

Three-Dimensional Printable Nanoporous Polymer Matrix Composites for Daytime Radiative Cooling

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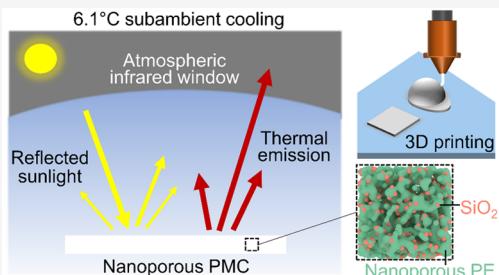
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ABSTRACT: Daytime radiative cooling presents an exciting new strategy for combating global warming, because it can passively cool buildings by reflecting sunlight and utilizing the infrared atmospheric window to eject heat into outer space. Recent progress with novel material designs showed promising subambient cooling performance under direct sunlight. However, large-scale implementation of radiative cooling technologies is still limited by the high-cost and complex fabrication. Here, we develop a nanoporous polymer matrix composite (PMC) to enable rapid production and cost reduction using commercially available polymer processing techniques, such as molding, extrusion, and 3D printing. With a high solar reflectance of 96.2% and infrared emissivity $> 90\%$, the nanoporous PMC achieved a subambient temperature drop of 6.1°C and cooling power of 85 W/m^2 under direct sunlight, which are comparable to the state-of-the-art. This work offers great promise to make radiative cooling technologies more viable for saving energy and reducing emissions in building cooling applications.

KEYWORDS: radiative cooling, polymer matrix composite, nanoporous polyethylene, 3D printing, thermal management



Space cooling, as a major necessity in modern society, consumes a significant amount of electricity,¹ which will continue to rise under the likelihood of extreme weather in the next decades.² However, traditional vapor-compression-based cooling systems have a net heating effect on the global climate and use refrigerants with a strong green-house effect.³ Recently, daytime radiative cooling has attracted intense interest as an energy-saving and environmentally friendly strategy for space cooling applications, because it demonstrates a subambient cooling effect even under intense solar irradiance.⁴ Daytime radiative cooling utilizes material surfaces that can reflect inward sunlight and simultaneously emit thermal radiation into the cold outer space ($\sim 3\text{K}$) through the atmospheric transparency window (i.e., $8\text{--}13 \mu\text{m}$).^{5\text{--}8} When the heat loss by thermal radiation exceeds the heat gain from solar absorption and parasitic heat, radiative cooling decreases its temperature until reaching the equilibrium at a subambient point. In previous studies, the subambient temperature drop up to 42°C and maximum cooling power up to 96 W/m^2 had been experimentally demonstrated under direct sunlight,^{9,10} revealing the great promise of daytime radiative cooling.

To achieve daytime radiative cooling, high solar reflectivity to minimize sunlight absorption and high infrared emissivity in the atmospheric transparency window of $8\text{--}13 \mu\text{m}$ to maximize outward thermal radiation are required. This stringent property requirement was not realized for a long time until the recent development of novel material designs, including photonic structures,^{4,9,11\text{--}15} polymer multilayer films,¹⁶ glass-polymer metamaterials,¹⁷ nanoparticle-based

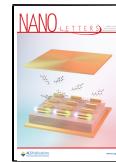
emitters,^{18\text{--}20} hierarchically porous paints,^{21,22} polyethylene aerogels with a thermal emitter,¹⁰ structural woods,²³ polydimethylsiloxane-based selective emitters,^{24\text{--}26} and poly(ethylene oxide) fibers.²⁷ However, most designs demand a complex synthesis process and/or expensive raw material. For example, the photonic structure with alternating photonic layers needs expensive and complicated vacuum deposition;⁴ the glass-polymer hybrid metamaterial uses precious metal silver as the substrate to enhance solar reflectivity;¹⁷ and the low-thermal-conductivity polyethylene aerogel requires complex, multistep solvent extraction to obtain the porous structure.¹⁰ To date, simple and low-cost fabrication of daytime radiative cooling materials is still challenging, which remains as the key bottleneck for large-scale practical implementation.

