# Supplementary Materials

## Supplementary Notes

### 1. Relationship between PEA thickness and emitter temperature

To better understand the effect of PEA thicknesses on the temperature of underlying emitter, we simplified the thermal process as shown in **Figure. S3a**. A heat flux is driven by the temperature difference between ambient air and the emitter. The overall thermal resistance consists of thermal resistance $\frac{D_{PEA}}{k_{PEA}}$ across the PEA and external thermal resistance $\frac{1}{h_{ext}}$ between PEA and environment. Therefore, the heat flux $q$ can be expressed as follows:

$$q = \frac{(T_{amb} - T_{emi})}{(\frac{D_{PEA}}{k_{PEA}} + \frac{1}{h_{ext}})} \tag{S1}$$

where $T_{amb}$ is the ambient temperature, $T_{emi}$ is the emitter temperature, $D_{PEA}$ is the thickness of PEA, $k_{PEA}$ is the thermal conductivity of PEA, $h_{ext}$ is the convective heat transfer coefficient. The relationship between PEA transmittance and thickness according to Beer-Lambert Law is as follows:

$$\tau(\lambda) = e^{-\alpha \cdot D_{PEA}} \tag{S2}$$

where $\tau(\lambda)$ is the transmittance of PEA, $\alpha$ is extinction coefficient of PEA, which is obtained by measuring the transmittance of PEA samples. The results of measured $\tau(\lambda)$ and calculated $\alpha$ are shown in **Figure. S3b**. The heat transfer model of PEA+Emitter is shown in **Figure. S5b**. The energy conservation equation of emitter-PEA surface and PEA upper surface is as follows:

$$\tau_{amb}\tau(\lambda)\sigma\left(T_1^4 - T_{spa}^4\right) = k_{PEA}\frac{(T_2 - T_1)}{D_{PEA}} \tag{S3}$$

$$k_{PEA}\frac{(T_2-T_1)}{D_{PEA}} = h_{ext}(T_0 - T_2) \quad \text{(S4)}$$

where $\tau_{amb}$ is atmospheric transmittance; $T_1$ is the temperature of emitter; $T_2$ is the temperature of PEA; $T_{spa}$ is the temperature of outer space, which temperature is 3 K. Through iterative calculation, $T_1$ under different atmospheric transmittance $\tau_{amb}$ and convective heat transfer coefficient $h_{ext}$ is calculated, as shown in **Figure. S3c** and **Figure. S3d**, respectively.

## 2. The calculation of $P_{cool,net}$

The heat transfer model of PEA+Hydrogel, PEA+Emitter and P(VdF-HFP) samples in **Figure. 3a** is simplified as shown in **Figure. S5**. Due to the infrared transmittance of PEA, hydrogel/emitter placed in front of PEA can conduct heat transfer with outer space through PEA. Due to the low thermal conductivity of PEA, the temperature of the PEA+Hydrogel/PEA+Emitter interface is lower than that of the PEA-ambient interface. Therefore, the $P_{cool,net}$ of PEA+Hydrogel can be expressed as follows:

$$P_{cool,net} = P_{rad} + P_{eva} - P_{sun} - P_{amb} \quad \text{(S5)}$$

Similarly, the $P_{cool,net}$ of PEA+Emitter can be expressed as follows:

$$P_{cool,net} = P_{rad} - P_{sun} - P_{amb} \quad \text{(S6)}$$

Because of the high infrared emissivity of P(VdF-HFP), the interface of P(VdF-HFP) for radiative cooling is mainly the upper surface. The $P_{cool,net}$ of P(VdF-HFP) can be expressed as follows:

