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Supplemental material

Near-room-temperature waste heat recovery through radiative cooling for both

daytime and nighttime power generation

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Methods

Sample fabrication

ZnO powder (purity: 99.9%) was purchased from Sigma–Aldrich with an initial diameter (d_{50}) of 3.048 µm. The ZnO powder was ground to a nanometer-size powder $(d_{50} = 0.126 \ \mu\text{m})$ by using an agitator bead mill (NETZSCH LabStar 1). Micro h-BN flakes (purity: 99.9%; $d_{50} = 10 \ \mu m$) were purchased from UNIGUE Enterprise. The micro h-BN flakes were ground to a size (d_{50}) of 6 µm. A particle size analyzer (Malvern Mastersizer 2000) was used to measure the size distributions of the ZnO powder and h-BN flakes. The nano ZnO powder and the micro h-BN were mixed at a volume ratio of 1:1. The well-mixed powder (2 g) was pressed into a 1-inch-diameter ingot at a pressure of 70 kg cm⁻² for 120 s. The ingots of both the pure ZnO powder and well-mixed powder were sintered at 900 °C for 2 h. The thickness of the sintered mixed powder was 2.2 mm. For the pure h-BN ingot, the sintering temperature was increased to 1050 °C to increase the degree of densification. Poly(vinylidene fluoride) (PVDF) powder ($M_w = ca. 534,000$) was purchased from Sigma–Aldrich. For PVDF ingots, the as-pressed ingots were sintered at 150 °C for 2 h. The thickness of the powder-sintered PVDF was 2.6 mm.

Sample characterization

UV–Vis–near-IR (NIR) spectra were recorded using a spectrometer (Hitachi UH-4150) equipped with a 60-mm integral sphere to ensure the collection of diffused light. MIR spectra were recorded using a Fourier transform infrared (FTIR) spectrometer (Bruker V70) equipped with a gold-coated integral sphere. The thermal diffusivity (α) was measured using a flash apparatus (NETZSCH LFA 447). The specific heat capacity (C_p) was measured through differential scanning calorimetry (DSC, TA Q200). The density (D) was measured by dividing the mass by the volume. The thermal conductivity (κ) was calculated using the equation

 $\kappa = \alpha C_{\rm p} D$

Cooling power measurement

The DRC samples were attached to a Kapton heater (diameter: 1 inch) to characterize their DRC properties. A K-type thermocouple was used to measure the temperature at the bottom of a sample (T_{sample}), the temperature of the surrounding ($T_{surrounding}$), and the ambient temperature (T_{amb}). The heater and samples were placed in an acrylic box filled with Styrofoam to minimize environmental perturbation. A clean IR-transparent polyethylene (PE) film (thickness: *ca*. 10 µm) was used to seal the acrylic box and maintain the free transportation of thermal radiation. A DAQ module (NI-9213, National Instrument) was used to collect the thermocouple data. The heater was connected to a DC power supply (2280S Keithley). The cooling power of the samples was measured using a feedback control system, to maintain the sample temperature equal to the surrounding temperature in the acrylic box. The temperature was regulated using a proportional–integral–derivative (PID) control algorithm. The solar irradiance was measured using a pyranometer (Kipp & Zonen, CMP10). A weather station recorded the wind speed and relative humidity. The experiments were performed on March 10, 2022.

Thermoelectric power measurement

Commercial thermoelectric generators (TEC1-049042020, Jin Hua Electronic) were used to verify the near-room-temperature waste heat recovery. The thermoelectric generator (20 mm*20 mm) consists of thermoelectric materials [(Bi, Sb)₂Te₃ alloys] covered by gray outer shells (mostly sintered alumina) at both hot-side and cold-side. The thermoelectric material is fixed inside the shell with tin solder (Fig. S1). A Kapton heater was used to simulate a near-room-temperature heat source with temperatures from 35 to 60 °C. NASBIS thermal insulation pads were used to minimize heat loss. The temperature of the Kapton heater was regulated using a DC power supply (2280S, Keithley). The thermoelectric voltage was measured using a DAQ device (NI USB-6003). The internal resistance of the TEG in a four-wire configuration was measured by a source meter (2400, Keithley) to be 1.29 Ω . The thermoelectric power was calculated under impedance matching conditions. The amounts of thermoelectric power generated in the daytime and at night were measured on March 4 and 14, 2022, respectively.



Fig. S1. (b) top-view of the commercial thermoelectric generator and (c) side-view of the commercial thermoelectric generator.

S1 Calculation of power flux in a radiative cooler



Fig. S2. Schematic representation of the power flux in a radiative cooler.

