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Solar harvesting and energy generating building skins with photothermal–photovoltaic dual-modality based on porphyrin thin films

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Abstract

In solar harvesting for energy sustainability, the porphyrin compounds have been found to exhibit both photovoltaic (PV) and photothermal (PT) effects due to their unique structures and properties. Porphyrin compounds are structurally characterized by a large ring molecule consisting of four pyrroles, denoted as the porphyrin ring. The optical properties of these compounds typically exhibit strong absorption near the UV and NIR regions. The nanoscale thin films of porphyrins have been achieved to be highly transparent with a high average visible transmittance. The porphyrin compounds are well known for making dye-sensitized solar cells (DSSC), bulk-heterojunction solar cells (BHJSC), and perovskite solar cells (PSC). Some of the porphyrin compounds have been shown to exhibit strong photothermal effects. With specially designed porphyrin films, solar light can be spectral-selectively harvested and converted to electricity (PV) or thermal energy (PT). In this study, transparent porphyrin thin films of chlorophyllin, phthalocyanine, and their hybrids are synthesized for developing a unique multifunctional building skin design capable of solar harvesting and energy generation based on a PT–PV dual-modality mechanism. The porphyrin film is deposited on the outer pane for photothermal heating to reduce the heat loss; the DSSC on the inner pane harvests the solar light for electricity generation. Further, the $Fe_3O_4@Cu_{2-X}S$ film is also deposited on the outer pane to remove the IR portion to reduce the PV surface temperature so that the power conversion efficiency (PCE) is enhanced. We report the experimental results on the synthesis and characterization of the porphyrin films for energy-efficient building skin application. Also discussed are the synergistic mechanisms of solar harvesting, wavelength segregation, and energy generation via the PT–PV dual-modality system.

Introduction

To meet the mission of net-zero by 2050, declared at COP26, energy-efficient building skin will play a critical role in achieving systems that are energy neutral, zero emission, and climate positive since a major energy consumption is through buildings especially in densely populated megacities. The U.S. consumes about 30 percent of building heating and cooling energy, representing an annual impact of 1.1 quadrillion British thermal unit (BTU) of primary energy.[1] A modern building skin is no longer a conventional barrier to shield from environmental disturbances but a multifunctional layer, from interior to exterior, not only architecturally designed to exhibit the cultural and esthetic characteristics, but also structurally engineered to be the overall technological component of high rises, façades, skylights, walkways, and glass box extensions. In recent years, the energy efficiency of buildings has been the most critical issue in architectural design for sustainability. Great challenges remain, however, in terms of heat loss, energy efficiency, and lighting requirements. Although various glazing and coating technologies have been developed, including low-emissivity coating and double/triple panes, the huge consumption of energy will not be resolved until fundamentally different new concepts and engineering innovations are developed.

A major challenge in energy saving is inefficient thermal insulation, especially for large-surface area high-rise public buildings in cold climates. The conventional approach mainly relies on optimization of the thermal insulation but is severely hindered by the conflicting intrinsic material properties (i.e., thermal insulation vs. transparency). The current technology for efficient windows is typically based upon the double-pane insulated glass unit (IGU) with a low-emissivity coating. Heat loss is characterized by the so-called U-factor, which is defined as a measure of thermal transmittance through conduction, convection, and radiation.[2] The U-factor is quantitatively measured by the ratio of the heat flux H per unit area through the pane to the temperature difference ΔT between its interior and exterior, or the heat energy transferred per unit of time and per unit of surface area divided by the temperature gradient, which is the temperature difference divided by the distance between the two surfaces (the thickness of the material), expressed in watts per kelvin per meter. Lower U factor implies an improved thermal insulation. The U-factor is currently only improved by the double-pane IGU, which ultimately limits further improvement via means of limited insulators (transparent gases). This key challenge can be addressed by an entirely different thermal insulation mechanism via optical means without relying on any conventional glazing technologies.

In our previous works, we developed a novel concept of Optical Thermal Insulation (OTI) without relying on thermal intervention medium, such as air or argon, as often used in conventional window glazing.[3] With a spectral selective thin film coating, the single pane can preferentially absorb sunlight in the UV and NIR regions but permit high average visible transmittance (AVT). The UV and NIR absorptions are converted to heat via the pronounced photothermal (PT) effect of the coating that effectively increases the single-pane surface temperature. Under solar irradiation, the temperature difference, ΔT, between the window surface and room interior can be reduced to effectively lower heat transfer through the window, therefore achieving the goal of energy saving without double or triple pane. Our previous research has shown U-factors well below those of single or double panes without photothermal coatings.[3–5] We have demonstrated that the single pane coated with chlorophyll film exhibits both efficient photothermal heating of the window surface and high visible light transmittance, resulting in much lower U-factors.[5] The engineering implications of the photothermally activated single pane show great promise in both energy and materials savings for sustainability.

Although OTI has proved to be effective in lowering the U-factor of single pane that is comparable to double pane, other issues need to be addressed for different seasons in a cold climate. While the OTI concept can be well applied to the winter season in a cold climate with the photothermally heated windows, the warm windows in the summer may increase the energy consumption of air conditioning. We have therefore developed a new concept of photothermal (PT)–photovoltaic (PV) dual-modality building skin that can be seasonably altered for the most efficient solar harvest and energy generation.[6] In this design, the building skin is no longer a passive thermal insulator but an active energy device. The smart building skin with PT–PV dual modality is not only optically insulating for reduced heat loss in the winter but also performs as a PV panel for producing electricity all year round. Furthermore, the IR portion of the sunlight is removed (absorbed) by the PT layer, so the PV efficiency can be enhanced due to reduced surface temperature under prolonged solar irradiation.

The PT–PV dual-modality structure is schematically illustrated in Fig. 1. As shown in this figure, the PT–PV dual modality is developed on the double-pane structure with the spectral selective PT coating on the outer pane and the PV on the inner pane (both coatings are applied on the inner sides of the double pane). The PT and PV coatings are developed with several key characteristics: (1) both coating films are highly transparent in the visible range for window applications; (2) the PT coating on the outer pane can spectral selectively absorb solar light in the UV and IR regions, which are converted to thermal energy in the winter for lowering the U-factor, according to the optical thermal insulation principle, and (3) a porphyrin-based dye-sensitized photovoltaic cell (DSSC) is deposited on the inter pane for producing electricity all year round. The dual modality can be switched easily depending upon the seasonal changes.

