. 3. In cold weather, the light can be converted to heat through the photothermal effect with high conversion efficiency.

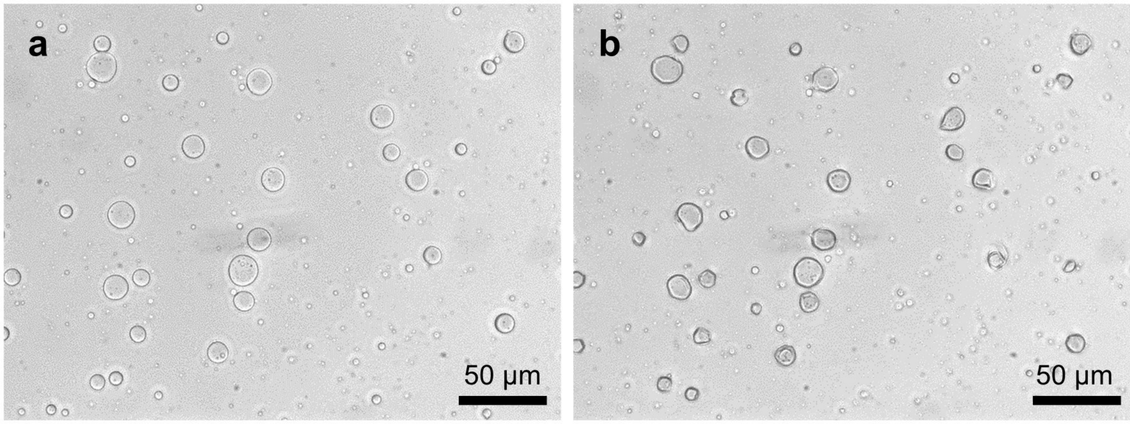

Fig. S1 Optical micrographs of the DDF-BPA-TA microspheres dispersed in (**a**) PVA solution and (**b**) PVA film, respectively. The DDF-BPA-TA microspheres were slightly deformed during the drying process.

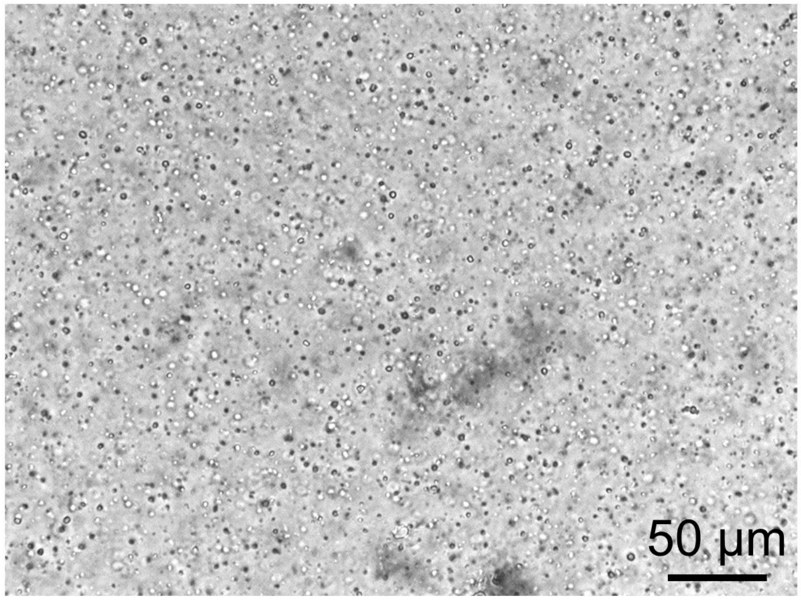

Fig. S2 Optical micrograph of the DDF-BPA-TA microspheres prepared at a stirring speed of 10,000 rpm. The diameters of the DDF-BPA-TA microspheres varied in the range of 1–5 μm.