$$P_{cool,net} = P_{rad} - P_{sun} - P_{amb} \quad \text{(S7)}$$

**Supplementary Figurers**

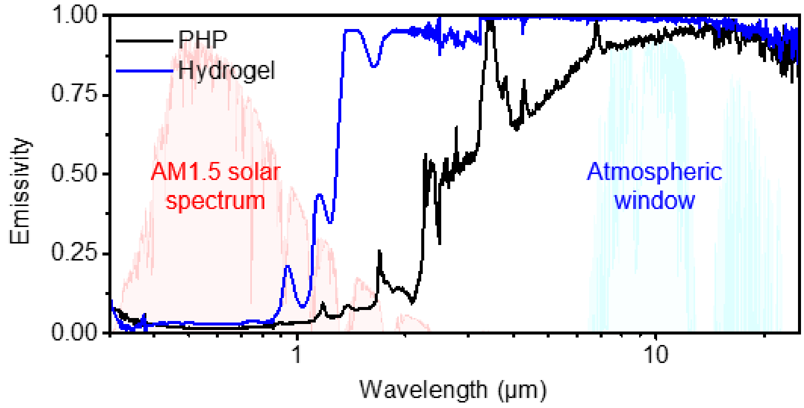


**Figure. S1:** Emissivity of PHP membrane and hydrogel sample along with the normalized AM 1.5 solar spectrum and the atmospheric transmittance

**Figure. S2:** Photograph of the cooling performance experimental setup

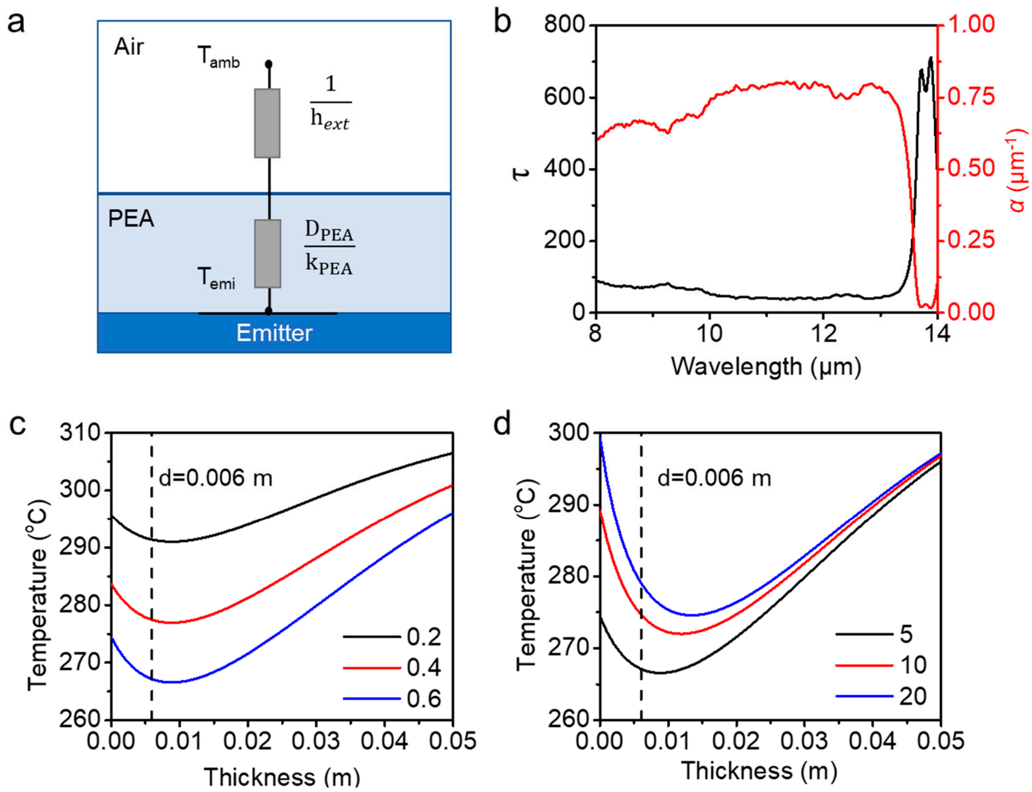


**Figure. S3:** Heat transfer model of PEA+Emitter sample with different thickness. (**a**) Resistance network of heat transfer between the emitter and ambient air. (**b**) Absorptivity and extinction coefficient of PEA samples in the atmospheric window. (**c-d**) Simulated variation of emitter temperature with PEA thickness in different atmospheric transmittance (**c**) and convective heat transfer coefficients (**d**)