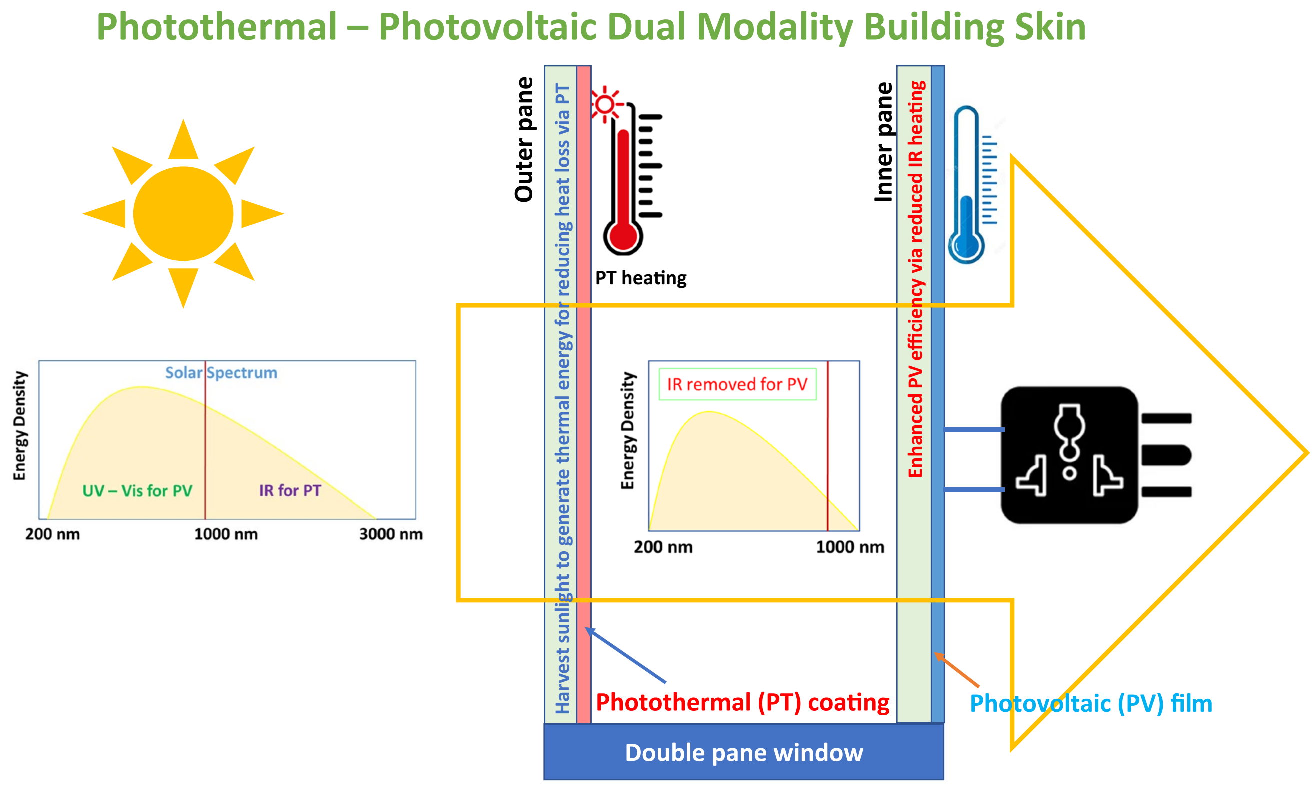

Figure 1. Schematic diagram of PT–PV dual-modality structure for double-pane windows.

Most importantly, the IR portion of the solar light can be filtered by the outer pane PT film to reduce the heating on the DSSC. As is well known, PVs suffer from the temperature dependence of the power conversion efficiency (PCE).[7] On an average, the temperature coefficient of 0.25% per °C means that for every 1°C temperature change above 25°C (hotter), the PV panel loses 0.25% of its voltage. In this dual-modality design, the PT coating is to absorb a large fraction of IR from the solar light, which will effectively reduce the heating of PV panels. The outer PT film can therefore serve two purposes: (1) photothermally heating up the window surface to lower the U-factor in winter; and (2) absorbing most of the IR to reduce heating on the DSSC, which is deposited on the inner layer.

As described above, the PT–PV dual modality operates in the following fashion: in the wintertime, the heat loss is the major issue; therefore, the PT film on the outer pane photothermally increases the window surface temperature to reduce U-factor. Under this condition, the PT–PV modality building skin (Fig. 1) operates mainly in the optical thermal insulation mode. In the summertime, since the exterior temperature is higher than the interior room temperature, the PV on the inner pane is the main device to generate electricity. Meanwhile, the PT film can remove some IR portion of the solar light to reduce the surface temperature of PV for enhanced PCE. In this way, the PT–PV dual-modality building skin fully utilizes IR from solar light for two purposes: 1) heating the outer pane in the winter for reducing heat loss and 2) removing IR in the summer to lower the PV temperature on the inner pane. Note that the PV on the inner pane functions all year round, however, its efficiency may depend on the incident angle and intensity of solar light.[8]

This study focuses on the fundamental studies of the PT and PV materials with spectral selective spectra for the most efficient photon-to-heat and photon-to-electricity conversions based on highly transparent porphyrin thin films. The operating physical mechanisms governing the PT conversions are identified for several systems, including $Fe_3O_4@Cu_{2-X}S$, Chlorophyllin, Phthalocyanine, and Chlorophyllin:Phthalocyanine hybrids.