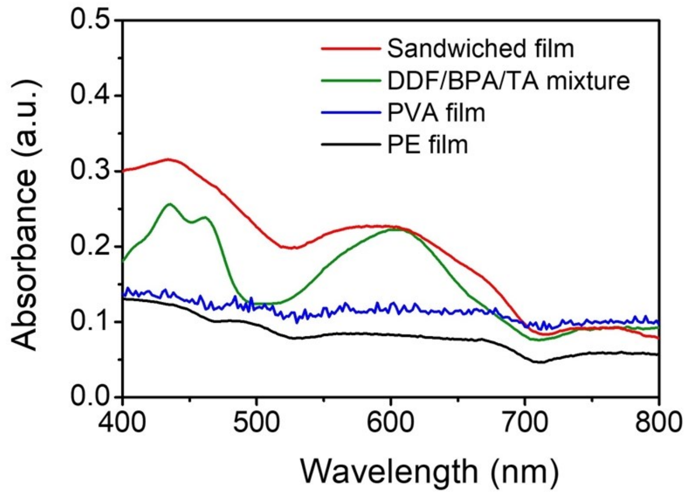

Fig. S3 UV-vis absorption spectra recorded from the DDF-BPA-TA mixture, the sandwiched film, PVA film, and PE film, respectively.

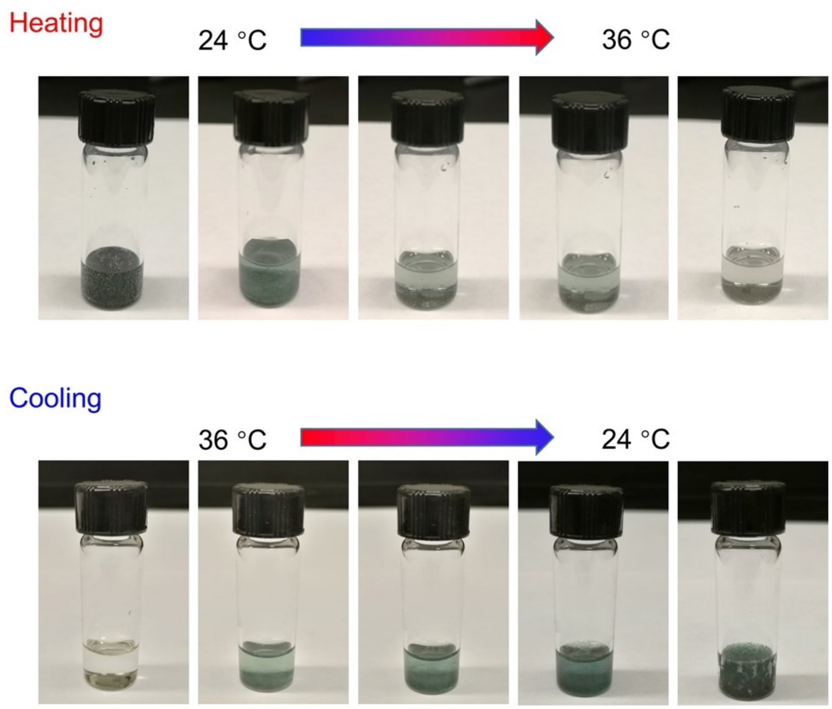

Fig. S4 Digital photographs of the DDF-BPA-TA mixture during the heating from 24 to 36 °C and cooling from 36 to 24 °C. The color of the mixture faded as the temperature was increased, resulting in a colorless solution at 36 °C. Recovery of the color was observed when the temperature was cooled down to 24 °C.