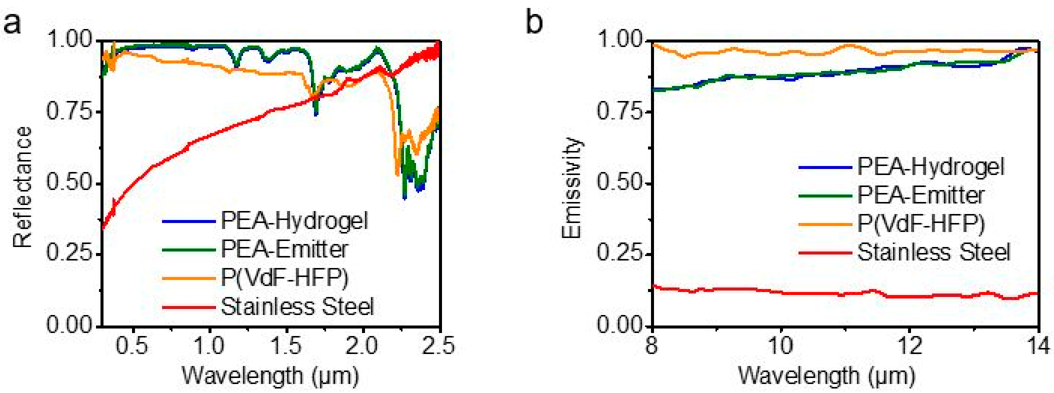


**Figure. S4:** Reflectance spectrum in the AM 1.5 solar spectrum range (**a**) and emissivity in the infrared range (**b**) of PEA+Hydrogel sample, PEA+Emitter sample, P(VdF-HFP) sample and stainless-steel substrate