Experimental section

Material synthesis

The chemicals of this research include Iron (III) acetylacetonate ($Fe(acac)_3$, ≥99.9%), copper (II) acetylacetonate ($Cu(acac)_2$, ≥99.9%), oleylamine (70%), sulfur (99.998%), N-methyl-2-pyrrolidone (NMP, 99.5%), chloroform (≥99.9%), tetrahydrofuran (THF, ≥99.9%), polyethylene glycol (PEG, Mw = 6000), titanium (IV) isopropoxide (TIP, 97%), ethylene glycol (≥99%), titanium(IV) chloride (≥99%), copper chlorophyllin, titanium chloride ($TiCl_4$, ≥99%) (Sigma-Aldrich), Cyclohexane (Tedia Inc), Titanium (IV) oxide (Aeroxide P25) (ACROS organics), Citric acid monohydrate (Fisher Scientific), Iodolyte AN-50 (Solaronix), [5-[Bis(4-hexylphenyl)amino]-15-[2-(4-carboxyphenyl)ethynyl]-10,20-bis(3,5-di-tert-butylphenyl)porphyrinato]zinc(II) (YD2, >97%), copper (II) phthalocyanine (β form) (Phthalocyanine, >93%) (Tokyo Chemical Industry Co., Ltd.), and 2.2 mm 7–8 Ohm/Sq FTO TEC 7 fluorine-doped SnO_2 (FTO) glasses (MSE supplies).

The synthesis of $Fe_3O_4@Cu_{2-X}S$ nanoparticles was carried out by following a modified procedure from the literature.[3] Specifically, the amount of oleylamine was heated to 300°C and stirred for 30 min in a nitrogen environment to remove residual water and oxygen. Subsequently, a mixture containing 0.5 mmol $Fe(acac)_3$ in oleylamine/NMP (3:2, v/v) was injected into pre-heated oleylamine to form Mixture A. Then Mixture A was stirred at 300°C for 10 min, and then cooled down to 70°C. In the meantime, Mixture B containing 1 mmol of sulfur in oleylamine/cyclohexane (6:5, v/v) was prepared and injected into Mixture A to form Mixture C, which was kept at 70°C for 10 min. Mixture D containing 0.5 mmol $Cu(acac)_2$ in oleylamine/chloroform (1:4, v/v) was injected into Mixture C to form the final mixture. The final mixture was stirred at 70°C for 30 min and then cooled to room temperature. $Fe_3O_4@Cu_{2-X}S$ nanoparticles were collected by a strong magnet and washed with methanol, and then freeze-dried overnight. After drying, $Fe_3O_4@Cu_{2-X}S$ nanoparticles were dispersed in THF for later use.

The TiO_2 paste was synthesized based on a modified procedure from the literature.[9] Briefly, 1.5 g of ethylene glycol was heated to 60°C in a beaker. Subsequently, 0.284 g of TIP was added and stirred to form a uniform mixture. Finally, 1.260 g of citric acid was added, and then the temperature was increased to 90°C. When the solution turned clear, 0.56 g of P25 was added into the clear solution and mixed in a mortar grinder to form a TiO_2 paste.

DSSC architecture and fabrication

The structure of DSSC is schematically illustrated in Fig. 2(a). As shown in the figure, the DSSC consists of a photoanode, dyes, electrolyte, and counter electrode. The substrate for the DSSC is a transparent conductive oxide (TCO) glass, made of fluorine-doped tin dioxide (FTO). Metal oxide TiO_2 is often used for making photoanode of DSSC, to transport the electrons, which is also called the electron transport layer. Electrolyte is an essential mediator between the photoanode and counter electrode in DSSC. Electrolyte regenerates the dye sensitizer from an oxidized state back to a ground (steady) state by gaining electrons from redox mediator. Photosensitizer plays a critical role in DSSC in producing the photon-induced electrons and injecting the electrons into the conduction band of the photoanode. In this study, the porphyrin compound YD2 was used as the dye for DSSC.

The YD2 dye solution (0.2 mM) was prepared in ethanol. The TiO_2 layer was deposited by using the doctor balding technique on FTO glass. FTO substrates were ultrasonically cleaned with acetone and isopropyl alcohol (IPA) before use. The TiO_2 layer was dried at 60°C for 30 min and then sintered at 500°C for 30 min to form a photoelectrode on FTO glass. Subsequently, the photoelectrode was immersed in a 40 mM $TiCl_4$ solution for 30 min at 70°C in an oven, followed by calcination