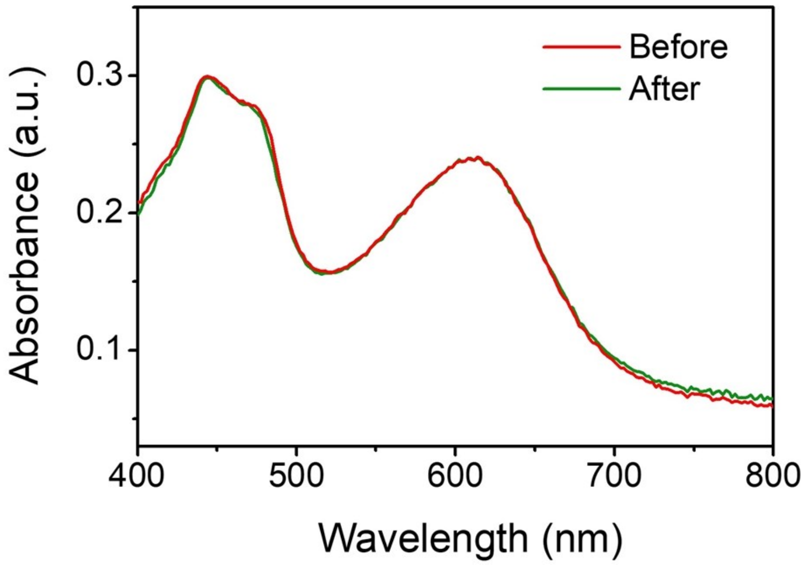

Fig. S5 UV-vis absorption spectra recorded from a sandwiched photo-thermochromic film before and after ten rounds of heating and cooling between 24 and 36 °C.

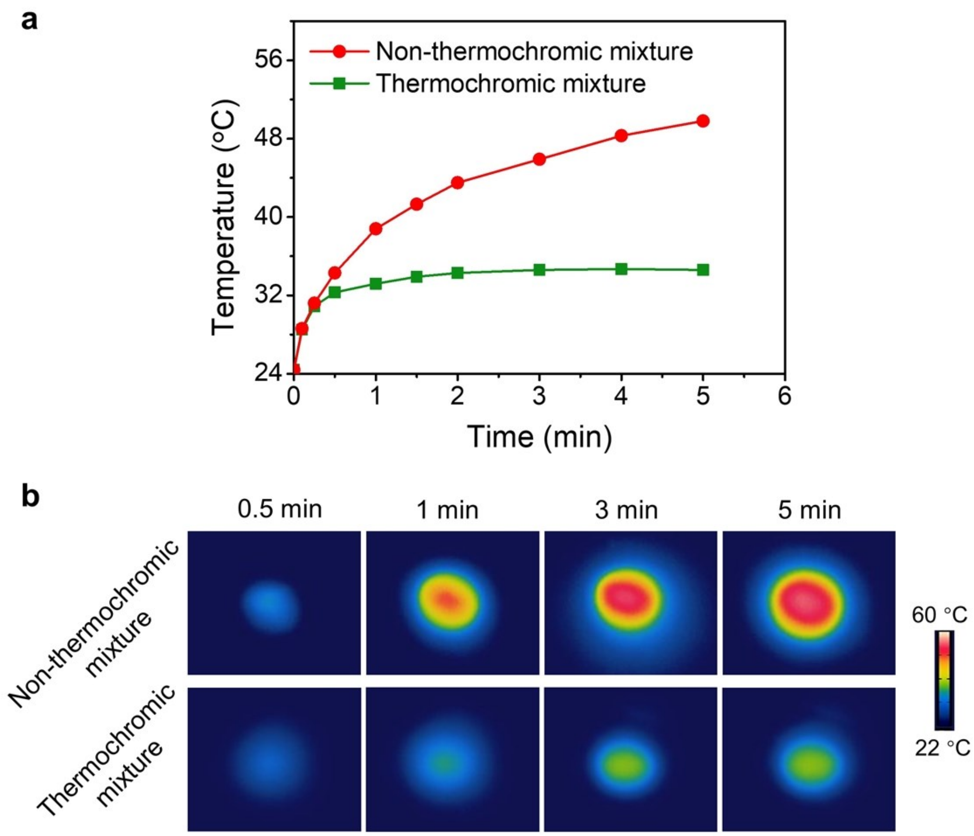

Fig. S6 a) Temperature increase of the DDF-BPA-TA (thermochromic) and DDF-BPA-LA (non-thermochromic) mixtures upon irradiation with the 660-nm laser at an irradiance of 0.4 W/cm^2, respectively. b) IR-camera images showing the rise in temperature for the thermochromic and non-thermochromic mixtures upon irradiation by the laser at an irradiance of 0.4 W/cm^2. Note that a plateau in temperature (around 34 °C) was achieved for the thermochromic mixture, in marked contrast to the non-thermochromic control, which showed continuous increase in temperature up to 52 °C during the laser irradiation.

