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Nanophotonic-Engineered Photothermal Harnessing for Waste Heat Management and Pyroelectric Generation

Xiao-Qiao Wang,[†] Chuan Fu Tan,[†] Kwok Hoe Chan,[†] Kaichen Xu,[†]® Minghui Hong,[†]® Sang-Woo Kim,*^{,‡}® and Ghim Wei Ho*^{,†}®

[†]Department of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, Singapore 117583, Singapore

[‡]School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 440-746, Republic of Korea

Supporting Information

ABSTRACT: At present, there are various limitations to harvesting ambient waste heat which include the lack of economically viable material and innovative design features that can efficiently recover low grade heat for useful energy conversion. In this work, a thermal nanophotonic-pyroelectric (TNPh-pyro) scheme consisting of a metamaterial multilayer and pyroelectric material, which performs synergistic waste heat rejection and photothermal heat-to-electricity conversion, is presented. Unlike any other pyroelectric configuration, this conceptual design deviates from the conventional by deliberately employing back-reflecting NIR to enable waste heat reutilization/recuperation to enhance pyroelectric generation, avoiding excessive solar heat uptake and also retaining high visual transparency of the device. Passive solar reflective cooling up to 4.1



°C is demonstrated. Meanwhile, the photothermal pyroelectric performance capitalizing on the back-reflecting effect shows an open circuit voltage (V_{oc}) and short circuit current (I_{sc}) enhancement of 152 and 146%, respectively. In addition, the designed photoactive component (TiO_2/Cu) within the metamaterial multilayer provides the TNPh-pyro system with an effective air pollutant photodegradation functionality. Finally, proof-of-concept for concurrent photothermal management and enhanced solar pyroelectric generation under a real outdoor environment is demonstrated.

KEYWORDS: photothermal, nanophotonic, solar pyroelectric, daytime passive cooling, waste heat management

lolar heat presents a rich and ubiquitous source of ambient thermal energy, however, exploitation of its indirect low grade waste heat for practical application has always been challenging. Noticeably, the photothermal effect associated with solar heat has recently garnered immense interest in photo/electro-catalysis,¹⁻⁴ steam generation,⁵⁻⁷ energy harvesters,^{8–10} and actuators.^{11–15} In particular, a photothermal pyroelectric material that performs solar heatto-electricity conversion when subjected to temporal thermal fluctuations is especially attractive for pragmatic outdoor application since it does not require a spatially uniform temperature gradient.¹⁶⁻²¹ In addition, the unique combinatorial capabilities of thermo-electric conversion and spontaneous temperature reduction make pyroelectric materials highly desirable for waste heat utilization²² and related passive cooling applications.²³⁻²⁵ To date, a smart material system that performs sustainable solar waste heat rejection for passive cooling and photothermal waste energy utilization for pyro-

electricity generation has not been well-explored and remains a great challenge.

Here, we demonstrate a thermal nanophotonic-pyroelectric (TNPh-pyro) scheme for solar waste heat harnessing to achieve holistic passive reflective cooling, photodegradation, and heat-to-pyroelectricity conversion. One of the main challenges for most solar pyroelectric technology lies in the limited thermal fluctuation harvesting.²⁶ Unlike any other pyroelectric scheme, our design deviates from the conventional by deliberate channeling of the reflected near-infrared (NIR) heat onto pyroelectric material so as to offer a recurring chance of heat propagation (photon recycling),²⁷ resulting in an enhanced solar pyroelectric output. Specifically, a metamaterial is coated on the indoor side to meet the strict cooperative demands for heat reflection, visible transmission, and also UV absorption for

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Figure 1. (a) Schematic of nanophotonic-ferroelectric concept for the TNPh and (b) the deposition pathway that leads to TNPh. (c) Photograph of the TNPh-pyro prototype.

respective cooling, transparency, and photocatalysis, while the pyroelectric film is coated on the other side to harvest the reflected waste heat and solar insolation fluctuation for electric power output. Using the photonic nanostructure approach, flexible tunability in strong suppression of waste heat uptake and nonconflicting enhanced thermal harvesting that operate reliably at ambient outdoor condition can be realized. To this end, an exemplary unified and compact design is proposed for ultimate energy saving, involving natural daytime lighting, passive cooling, and air purification along with solar heat harvesting for pyroelectric generation.