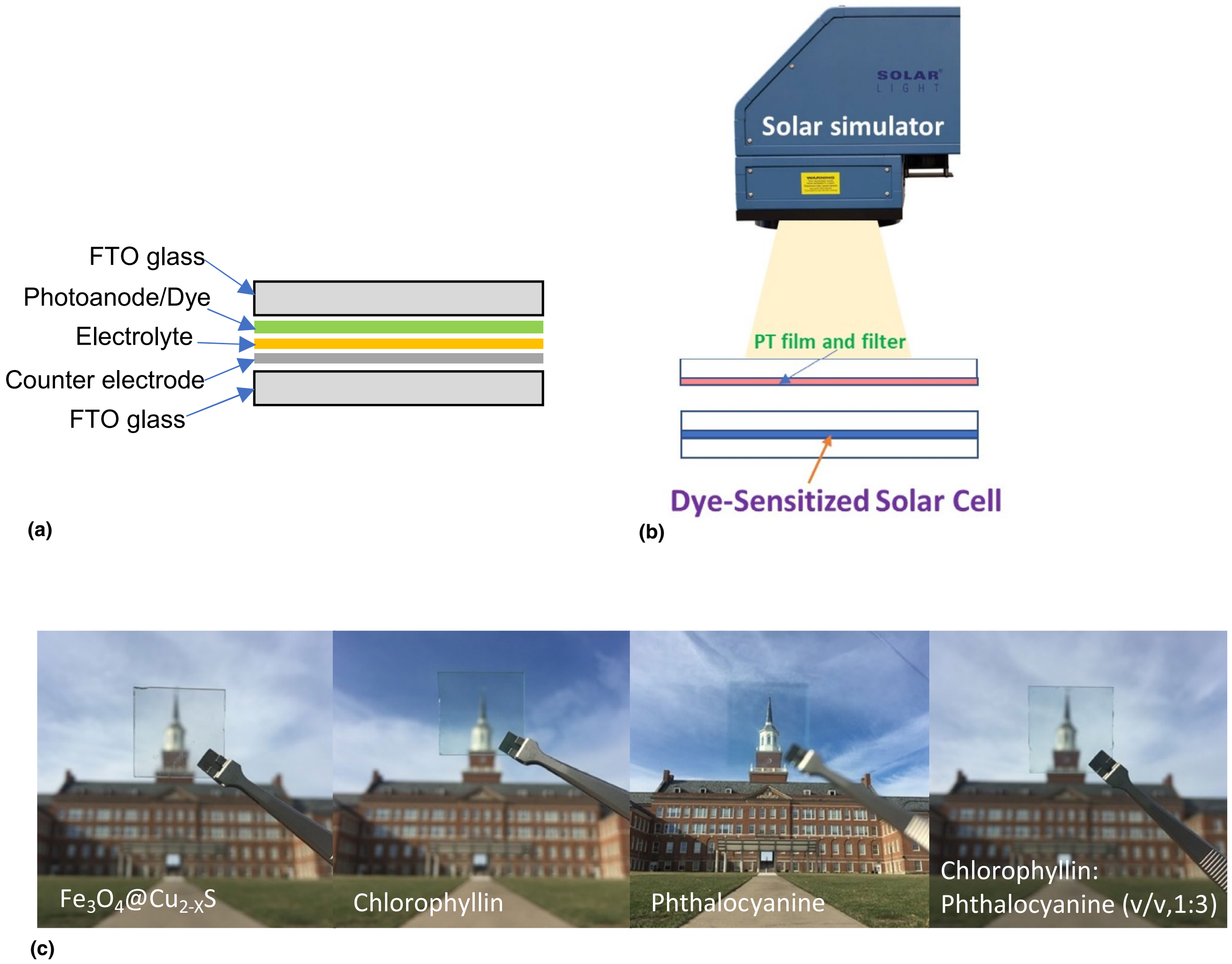

Figure 2. Schematic diagram of (a) DSSC cross-sectional structure and (b) experimental setup. (c) Optical photographs of $Fe_3O_4@Cu_{2-X}S$, chlorophyllin, phthalocyanine, and chlorophyllin:phthalocyanine (v/v,1:3) thin films in front of University of Cincinnati building showing high transparency of PT films.

at 570°C for 30 min. After $TiCl_4$ treatment, the resulting photoelectrode was immersed in a dye solution for 20 h. The counter electrode was prepared by spin coating an H_2PtCl_6 solution in isopropyl (1 wt.%) onto FTO glass and then sintered with the film at 450°C for 30 min. The solution was spin coated on FTO glass substrates for 30 s at 4000 rpm. Each glass slide was coated with 10 µl solution. To fabricate a DSSC device, the photoanode (TiO_2 on FTO glass) and cathode (Pt on FTO glass) were clamped together. Finally, an electrolyte solution was injected into the photoanode and cathode.

Photothermal film and light filter preparation

To prepare the PT thin film samples, $5 \times 5 \times 0.25$ cm^3 glasses were ultrasonicated in acetone for 15 min and in isopropyl alcohol for another 15 min; the cleaned substrates were then dried by compressed air. Solutions with various concentrations of chlorophyllin, phthalocyanine, and $Fe_3O_4@Cu_{2-X}S$ were compounded with a fixed amount of PEG in THF. 10 wt.% PEG solution was applied to every thin films.[10] The thin films were deposited on glass substrates by spin coating at 3000 rpm for 20 s. Each glass substrate was coated with 400 µL of solution, which contained 200 µL of photothermal materials and 200 µL of 10 wt.% PEG in THF.

Characterization

For current–voltage (I–V) characteristic and photothermal experiments, the samples were irradiated by simulated solar light (0.1 W/cm^2) using the Newport 150 W solar simulator (Lamp model 67,005) with a Xenon Lamp power supply (AM 1.5). The light power density of solar simulator was calibrated by an optical power meter (Newport, 1919-R). The active area of the DSSC was 1 cm^2. Current–voltage characteristics (I–V curves) of DSSCs were measured by using a Keithley 2400 source (Keithley Instruments, Inc., Cleveland, OH, USA). The temperature was recorded by a thermocouple (K type). The absorption and transmittance spectra were characterized by UV–VIS–NIR spectrometer (Lambda 900, PerkinElmer Inc.), and average visible transmittance (AVT) was measured by light transmittance meter LS116 (Linshang, Co. Ltd.).

Results and Discussion

As shown in Fig. 1, the PT coating on the outer pane can absorb the sunlight for two functions: 1) convert the UV and IR to photothermally heat up the surface temperature, which can effectively lower the U-factor of the outer pane; and 2) remove the IR portion from sunlight to reduce the heating on the PV on the inner pane, which can enhance power conversion efficiency (PCE). Obviously, all substrates and coatings must be transparent with high AVTs for building skin application. Following this strategy, an experimental apparatus was set up to characterize the PT and PV dual-modality system, as shown in Fig. 2(b). As shown in this figure, several substrates are positioned in parallel to simulate the double pane (Fig. 1). The PT film is coated on the lower surface of the top glass substrate while the DSSC is deposited between two FTO substrates. The air gap between the photothermal film and the top surface of DSSC is set at 1 cm. The surface temperatures of PT and DSSC were measured and recorded by using a thermal couple. Figure 2(c) shows the optical photographs of PT films with high visible transparency.

Figure 3(a)–(e) shows the absorption spectra of the chlorophyllin [Fig. 3(a)], phthalocyanine [Fig. 3(b)], YD2 [Fig. 3(c)], $Fe_3O_4@Cu_{2-X}S$ [Fig. 3(d)], and Chlorophyllin:Phthalocyanine (C:P) hybrid with 1:3 (v/v) ratio [Fig. 3(e)] solutions with the same concentration (0.01 mg/ml). Note that chlorophyllin is dissolved in water, phthalocyanine in THF, YD2 in ethanol, and $Fe_3O_4@Cu_{2-X}S$ in toluene. Following a procedure described in previous work,[10] a hybrid solution of Chlorophyllin:Phthalocyanine with a 1:3 (v/v) ratio was deposited on a glass substrate by spin coating.