In this work, we report a facile, scalable, and inexpensive process utilizing thermally induced phase separation to fabricate nanoporous polymer matrix composites (PMCs) for daytime radiative cooling. In this material design, the high solar reflectivity is achieved by tuning the nanoporous structure of the polymer matrix, which eliminates the need for expensive

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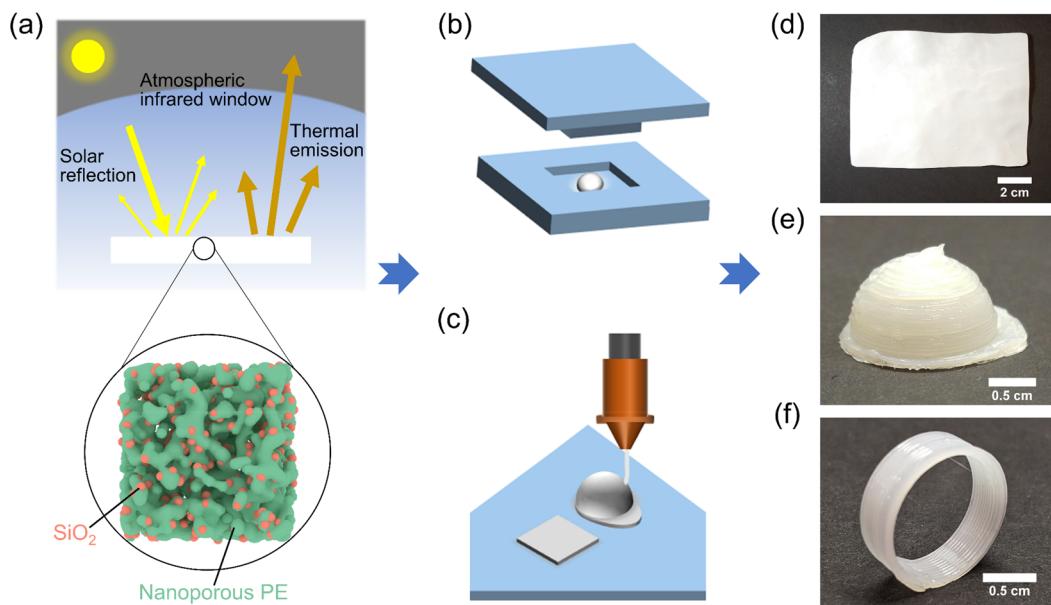


Figure 1. (a) Schematic of the nanoporous polymer matrix composite (PMC) material design with a nanoporous polyethylene matrix and randomly distributed SiO₂ particles for radiative cooling under direct sunlight. Schematic of (b) the compression molding and (c) the 3D printing processes for fabricating daytime radiative cooling (d) films and (e, f) complex structures using the nanoporous PMCs.

vacuum deposition of the reflective silver layer. In the meantime, the infrared emissivity is independently controlled by the concentration of selectively emitting fillers dispersed in the polymer matrix. By investigating the optimized processing parameters, we fabricated nanoporous PMCs with low-cost components of silicon dioxide and polyethylene, which demonstrate simultaneously high solar reflectivity (96.2%) in the wavelength of 0.3–2 μm and infrared emissivity (>90%) in the atmospheric transparency window of 8–13 μm. Thermal measurement under direct sunlight (>700 W/m²) showed that the nanoporous composite film can achieve a subambient temperature drop up to 6.1 °C and a cooling power of 85 W/m², which is comparable to the performance of state-of-the-art radiative cooling materials. Moreover, due to the thermoplastic nature of the polymer matrix, the nanoporous SiO₂–PE composites can be facilely formed into different shapes using a wide range of commercially available processing techniques, such as molding, extrusion, and 3D printing. Given its low cost, ease of fabrication, and high performance, the nanoporous PMCs demonstrated here will open a new opportunity to facilitate practical applications of daytime radiative cooling on a large scale.