RESULTS AND DISCUSSION

The integrated nanophotonic-ferroelectric scheme used for simultaneous NIR heat reflective, catalytic, and energy harnessing purposes is illustrated in Figure 1a. The thermal nanophotonic (TNPh) structure consists of hybrid metal oxidedielectric metamaterial film with a periodically layered structure. It is constructed by alternate spin-coating or dipcoating of titanium dioxide (TiO₂) and mesoporous silicon dioxide (SiO_2) films, and the topmost layer of mesoporous titanium dioxide/copper (TiO2/Cu) (Figure 1b). A ferroelectric poly(vinylidene difluoride) (PVDF) film is representative as an outdoor solar heat harvester, where direct conversion of thermal fluctuation to electric output occurs via change of spontaneous polarization in response to temperature change. Figure 1c shows the TNPh-pyro film which has high optical transparency and resistance against scratches and is well-suited for smart window and display applications.

Essentially, Figure 2a illustrates the TNPh design of precise composite multilayers that can achieve collective reflection of NIR, transmission of visible and absorption of UV rays for respective passive cooling, lighting, and air purification in addition to intensified waste heat scavenging, which will be discussed later. The alternating layers of high refractive index TiO₂/Cu and low refractive index mesoporous SiO₂ are mainly responsible for the primary NIR reflection, which follows the quarterwave principle.²⁸ The quarterwave layers of successive high and low refractive index materials are periodically stacked to achieve targeted wavelength, λ of maximum reflectivity. The



Figure 2. (a) Three-dimensional schematic of the nanophotonic design for TNPh. (b) SEM image of cross-section of TNPh and (c) surface of mesoporous TiO_2/Cu . (d) TEM image of the mesoporous SiO_2 .

optimal reflectivity for λ at normal incidence can be calculated following the Bragg condition $\lambda = 4n_{\rm h}d_{\rm h} = 4n_{\rm l}d_{\rm b}$ where the $n_{\rm h/l}$ and $d_{\rm h/l}$ are the refractive indexes and thicknesses of the high (h) and low (l) refractive index layers, respectively. Figure 2b shows the cross-section of a periodically layered TNPh with optimized thickness that exhibits a maximal reflectance at 920 nm. Evidently, the alternate layers of anatase TiO₂ (~110 nm) and mesoporous SiO₂ (~170 nm) are well-interfaced, while the



Figure 3. (a) Transmission spectra and (b) transmitted solar irradiance of glass, 6-layer, 8-layer, and 10-layer TNPh and TNPh-pyro with resonance wavelength at 920 nm, against power density of spectral solar irradiance (AM 1.5). (c) Time-dependent indoor blackbody and air temperature of a model house with a glass and TNPh-pyro window exposed to 100 mW/cm² simulated solar radiation. (d) Temperature and electric potential distribution of each device in PVDF-glass and TNPh-pyro film.

top mesoporous TiO₂/Cu layer (~140 nm) of high specific surface area $(127.6 \text{ m}^2/\text{g})$ is devised for superior photodegradation of volatile organic compounds (VOCs) air pollutants. The highly organized self-assembled mesoporous frameworks of TiO₂/Cu and SiO₂ are shown in Figure 2c,d, respectively. Cu nanoparticles of average diameter ~5.4 nm are observed to be dispersed within the mesoporous TiO_2 (Figure S1a-c). It is noted that the surfaces of these Cu nanoparticles are likely to be oxidized when exposed to air. The bulk XRD characterization of TiO2/Cu specimen shows an additional peak at 43.2° which is distinguished as the Cu (111) (Figure S2). Presumably, Cu oxide is not detected due to its thin covering layer on Cu nanoparticle surface. The refractive indexes of 2.00, 1.36, and 1.41 correspond to the anatase TiO_{24} mesoporous SiO₂, and mesoporous TiO₂, respectively (Figure S3). Importantly, the optically homogeneous film of high refractive index TiO₂ contrast to that of the low refractive index SiO₂ dielectric enables the metamaterial film to act as a wide waste NIR heat reflector for passive cooling.²⁹⁻³¹ Such a nanophotonic approach to achieve NIR reflective capacity has a distinct advantage in terms of versatility over the NIR reflection properties, including resonance wavelength, intensity, and full width at half-maximum (FWHM) of the resonance peak. By controlling the number of the layers and thickness parameters, peak reflection from 830 to 912, 1030, and 1190 nm with maximum intensity from ~57 to 70 and 85% can be readily customized (Figure S4a,b). The experimental NIR reflection characteristic is in good agreement with the simulation study, which proves the consistency of our design with the theoretical calculation (Figure S4c). Therefore, the nanophotonic structure design and materials selection fundamentally enable spectral