As shown in Fig. 3(a) and (b), chlorophyllin is typically characterized by peaks at 402 nm and 647 nm, while phthalocyanine exhibits peaks at 350 nm, 638 nm, and 730 nm. Since chlorophyllin, phthalocyanine, and YD2 are all porphyrin compounds, they show two characteristic absorption peaks in the region of 380–500 nm (B band) and 500–750 nm (Q band). Notably, both chlorophyllin and YD2 exhibit very similar absorption spectra with a strong sharp peak at around 400 nm and a small peak between 600 and 700 nm. Due to almost the identical absorption spectra, both chlorophyllin and YD2 show green color. Chlorophyllin:Phthalocyanine is similar to that of Phthalocyanine but with increased intensities at the UV and NIR peaks.

Porphyrins, their derivatives, and hybrids have been found to exhibit fascinating properties for a variety of applications such as PVs, diodes, rectifiers, and capacitors.[6] The porphyrins can be structurally altered to exhibit electro-photonic properties that are much different from the original homogeneous solutions and films, in particular the optical absorptions. The photonic behaviors of porphyrins can be tuned by chelation of a metal ion and substitution on the macrocycle which modifies their band gaps due to structural modulations.[6]

The band gap energy can be obtained by absorption spectra and estimated by using the Tauc equation[11]:

$$(\alpha hv)^{\gamma} = A\left(hv - E_g\right),$$

where α is the absorption coefficient, h is Planck's constant, v is the photon's frequency, γ is the nature of the electronic transition, A is the proportionality constant, and E_g is the band gap energy (eV).

The band gap energy is obtained from the first peak in the visible region. From the Tauc plots,[11] as shown in Fig. 3(f)–(j), the estimated direct band gap energies of chlorophyllin [Fig. 3(f)] and phthalocyanine [Fig. 3(g)] are 1.89 eV and 1.7 eV, respectively. In the same approach, the direct band gap energy of YD2 [Fig. 3(h)] is determined to be 1.83 eV. As shown in Fig. 3(i), the band gap of $Fe_3O_4@Cu_{2-X}S$ is 2.63 eV, which is in agreement with the published results.[8] The band gap of the chlorophyllin:phthalocyanine hybrid is slightly modified to 1.61 eV in comparison to that of phthalocyanine (Eg = 1.7 eV), as shown in Fig. 3(j). The band gap energy of the anatase phase TiO_2 is 3.2 eV[12,13] and that of the rutile phase TiO_2 is 3.0 eV.[13]

The X-ray diffraction patterns of TiO_2 photoelectrode with $TiCl_4$ post treatment are shown in Fig. 4(a). The pronounced diffraction peaks at 2 θ = 25.304°, 37.793°, 48.036°, 62.684°, and 68.755° can be assigned to (101), (004), (200), (204), and (116) planes of the anatase structure [98-000-0081]. In addition, the peaks at 2 θ = 27.440°, 36.079°, 41.240°, and 54.324° can be assigned to (110), (101), (111), and (211) planes of the rutile structure [98-000-0375]. They are the experimental evidence that the post treatment resulted in the anatase/rutile mixed phase in TiO_2 photoanode for DSSC.[14]

Figure 4(b) and (c) shows SEM images of TiO_2 photoanode with $TiCl_4$ post treatment. As shown in the figure, the thickness of the FTO film on the glass is about 700 nm and that of the photoanode is 7.6 µm. As can also be seen from the figure, the photoanode has a porous microstructure, which creates more surface area for absorbing the photosensitizer (dye). Intimate electrical contacts can be created between the TiO_2 nanoparticles with the $TiCl_4$ post treatment, leading to enhanced short-circuit current (I_{SC}).[15]

From the schematic diagram of Fig. 2(b), one can see that the simulated solar light passes through the top substrate first. Various PT coatings on the top substrate can absorb the simulated solar light in the UV and IR regions for photothermal heating. Figure 4(d) shows the heating curves of chlorophyllin, phthalocyanine, hybrid, and $Fe_3O_4@Cu_{2-X}S$ thin films. As can be seen from this figure, all four films can be photothermally heated to raise the surface temperature rather rapidly, among which the maximum temperature of the porphyrin hybrid can reach as high as 33.6 ºC. The temperature profiles