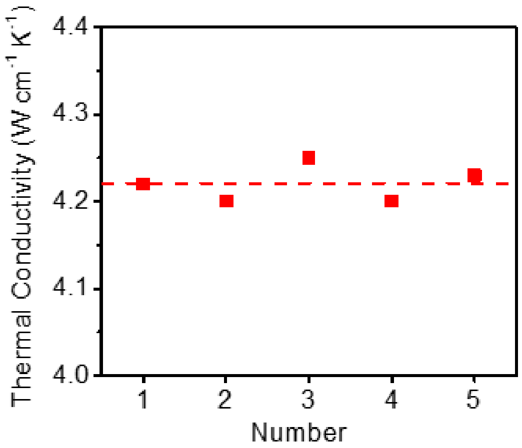


**Figure. S5:** Thermal conductivity measurement results of a P(VdF-HFP) sample in 5 times

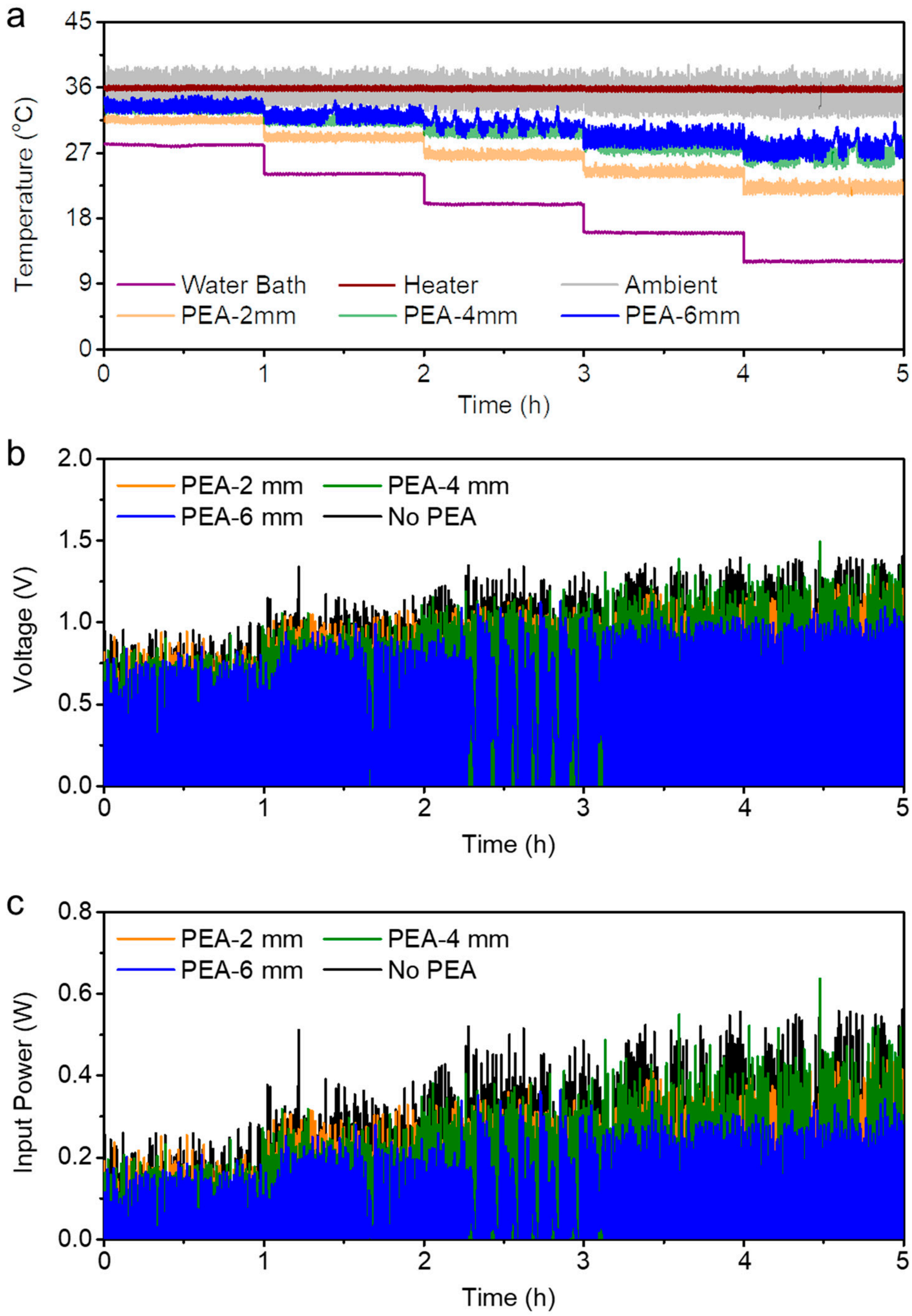


**Figure. S6:** Heat transfer experiment of PEA samples. (**a**) Temperatures recordings of different PEA thickness in different water bath temperatures. (**b**) Voltage that needs to be applied to the heater in order to maintain the same temperature with and without the PEA layer. (**c**) Corresponding input power of the heater calculated from its voltage and constant 3.5 Ω resistance

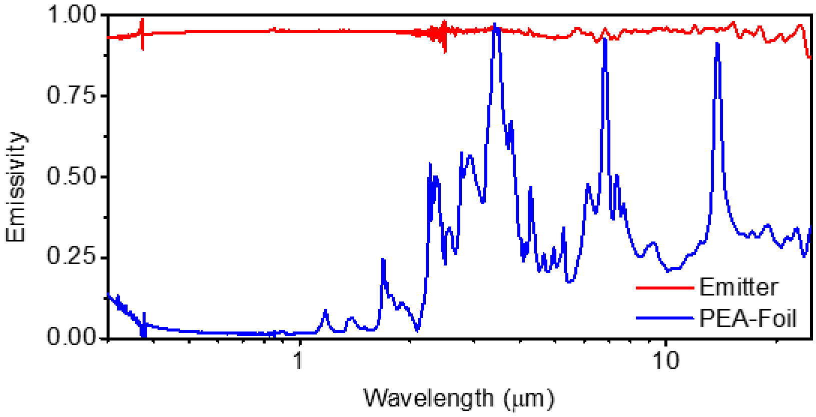


**Figure. S7:** Emissivity spectrum of emitter and PEA-Foil sample

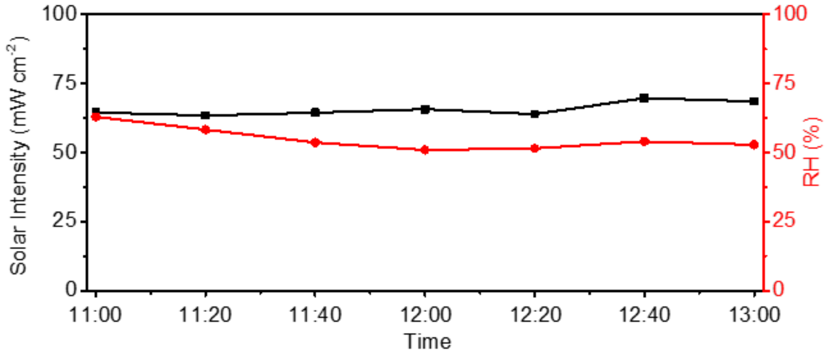


**Figure. S8:** Real-time solar intensity and environment humidity on Jul 7, 2022 in Wuhan, China