selectivity and tunability of the metamaterial system, which is essential in achieving macroscopic daytime passive NIR reflective cooling.

The solar transmittance to indoor is the key metric to access cooling performance based on the reflection characteristic of the TNPh, where optimal suppression of NIR waste heat and sufficient visible transmittance are required. ITO is noticeably incapable of blocking NIR in the range of 780-1200 nm, which represents a considerable proportion of solar heat. In order to complementary shield this portion of solar spectrum, various nanophotonic films are deliberately tuned with transmission resonance dip at 830, 920, and 1100 nm (Figures 3a and S5) to further suppress the solar heat gain. 6-layer TNPh (TNPh-6), 8-layer TNPh (TNPh-8), and 10-layer TNPh (TNPh-10) and TNPh-pyro (TNPh-10-pyro) with a transmission dip at 920 nm (Figure 3a) can achieve a minimum transmittance of 38, 26, 14, and 7.6%, respectively (Figure 3a). Selective UV, VIS, NIR spectral transmission tuning and systematic analysis of the solar irradiance transmittance for all samples were performed, and the results for TNPh films at 920 nm are representatively shown in Figure 3b. The percentage of energy transmittance corresponding to each spectral range is numerically summarized in Table S1. In consideration of combined visual transparency (VIS transmittance 80.2%) and waste heat rejection capabilities (NIR transmittance 49.2%), TNPh-10 with optimized transmission dip at 920 nm is adopted for the TNPh-pyro scheme, where waste solar heat gain is effectively reduced (NIR transmittance 35.0%) without compromising the desirable daylighting (VIS transmittance 69.5%), satisfying the typical transparency requirement of a window.



Figure 4. (a) Schematic of the solar pyroelectric measurement. (b) Reflection spectra of TNPh and absorption spectra of PVDF and TNPhpyro. (c) Open circuit voltage and (d) short circuit current for normal PVDF and TNPh-pyro at light oscillation of 9, 32, and 60 mHz. (e) Temperature and (f) rate of change of temperature of PVDF and TNPh-pyro at 9 mHz.

On the basis of the above solar irradiance analysis, we demonstrate the cooling performance by exposing a model house $(14 \times 14 \times 30 \text{ cm}^3)$ with TNPh/bare glass coverings to 100 mW/cm² simulated solar irradiation (Figure S6a). Figure 3c shows the blackbody and the air temperature with time for TNPh-pyro compared to bare glass. The indoor blackbody temperature of the bare glass covering increases quickly and reaches 33.1 °C after 1 h of light illumination, while the TNPhpyro exhibits slower temperature rise and stabilizes at 29.0 °C. The IR images taken at the blackbody surfaces show consistent cooling characteristics of the TNPh-pyro covering (Figure S6b). The corresponding indoor blackbody and air temperatures of TNPh-pyro effectively reduce by 4.1 and 1.3 °C when compared to that of bare glass, demonstrating its obvious cooling capability for indoor environment. According to the previous work, depending on the climate, a 1-4 °C decrease in the set point temperature could save up to 45% of energy required for the building's cooling.³² In addition, by virtue of TiO₂ being one of the key components in the nanophotonic structure, its photocatalytic properties are concurrently exploited for environmentally benign photocatalysis oxidation process. By photoreduction of aqueous copper(II) over illuminated TiO₂ film, Cu nanoparticles were homogeneously deposited as an efficient co-catalyst for photocatalytic air purification. The optimal TiO₂/Cu film shows VOCs, that is, ethanol, IPA, and formaldehyde degraded after 60 min UV irradiation (see details in Figures S7 and S8).