The net heat exchange of a DRC system (Fig. S2) can be defined as:

$$P_{net} = P_{rad} - P_{atm} + P_{con} - P_{sun}$$
 * MERGEFORMAT (1)

In equation (1), the power radiated by the surface is P_{rad} :

$$P_{rad}(T_{surf}) = \int d\Omega \cos\theta \int_0^\infty d\lambda I_{bb}(T_{surf}, \lambda) \varepsilon(\lambda, \theta) \qquad \qquad \land * \text{MERGEFORMAT}(2)$$

where $\varepsilon(\lambda, \theta)$ is the emissivity of the surface and I_{bb} is the spectral radiance of blackbody radiation:

$$I_{bb}(T,\lambda) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{(\lambda k_B T)}} - 1}$$
 * MERGEFORMAT (3)

 P_{atm} is the absorbed power from the thermal radiation emitted from the atmosphere; it can be calculated as follows:

$$P_{atm}(T_{amb}) = \int d\Omega \cos \theta \int_{0}^{\infty} d\lambda I_{bb}(T_{amb},\lambda) \varepsilon(\lambda,\theta) \varepsilon_{atm}(\lambda,\theta)$$
 * MERGEFORMAT (4)

where $\varepsilon_{atm}(\lambda,\theta) = 1 - t(\lambda)^{\frac{1}{cos}\theta}$ is the angular emissivity of the atmosphere and $t(\lambda)$ is the transmittance of the atmosphere in the zenith direction.

 $P_{\rm con}$ is the combined conductive/convective heat exchange; it can be expressed as follows:

$$P_{con}(T_{surf}, T_{amb}) = h(T_{surf} - T_{amb})$$
 * MERGEFORMAT (5)

where h is conductive/convective heat exchange coefficient.

 $P_{\rm sun}$ is the absorbed solar irradiance:

$$P_{sun} = \int I_{AM1.5G} \varepsilon(\lambda, \theta) d\lambda \qquad \qquad \backslash * \text{ MERGEFORMAT (6)}$$

According to the Kirchhoff's law, the absorptance (α) is equal to the emissivity (ε) at thermal equilibrium. Hence, in this study, we could replace the emissivity with the absorptance (*i.e.*, $\alpha = \varepsilon$).

S2 1D heat transfer model of DRC-TEG



Fig. S3. Schematic representation of the TEG cooperating with DRC.

A heat transfer model for TEG cooperating with DRC has been decribed by Liu *et* $al.^1$ For simplification, we consider a 1D heat transfer model based on the following assumptions:

- The energy flux is transported only along the out-of-plane direction. Heat losses from the edge of the TEG or daytime radiative cooler are neglected.
- The considered model is composed of waste heat source/thermal grease/TEG leg/thermal grease/daytime radiative cooler/sky.
- 3. The temperature of the waste heat source is kept constant at $T_{\rm w}$.

The energy balance equation can be written as:

$$P_{rad} + P_{con} - P_{atm} - P_{sun} + P_{TEG} + \frac{T_h - T_w}{R_{Gre}} = 0$$

$$\land * \text{ MERGEFORMAT (7)}$$

The values of P_{rad} , P_{con} , P_{atm} , and P_{sun} can be calculated using equations (2)–(6).

 R_i is the thermal resistance of the *i*th layer (*i* = thermal grease, TEG, or daytime radiative cooler); it can be written as:

$$R_i = \frac{L_i}{\kappa_i A_i}$$
 * MERGEFORMAT (8)

where L_i , κ_i , and A_i are the thickness, thermal conductivity, and area of the *i*th layer, respectively.

 P_{TEG} is the thermoelectric power generated by the TEG under impedance matching conditions; it can be written as:

$$P_{TEG} = \frac{(nS\Delta T)^2}{4A_{TEG} \times R_{in}}$$
 * MERGEFORMAT (9)

where *n* is the number of thermoelectric legs in series; *S* is the combined Seebeck coefficient of the P- and N-type legs; ΔT is the temperature difference between the hot $(T_{\rm h})$ and cold $(T_{\rm c})$ sides; $A_{\rm TEG}$ is the area of the TEG device; and $R_{\rm in}$ is the inner resistance of the TEG device. We assumed *S* to have a value of 183 μ V/K; *n* to have a value of 49; and $R_{\rm in}$ to have a value of 2 Ω . The other parameters used in the calculation are listed in Table S1. The energy conservation equations at the cold and hot sides are:

$$P_{c}A_{TEG} - \frac{T_{c} - T_{surf}}{R_{Gre} + R_{cooler}} = 0 P_{h}A_{TEG} + \frac{T_{h} - T_{w}}{R_{Gre}} = 0$$
 * MERGEFORMAT (10)

where $P_{\rm h}$ is the energy transfer into the TEG hot side and $P_{\rm c}$ is the energy transfer out

of the cold side; they can be calculated as follows:

$$P_{c} = (nSI_{TEG}T_{c} + \frac{T_{h} - T_{c}}{R_{TEG}} + \frac{1}{2}I_{TEG}^{2}R_{in})/A_{TEG}P_{h} = (nSI_{TEG}T_{h} + \frac{T_{h} - T_{c}}{R_{TEG}} - \frac{1}{2}I_{TEG}^{2}R_{in})/A_{TEG}$$

$$\land * \text{ MERGEFORMAT (11)}$$

where I_{TEG} is the current in the TEG.

Definition	Symbol	Value (mm)	Unit
Length	L _{cooler}	3	mm
	L _{Grease}	1	mm
	L_{TEG}	1.6	mm
Area	A _{cooler}	4	cm ²
	$A_{TEG-leg}$	0.4	cm ²
	A_{Grease}	4	cm ²
Thermal conductivity	κ_{cooler}	Variable number	W m ⁻¹ K ⁻¹
	κ_{Grease}	10	W m ⁻¹ K ⁻¹
	κ_{TEG}	1.5	W m ⁻¹ K ⁻¹
Number of	п	49	unitless
thermoelectric legs			
Combined Seebeck	S	183	μV/K
coefficient			
Internal resistance	R _{in}	2	Ω

Table S1. Parameters of 1D heat transfer model.

S3 Reflection losses of h-BN and ZnO

Fig. S4(a) presents the optical constants of h-BN in the in-plane direction and ZnO in the solar spectral region; these optical constants were obtained from Yoonhyku² and Sorar³. Fig. S4(b) displays the optical constants of h-BN in the in-plane and out-ofplane directions and of ZnO in the MIR region; these optical constants were obtained from Caldwell⁴ and Querry⁵. Fig. S4(c) presents the Fresnel reflections of ZnO and h-BN in the MIR region, calculated as follows:

$$R = \frac{(n+1)^2 + k^2}{(n-1)^2 + k^2}$$
 * MERGEFORMAT (12)

for a semi-finite substrate case in normal incidence.



Fig. S4. (a) Optical constants of h-BN and ZnO in the solar spectral region. (b) Optical constants of h-BN and ZnO in the MIR region. (c) Fresnel reflection of h-BN and ZnO in the MIR region.

S4 Impact of solar absorption on the energy flux

In the actual case, solar absorption is inevitable. We should consider solar absorption to discuss the energy flux in a real situation. We have calculated the P_{net} of the broadband emitter with various degrees of solar absorption (0%, 5%, 10%, 20%, 30%, and 50%) and compared the values with TEG and MNHZC. As shown in Figure R3, when the degree of solar absorption increases, the P_{net} decreases fastly. The absorption in the solar region impacts the cooling performance seriously. P_{net} of the broadband emitter decreases from 390.5 to -109.5 Wm⁻² at $T_{surf} - T_{amb} = 10^{\circ}$ C when solar absorption increases to 50%. For the reported MNHZC, the P_{net} is between the case of the broadband emitter with 5% and 10% solar absorption. On the other hand, the P_{net} of TEG is lower than the broadband emitter with 50% solar absorption. The significant impact of solar absorption indicates that optimization in the solar spectrum is crucial. Our MNHZC with P_{sun} of 47.2 W/m² shows superior cooling performance than TEG.



Fig. S5 Energy flux of the broadband emitter with various degree of solar absorption,

MNHZC and TEG.

S5 SEM image of h-BN, ZnO and h-BN/ZnO

(a)

Fig. S6(a) presents SEM images of the sintered ZnO, hBN, and h-BN/ZnO (MNHZC). The image of h-BN/ZnO reveals a 3D hierarchical structure; the surfaces of the micro h-BN flakes were covered with nano ZnO powder. The 3D hierarchical structure could excite the phonon resonance of ZnO at wavelengths in the range from 16 to 25 μm. This behavior could also be modeled through FDTD simulation (Supplemental Material S5). Fig. S6(b) displays an SEM image of the micro h-BN flakes that had not been subjected to the sintering process. The thicknesses of the h-BN flakes ranged from 100 to 300 nm.

Fig. S6. (a) SEM images of sintered ZnO, h-BN, and h-BN/ZnO (MNHZC). (b)

Measurement of the thicknesses of the micro h-BN flakes.