The proposed nanoporous PMC structure for daytime radiative cooling is shown in Figure 1a. It consists of nanoporous polyethylene (PE) as the polymer matrix and randomly distributed silicon dioxide (SiO₂) particles as the fillers. PE is intrinsically transparent in both the solar and the infrared wavelength regions. On the one hand, by creating air pores in nanoscale sizes that are comparable to the ultraviolet, visible, and near-infrared wavelengths inside the PE matrix, it can induce scattering effects to enable reflection of the incident sunlight.²⁸ On the other hand, the addition of SiO₂ particles, which function as selective emitters, could modify the infrared emissivity of the composite to allow strong thermal emission in the wavelengths of 8–13 μm. Thus, independent control of the optical properties of nanoporous PMCs in different wavelength regions can be made by engineering the nanoscale pores and the particle fillers, respectively. This makes it viable to achieve

simultaneously high solar reflectivity and selective infrared emissivity with the nanoporous PMC itself, eliminating the additional reflective Ag layer or thermal emitter that has often been needed in previous works.

To fabricate the nanoporous PMCs, high-density PE pellets (HDPE, melt index 2.2 g/10 min, Sigma-Aldrich), ultrahigh molecular weight PE powder (UHMWPE, Alfa Aesar), and SiO₂ particles (<10 μm, Sigma-Aldrich) are mixed in the paraffin oil (light, Fisher Chemical) at 180–200 °C for 30 min using an overhead stirrer. After sufficient stirring, a homogeneous polymer mixture is obtained, which can be further used to form the designed shapes by different processing techniques, such as compression molding and 3D printing (Figure 1b–f). During the forming process, the mixture is heated to an elevated temperature at which it softens and then cooled to room temperature after the desired shape is attained. After solidification, demixing of the homogeneous polymer solution occurs, which separates it into a polymer-rich solid phase and an oil-rich liquid phase due to thermally introduced phase separation.^{29,30} Finally, the paraffin oil is extracted by methylene chloride (99.99%, Fisher Chemical), and an interconnected nanoporous polymer network is created. It should be noted that, in addition to its compatibility with conventional polymer processing techniques for the large-scale fabrication of thin films, the material design of nanoporous PMC enables the use of 3D printing to construct complex geometric structures with a radiative cooling capability for the first time (Figure 1e,f). Considering the increasing importance of 3D printing, especially in the construction and architecture industry, this could provide the advantages of flexible customization, rapid production, and cost reduction to broaden the practical application of radiative cooling technologies in buildings.

To achieve the desired properties for daytime radiative cooling, we investigated the effects of different processing parameters on the fabrication of nanoporous PMCs. First, the solar reflectance was optimized by tuning the nanoporous structure of the PE matrix with varied PE:oil ratios, heating