Apart from the indoor cooling and air purification functionalities, the TNPh-pyro scheme capitalizes the NIR waste heat back reflection functionality for enhanced solar pyroelectric harvesting. Compared to the widely researched piezoelectric, $^{33-36}$ triboelectric, $^{37-40}$ and photovoltaic materials, $^{41-43}$ pyroelectric nanogenerators offer a viable means of harvesting various ambient waste thermal energy. ^{44,45} The ubiquitous waste heat can be tapped from a few main sources of time-dependent ambient temperature variations namely the day-night cycle, wind, and the cloudiness of the sky as well as discrete temperature fluctuations from environmental/structural heating and cooling sources. Here, a transparent ferroelectric β -phase PVDF film (Figure S9) is chosen as the pyroelectric harvester within TNPh-pyro system due to its high mechanical flexibility, chemical resistance, and low cost merits, which makes it suitable for practical application. In order to gain insights on the NIR back reflecting effect on the pyroelectric conversion, simulations of temperature variance and corresponding electrical potential distribution were conducted first using COMSOL Multiphysics. A solar intensity of 100 mW/cm² is illuminated onto PVDF and TNPh-pyro film, where the simulated temperature as a function of time is shown in Figure S10. Within a minute of light irradiation, the temperature of TNPh-pyro is 3 °C higher than the PVDF film. The pyroelectric potential is simulated based on the temperature distribution (Figure 3d),²⁰ where the change of surfacebound charge density can be expressed as eq 1:

$$\Delta \sigma = \frac{I\Delta t}{A} = p\Delta T \tag{1}$$

Along the thickness of the PVDF film, the potential difference V between the top and bottom electrodes can be given by eq 2:

$$V = Ed = \frac{\Delta\sigma d}{\varepsilon_r \varepsilon_o} = \frac{pd}{\varepsilon_r \varepsilon_o} \Delta T$$
⁽²⁾

where *E* is the electric field intensity, *d* is the thickness of the PVDF film, and ε_r and ε_0 are the relative and vacuum dielectric constants, respectively. The pyroelectric coefficient is set as 2.7 nC cm² K⁻¹ and the interface between the PVDF and glass is grounded. The maximum simulated potential is approximately 44 V for the TNPh-pyro as compared to 33 V for the PVDF film, and thus the augmented electrical potential distribution of the TNPh-pyro can lead to the higher pyroelectric output.



Figure 5. (a) Model houses with roofs installed with integrated TNPh (left) and glass window (right). (b) Indoor blackbody and air temperature for the TNPh house and glass window house and corresponding solar irradiance and wind speed depending on time of day. (c) Infrared image of the two houses taken at 11:30. (d) Time-dependent shortcircuit current, open circuit voltage, and temperature of TNPh from 11:50 to 12:10.

Based on the positive simulation result, we experimentally compared the solar pyroelectric performance between the TNPh-pyro and PVDF. Figure 4a shows the setup for solar pyroelectric harvesting where an integrated TNPh-pyro film is exposed to intermittent solar radiation which enables timedependent temperature variation change of spontaneous polarization (Figure S11). The observed solar pyroelectric effect is due to the cyclic temperature fluctuation via NIR heat absorption when the light is unblocked and convective cooling when the light is blocked off. One of the main challenges for PVDF solar pyroelectric functionality lies in the limited light absorbance for consequential thermal harvesting. As shown in Figure 4b, the TNPh is highly reflective at the NIR region from 780 to 1200 nm, which coincides with the enhanced absorption of the rejected NIR radiation by PVDF for improved solar heat harnessing. The open circuit voltage (V_{oc}) and short circuit current (I_{sc}) for PVDF and TNPh-pyro under different frequencies of light oscillations (9, 32, and 60 mHz) were measured (Figure 4c,d). It is observed that the V_{oc} decreases with increasing frequencies. Evidently, the TNPh-pyro exhibits voltage enhancement for all three different frequencies up to 152% at 9 mHz with $V_{\rm oc}$ of the TNPh-pyro and PVDF at 8.2 and 5.4 V, respectively. The temperature profile of PVDF shows ΔT of 11.3 °C, while TNPh-pyro results in a larger ΔT of 15.9 °C over 55 s, which effectively increases by 141% (Figure 4e). When light oscillation frequencies increase to 32 and 60 mHz, a relatively smaller increase of ΔT was measured (see details in Figure S12a,b), which is consistent with the voltage output. Furthermore, the TNPh-pyro displays higher rates of temperature change (dT/dt), calculated using the time derivative as compared to PVDF which lead to enhanced I_{sc} for all light oscillation frequencies (Figures 4d,f and S12c,d). The peak current of TNPh-pyro is 24.5 nA at 9 mHz, which is ~146% higher than PVDF of 16.8 nA. As a result, our TNPhpyro film demonstrates enhanced solar waste heat-to-electricity conversion benefiting from the photon recycling path.