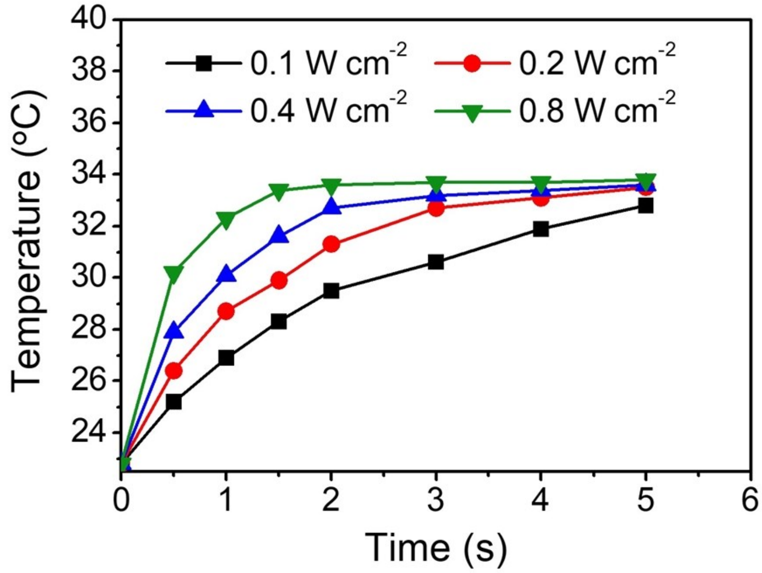

Fig. S7 Temperature increase when the sandwiched film (containing 32.2 wt.% for the photo-thermochromic mixture) was exposed to the laser at different irradiations of 0.1, 0.2, 0.4, and 0.8 W/cm^2, respectively, for up to 5 s. The temperature increased more rapidly when the irradiance was increased.

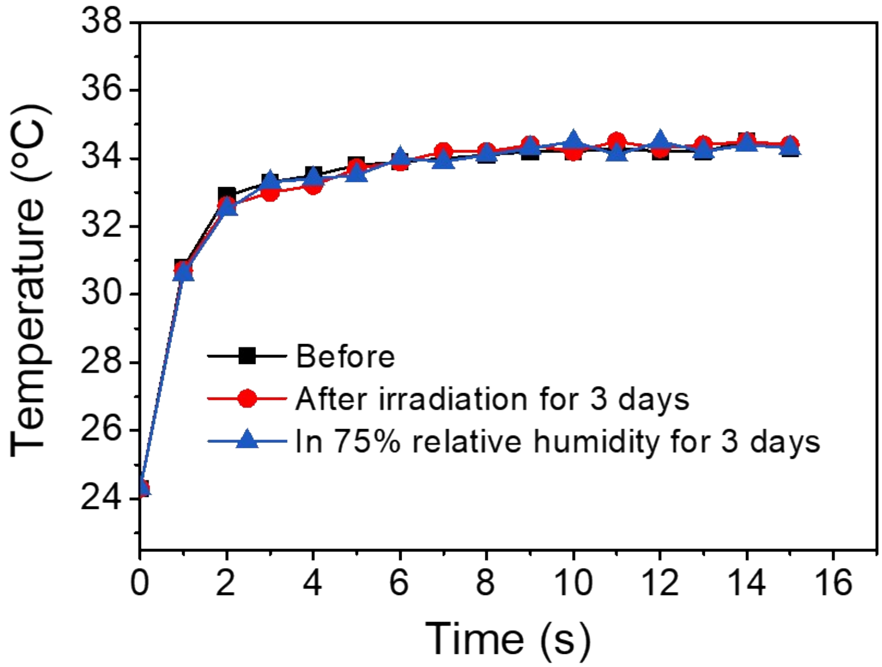

Fig. S8 Temperature elevation of the sandwiched photo-thermochromic film (containing 38.7 wt.% for the mixture) after irradiation of the sunlight for 3 continuous 3 days or storage in 75% relative humidity for 3 days. The films were irradiated at a laser density of 0.2 W/cm^2.