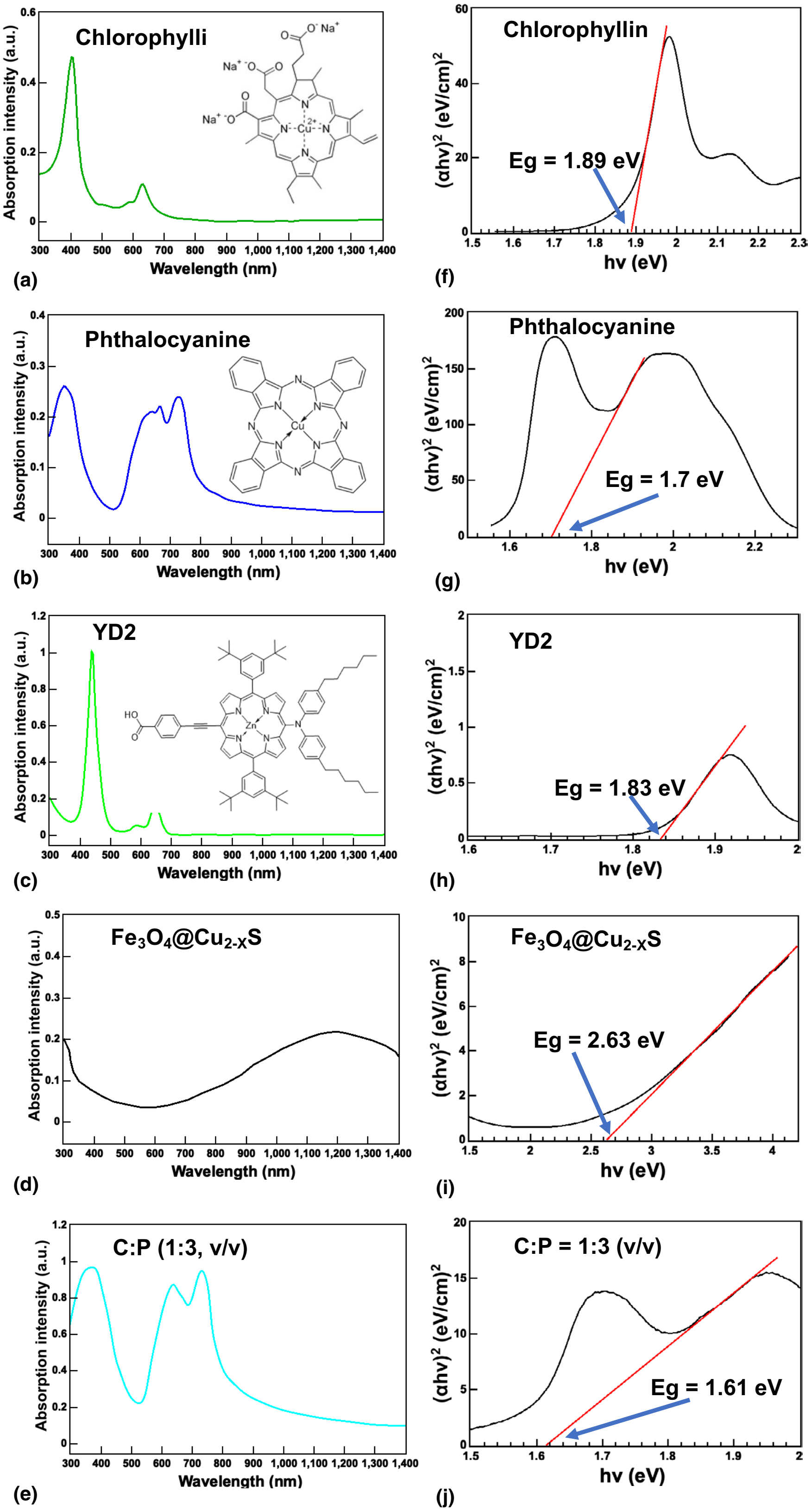

Figure 3. UV–Vis absorption spectra of solutions of (a) chlorophyllin, (b) phthalocyanine, (c) YD2, (d) $Fe_3O_4@Cu_{2-X}S$, and (e) chlorophyllin:phthalocyanine (C:P) with 1:3 (v/v) ratio. All solutions are the same concentration (0.01 mg/ml). The insets show the molecular structures of chlorophyllin, phthalocyanine, and YD2. Extrapolation of the Tauc plot for band gap calculations of (f) chlorophyllin, (g) phthalocyanine, (h) YD2, (i) $Fe_3O_4@Cu_{2-X}S$, and (j) hybrid of chlorophyllin:phthalocyanine with 1:3 ratio. The intercept of the red solid line with the x-axis determines the direct band gap energy of each material as indicated.