S6 Single scattering albedo (σ) of micro/nano hybrid h-BN/ZnO flake

We performed 3D FDTD simulations to verify the optical behavior of the MNHZC. As displayed in Fig. S7(a), a total-field scattered-field source was used to simulate the scattering/absorption cross-section. The h-BN flake was assumed to be a square of width *L* and thickness *t*. A thin layer of ZnO was coated onto the h-BN. The width of the h-BN was varied from 0 to 10 μ m. The thickness of the ZnO layer ranged from 0 to 700 nm. To study the optical behavior of the MNHZC, we calculated its single scattering albedo (σ) as follows:

$$\sigma = C_{\rm sca} / (C_{\rm abs} + C_{\rm sca})$$

The single scattering albedo represents the portion of scattered light during a scattering event. Hence, $(1 - \sigma)$ represents the portion of absorbed light; it can be used to estimate the absorption ability of a turbid medium. Fig. S7(b) presents the contour map of $(1 - \sigma)$ simulated with various thicknesses of ZnO. The bare h-BN exhibited low absorption beyond its two Reststrahlen bands; the h-BN presenting various thicknesses of ZnO offered higher absorptions beyond its Reststrahlen bands. The ZnO and h-BN displayed complementary absorption properties in the MIR range.



Fig. S7. (a) Schematic representation of the FDTD simulation setup. (b) Simulated single scattering albedo (σ). The values of $(1 - \sigma)$ are plotted to emphasize the absorption ability of the MNHZC.

S7 Scattering cross section of micro h-BN flake



Fig. S8. Measured reflectance of sintered h-BN and the simulated scattering crosssection of an h-BN flake; dashed lines: simulated scattering cross-sections of h-BN flakes of various sizes; *L*: length of the h-BN flake.

S8 Oxidation of hBN at high temperature

To examine the oxidation behavior of h-BN, we measured its UV–Vis–NIR and ATR-FTIR spectra before and after the sintering process. Fig. S9 (a) reveals that the reflection of h-BN in the NIR region decreased strongly as a result of the presence of B_2O_3 . The ATR-FTIR spectra confirmed this behavior. The peak position of B_2O_3 was coincident with that reported previously from a study of the annealing of h-BN under atmospheric conditions⁶



Fig. S9. (a, b) Measured spectra of h-BN before and after sintering: (a) solar and (b)

MIR regimes.

S9 Calculation of radiative cooling power under various relative humidities

The radiative cooling power is a crucial figure of merit for a radiative cooling system. The value of the radiative cooling power depends on the ambient temperature, surrounding temperature, humidity, wind speed, and solar irradiance. In terms of humidity, the transparency of the atmosphere windows would be affected dramatically by the local relative humidity⁷. Nevertheless, accurate quantitative analysis of the atmospheric transmittance requires detailed simulation of radiation transport in the atmosphere, but such simulation was beyond the scope of this study. We used a free online radiative-transfer suite provided by NASA (Planetary Spectrum Generator, PSG)⁸ to calculate [Fig. S10(a)] the atmospheric transmittance under various total water columns (TWCs). The transparency of the atmosphere depends strongly on the TWC. Fig. S10(b) presents the cooling powers calculated for various TWCs, in both the daytime and nighttime. The environmental parameters $(T_{amb}, T_{surrounding}, h)$ are based on the measured values recorded by the weather station and pyrometer [Figs. 4(b) and 4(d)]. Fig. S10(b) plots the cooling powers measured in the daytime and nighttime as dashed lines. According to the recorded values from the weather station, the relative humidities (RH) were approximately 30% in the daytime and approximately 55% at night. Values of RH of 30 and 55% corresponded to TWCs of 0-1000 and 1000-3000

atm-cm, respectively⁹. Our measured cooling powers were close to the estimated cooling powers under the TWCs in the specific ranges of RH.



Fig. S10 (a) Atmospheric transmittance at various TWCs. (b) Cooling powers of the

MNHZC, calculated for daytime and nighttime with various TWCs.

S10 Absorptance spectra of PVDF

Because of the strong scattering of air pores and IR absorption, the powdersintered PVDF exhibited an average solar reflection of approximately 97% and an average MIR absorption of approximately 95%.



Fig. S11 Absorptance spectra of the MNHZC, PVDF, and bare TEG at wavelengths of

(a) 0.26–2.5 and (b) 2.5–25 μ m.

S11 Thermal conductivity measurement



Fig. S12 Measured thermal conductivities of the MNHZC and powder-sintered PVDF.

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