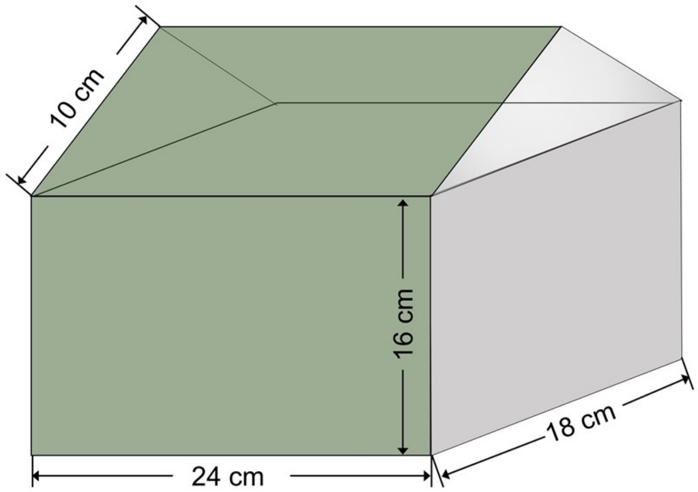

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Fig. S8 Schematic illustration showing the dimensions of the home-made building model used for indoor temperature measurements.

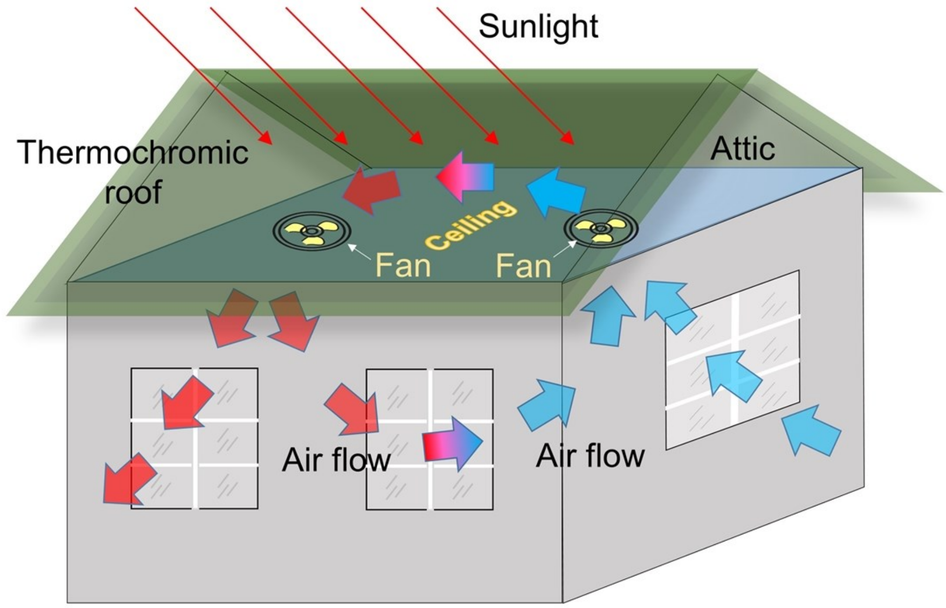

Fig. S9 Schematic illustration showing how the smart coating can be applied to a building with an attic that is common in the US. In cold weather, the fans on the ceiling are turned on to ensure cross-ventilation and heat diffusion. In hot climate, the fans are turned off to prevent heat diffusion between the attic and the main floor.