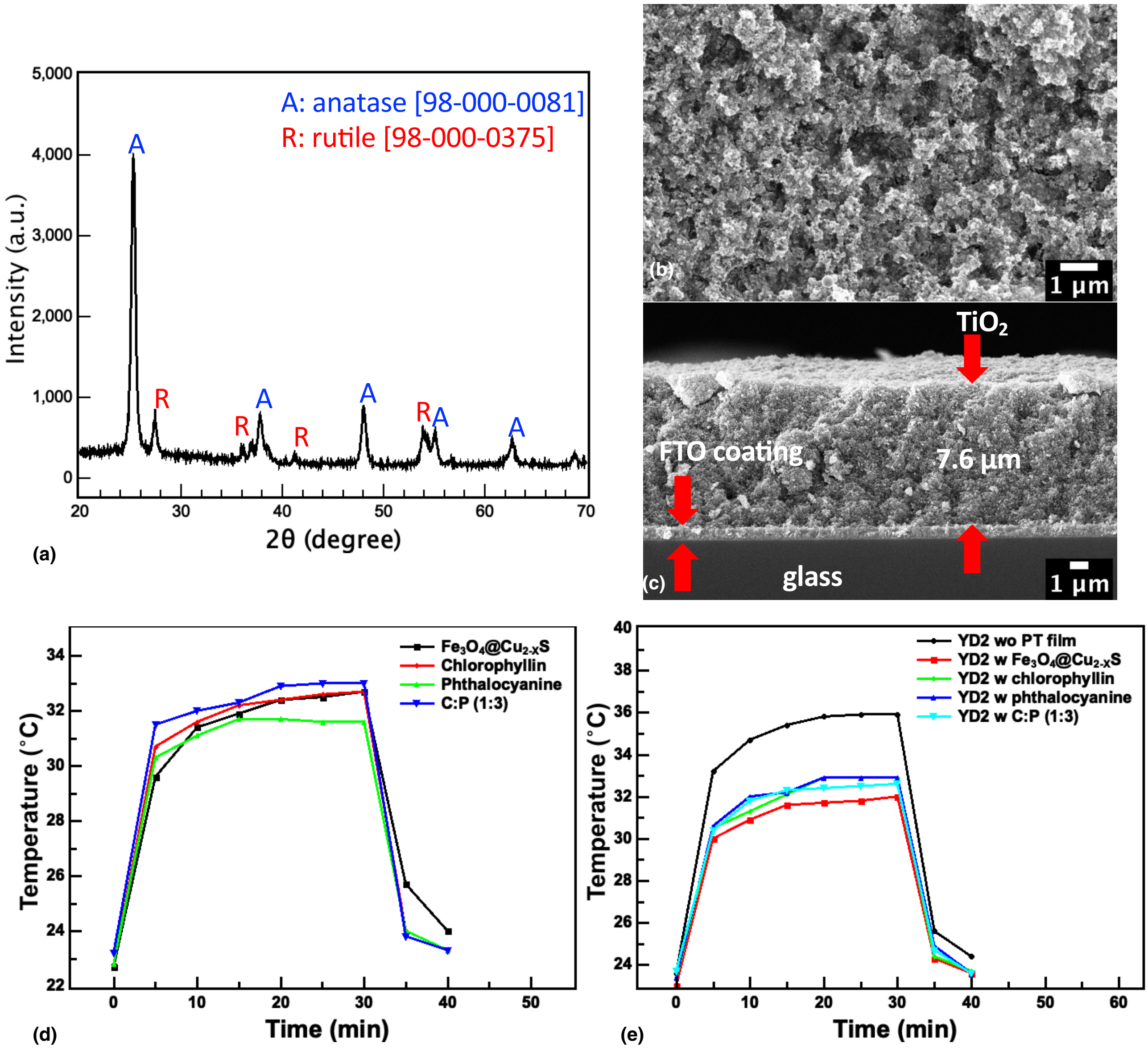

Figure 4. (a) XRD pattern of TiO_2 photoanode with $TiCl_4$ post treatment. SEM images of (b) the surface morphology and (c) the cross section of TiO_2 photoanode with $TiCl_4$ post-treatment film. (d) Heating curves of chlorophyllin, phthalocyanine, hybrid, and $Fe_3O_4@Cu_{2-X}S$ thin films. (e) DSSC-YD2 surface temperatures as function of time with different solar light filters as indicated.

of other films are quite comparable. As shown in our previous studies,[3] photothermal heating can effectively reduce the thermal loss of the window in the winter, as characterized by the low U-factors which are to be calculated in the following session.

Furthermore, these PT coatings also function as light filters (or wavelength segregators) to selectively remove the IR portion to reduce the DSSC surface temperature on the bottom layer [Fig. 2(b)]. Figure 4(e) shows the DSSC-YD2 top surface temperature as a function of time for various PT films coated on the top substrate [Fig. 2(b)]. As shown in Fig. 4(e), without the PT film light filter, the top surface temperature of DSSC-YD2 increases rapidly, approaching a maximum at 36.0 °C. However, with the PT film of $Fe_3O_4@Cu_{2-X}S$, the temperature is reduced to 32.0°C (red curve) due to the significant removal of IR [Fig. 4(e)]. Chlorophyllin, phthalocyanine, and their hybrids also reduce the temperature as shown in Fig. 4(e), but to lesser degrees for they do not have significant IR absorptions (Fig. 3).

Power conversion efficiency, photothermal efficiency, and U factor

The power conversion efficiency (PCE) of the DSSC is calculated by using the following equation[16]:

$$\mathrm{PCE} = \frac{P_{\mathrm{Max}}}{P_{\mathrm{in}}} = \frac{I_{\mathrm{SC}} \times V_{\mathrm{OC}} \times \mathrm{F.F.}}{P_{\mathrm{in}}} \times 100\%, \qquad (1)$$

where PCE is power conversion efficiency (%), P_{Max} is the maximum power (W), P_{in} is the incident light intensity (W), I_{SC} is the short-circuit current (A), V_{OC} is the open-circuit voltage (V), and F.F. is the fill factor.

Open circuit voltage (V_{OC}), short-circuit current (I_{SC}), voltage at maximum power point (V_{MP}), and current at maximum power point (I_{MP}) can be obtained from the I–V curves. The maximum power (P_{Max}) and power conversion efficiency (PCE) can be calculated by Eq. 1. We found that the DSSC-YD2 can convert sunlight to electricity with reasonable *PCEs* under the conditions depicted in Fig. 2(b), although varied with different PT films (or solar light filters). The PCE of DSSC-YD2 without a solar light filter is 4.57%; the PCE of DSSC-YD2 with $\mathrm{Fe_3O_4@Cu_{2-X}S}$ film as a solar light filter is 5.06%; the PCE of DSSC-YD2 with chlorophyllin film as a solar light filter is 2.95%; the PCE of DSSC-YD2 with phthalocyanine film as a solar light filter is 3.34%; and DSSC-YD2 with chlorphyllin:phthalocyanine hybrid film as a solar light filter is 3.31%. These results demonstrate the viability of the PT–PV dual-modality building skin. We can see that the PCE of DSSC-YD2 without a solar light filter is 4.57%, and it increases to 5.06% with the $\mathrm{Fe_3O_4@Cu_{2-X}S}$ film as a solar light filter, which is the highest as compared to those with the porphyrin-based films. The PCEs of DSSC-YD2 are consistent with the data shown in Fig. 4(e) that the $\mathrm{Fe_3O_4@Cu_{2-X}S}$ film can remove a large IR portion from sunlight, resulting in a significantly reduced PV surface temperature due to its UV–Vis characteristic [Fig. 3(d)].

The photothermal efficiency (η_{PT}) is defined as the ratio of the thermal energy generated by the sample to the incident photon energy. The photothermal efficiency for solar light was given by[17]

$$\eta_{\mathrm{PT}} = \frac{\left(C_{\mathrm{glass}} m_{\mathrm{glass}} + C_{\mathrm{PT\ material}} m_{\mathrm{PT\ material}} + C_{\mathrm{polymer}} m_{\mathrm{polymer}}\right)\Delta T_{\mathrm{max}}}{IA\Delta t} \qquad (2)$$

and since the mass of PT material and polymer is much lower than the glass substrate, the equation can be expressed as following[3]:

$$\eta_{\mathrm{PT}} \approx \frac{C_{\mathrm{glass}} m_{\mathrm{glass}} \Delta T_{\mathrm{max}}}{IA\Delta t}, \qquad (3)$$

where c is the specific heat capacity (J/g°C), m is mass (g), ΔT_{max} is the maximum change in temperature increase of the sample (°C), I is the incident light power density ($\mathrm{W/cm^2}$), A is the surface area of the sample, and Δt is the time for sample to achieve the maximum temperature (sec). In this research, the specific heat of glass is 0.84 J/g·°C, and the surface area of substrate is $5 \times 5\ \mathrm{cm^2}$.