To this end, we tested the outdoor solar reflective cooling and energy generation performance of the TNPh-pyro film (see details in Figure S13). Two identical house models with roofs installed with bare glass and TNPh-pyro panels were placed out in the open, while the indoor blackbody and air temperatures were monitored (Figure 5a). The solar irradiance, wind speed, and corresponding temperature data are shown in Figure 5b. Apparent indoor cooling is observed shortly under sun exposure where the blackbody temperature difference increases up to ~4.0 °C at noon time (from 11:30 to 12:30). The infrared image taken at 11:30 visually shows that the blackbody temperature of TNPh-pyro-roofed house is 58.5 °C, which is 4.2 °C lower than 62.7 °C for the glass-roofed house (Figure 5c). In the context of the indoor air, maximal temperature difference of ~1.2 °C is exclusively observed up to 11:30. This is expected since the confined air within the small capacity house model heats up quickly with time which can be attributed to heat trapping effect. As the temperature rises, the difference in temperature between the two house models diminishes due to higher heat loss of the glass-roofed house to the ambient. This should deviate from a real building scenario where the indoor air temperature is anticipated to be potentially lower and more consistent with time. The solar pyroelectricity output of the TNPh-pyro-roofed house was also measured while monitoring the temperature variation (Figure 5d). The maximum V_{oc} and I_{sc} obtained are -126.5 nA and -32.2 V respectively, which results from the temperature fluctuation derived from solar insolation with variable cloud cover and ambient wind cooling. Therefore, this demonstrates the proofof-concept for concurrent passive cooling and enhanced solar pyroelectric generation under real outdoor environment.

CONCLUSIONS

We propose the use of low cost and scalable nanophotonic multilayered structure for reutilizing waste thermal emission from solar reflective film for simultaneous passive daytime cooling and energy generation. Under simulated noon time solar irradiation conditions, we have successfully verified passive cooling of an indoor environment with blackbody and air temperature reductions of 4.1 and 1.3 °C, respectively. In addition, the TNPh exhibits effective photocatalytic degradation of VOCs due to the presence of photoactive TiO_2/Cu constituents in the metamaterial structure. Under 1 sun irradiation at 9 mHz light oscillation, the TNPh-pyro film

shows 152 and 146% enhancement in open circuit voltage and short circuit current output, respectively. The theoretical simulations on the influence of the back reflected light on solar pyroelectric conversion testify the appreciable gain in temperature and electric potential distribution. Finally, the real outdoor solar reflective cooling up to 4.2 °C and maximum pyroelectric V_{oc} of -126.5 nA and $I_{sc} -32.2$ V were delivered. This work described herein offers conceptual and technological possibilities for broad implications in other solar optical and heat manifestations such as photovoltaic/thermophotovoltaics, thermoelectric energy conversion, nanoscale heat management, photodetectors, smart window, optical data storage, *etc.*

EXPERIMENTAL SECTION

Details of materials fabrication steps, test structures, optical measurement and analysis, photocatalytic degradation of VOC measurement, and indoor/outdoor cooling performance and solar pyroelectric power output measurement including the setup design appear in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications Web site. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b06025.

Setup design and additional details (PDF)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: elehgw@nus.edu.sg. *E-mail: kimsw1@skku.edu.

ORCID [©]

Kaichen Xu: 0000-0003-4957-3144 Minghui Hong: 0000-0001-7141-636X Sang-Woo Kim: 0000-0002-0079-5806 Ghim Wei Ho: 0000-0003-1276-0165

Notes

The authors declare no competing financial interest.

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