The U factor is related to thermal transmittance, indicating the National Fenestration Rating's (NFRC) insulation ability standard for window manufacturers.[18] It refers to the window assembly's energy efficiency. A lower U-factor indicates better thermal insulation. Energy efficiency and sustainable materials for thermal insulators are becoming increasingly important as energy prices rise. The NFRC has published the general specification of the U factor for windows.[18] Even though the U factor requirement varies depending on the climate zone, the maximum U- factor requirement for windows is 1.7 W/m^{2}K. According to ASTM C1199-14,[19] the U factor can be expressed as follows:

$$U = \frac{1}{\frac{1}{h_{\mathrm{h}}} + \frac{1}{h_{\mathrm{c}}} + \frac{1}{U_{\mathrm{L}}}}, \qquad (4)$$

where h_{h} and h_{c} are, respectively, the interior and exterior heat coefficients, and U_{L} is the heat transfer coefficient of the windowpane. For a double-pane window, the U factor can be expressed as follows:

$$\frac{1}{U} = R_{\mathrm{h}} + 2R_{\mathrm{g}} + R_{\mathrm{s}} + R_{\mathrm{c}}, \qquad (5)$$

where R_{h} and R_{c} are $1/h_{\mathrm{h}}$ and $1/h_{\mathrm{c}}$, respectively. R_{g} is the thermal resistance of one of the window glass panes. R_{s} is the net thermal resistance of the gas or air in the gap between the windowpanes.

The photothermal material on the inner surface of the cold-facing pane will result in a net reduction in heat flow out of the window from the room to the exterior environment.

$$\dot{q}_{\mathrm{net}} = \dot{q} - \dot{q}_{\mathrm{Photothermal}}, \qquad (6)$$

where q_{net} is the net heat flow with the photothermal material, q is the heat flow that would occur in the double-pane window without the photothermal included, $q_{photothermal}$ is the reduction in heat flow due to the photothermal heating. Using the definition of U-factor, the net heat flux can be expressed as follows:

$$\dot{q} = (T_{\mathrm{out}} - T_{\mathrm{in}})\, U - \dot{q}_{\mathrm{PT}}\left(R_{\mathrm{o}} + R_{\mathrm{g}}\right)\mathrm{U}, \qquad (7)$$

where T_{in} is the interior room temperature, T_{out} is the exterior environment temperature.

Rearranging Eq. 7,

$$\dot{q} = (T_{\mathrm{out}} - T_{\mathrm{in}})\, U\left[1 - \dot{q}_{\mathrm{PT}}\frac{(R_{\mathrm{o}} + R_{\mathrm{g}})}{(T_{\mathrm{out}} - T_{\mathrm{in}})}\right]. \qquad (8)$$

The photothermal heat generation is given by

$$\dot{q}_{\mathrm{PT}} = \eta_{\mathrm{PT}} I_{\mathrm{Sun}}, \qquad (9)$$

where I is the intensity of solar light at the photothermal film.

Combining Eqs. 8 and 9 and using the definition of thermal resistance, an effective U factor (U_{eff}) for the double-pane window including the photothermal film can be expressed as follows:

$$U_{eff} = U\left[1 - \frac{\eta_{PT} I_{sun}\left(\frac{1}{h_o} + \frac{1}{h_g}\right)}{T_{in} - T_{out}}\right]. \qquad (10)$$

where h_o is 18 W/cm^{2}K and h_g is 306 W/cm^{2}K.[2] U is the U factor of the double-pane window without photothermal film, which is 1.265 W/cm^{2}K. η_{PT} is the photothermal efficiency of the PT film, I_{sun} is the incident light power density (W/cm^2) assumed to be approximately 900 W/m^2, T_{in} is the inside room temperature (°C) assumed to be 21.11°C, and T_{out} is the outside temperature (°C) taken as − 17.78 °C.[2]

The maximum steady temperatures (ΔT_{Max}) for $Fe_3O_4@Cu_{2-X}S$, chlorophyllin, phthalocyanine, and chlorophyllin:phthalocyanine hybrid thin films, respectively, is 9.30 °C, 9.30 °C, 8.80 °C, and 10.40 °C, respectively. The U factors, photothermal conversion efficiency (η), and the effective U factor for a double-pane window with the photothermal film (U_{eff}) were calculated. The outer pane of a double-pane window made of $Fe_3O_4@Cu_{2-X}S$, chlorophyllin, phthalocyanine, and chlorophyllin:phthalocyanine hybrid thin films has U_{eff} values of 1.214 W/m^{2}K, 1.212 W/m^{2}K, 1.214 W/m^{2}K, and 1.207 W/m^{2}K, respectively. We found that the photothermal heating considerably enhances the U factor (U_{eff}). Compared to the U factor without any photothermal heating, the U_{eff} of the photothermally heated windowpane is lowered considerably, all below 1.265 W/m^{2}K, indicating reduced thermal energy loss. Meanwhile, the PT–PV dual modality can also produce electricity via the DSSC on the inner pane. The combined effects of PT and PV will lead to a more energy-efficient building skin.

Conclusions

Based on the design as illustrated in Fig. 1, the PT–PV dual-modality assembly can spectral selectively harvest solar light in the UV and IR regions for both photothermal heating and removal of the IR through transparent porphyrin films. Sunlight is utilized to heat up the outer pane, thus photothermally reducing the thermal energy loss in the winter season. The heating curves from Fig. 4(d) show strong photothermal effects of the porphyrin and $Fe_3O_4@Cu_{2-X}S$ films, which are responsible for the low U factors. More important, due to high AVTs of these PT films, sunlight can mostly reach the DSSC on the inner pane to generate electricity. Since the IR portion is largely removed by the $Fe_3O_4@Cu_{2-X}S$ films, the PV surface temperature is effectively reduced as shown in Fig. 4(e). As a result, the PCE of the porphyrin-based DSSC is enhanced. In this fashion, the porphyrin-based PT and PV films synergistically generate thermal and electrical energy with dual modality.

The experimental results from this study show a proof-of-concept prototype to demonstrate the viability of the PT–PV dual modality for building skin applications. Particularly in building skin applications, the moderate PCEs of DSSCs can be compensated by the large surface areas of the building skin. The PT–PV dual-modality principle provides a fundamental basis for the design of next-generation building skins that are not only capable of energy saving but also energy generation.

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Data availability

Data available in a publicly accessible repository.

Declarations

Conflict of Interest

The authors declare no conflict of interest.

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