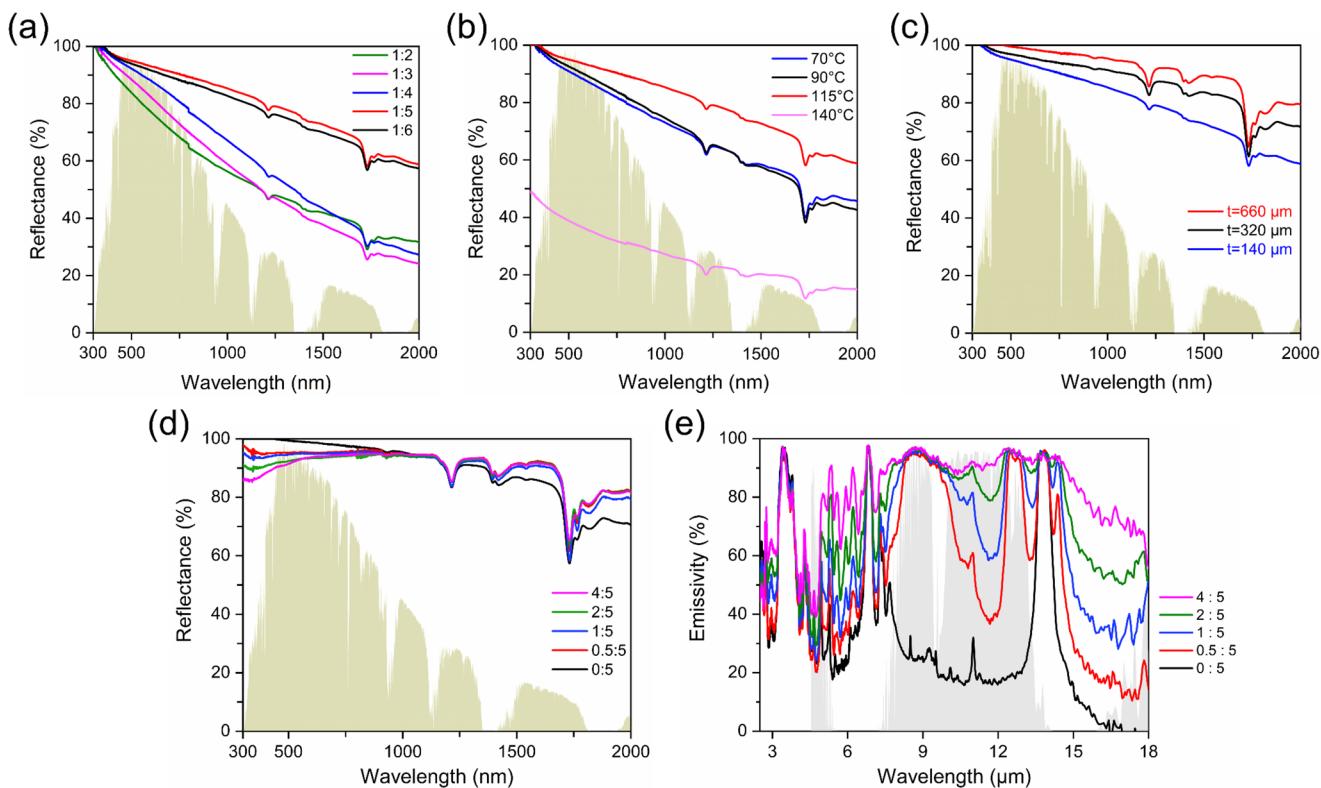


Figure 2. UV–vis–NIR reflectance measurement of the nanoporous polyethylene film with different (a) ratios of polyethylene to paraffin oil, (b) temperatures, and (c) thicknesses, for which SiO₂ particles were not added. (d) UV–vis–NIR reflectance and (e) FTIR emissivity measurements for nanoporous PMCs with different weight ratios of SiO₂:PE. Yellow shaded areas in (a)–(d) are the AM 1.5G solar spectra. Gray shaded area in (e) is the atmospheric transparency window.

temperatures, and film thicknesses. Figure 2a–c shows the solar reflectance of the nanoporous PE film measured using an ultraviolet–visible–near-infrared (UV–vis–NIR) spectrometer (Cary 5000, Agilent) with an integrating sphere (DRA 2500, Agilent). In order to elucidate the effect of the nanoporous polymer matrix for attaining high solar reflectance, SiO₂ particles were not added into the mixture for these samples. It was found that the overall solar reflectance first increases and then decreases with an increased PE:oil ratio (Figure 2a), reaching the optimum value at PE:oil = 1:5 (i.e., the volume of paraffin oil in milliliters is five times the total weight of PE in grams, where the weight ratio of HDPE to UHMWPE is fixed at 4:1). This is because the PE:oil ratio directly influences the solid–liquid phase separation upon cooling from the homogeneous PE-oil solution, thus determining the final pore size and distribution after oil extraction. The thermally induced phase separation can also be affected by the heating temperature, for which the optimal condition was 115 °C (Figure 2b). When the heating temperature is too low, PE and oil cannot sufficiently mix into a homogeneous one-phase solution which is a prerequisite to induce the phase separation during the cooling step. When the temperature is too high, the paraffin oil will diminish due to fast evaporation, which impedes the formation of the porous structure after oil extraction. Figure 2c illustrates that the solar reflectance can be further enhanced by increasing the film thickness. At the thickness of 660 μm, the nanoporous PMC film fabricated with a heating temperature of 115 °C and PE:oil = 1:5 achieved a high solar reflectance of 96.2% (normalized over the solar spectrum in the wavelength range of 300–2000 nm).

Next, the infrared emissivity of nanoporous PMCs was modulated by adding SiO₂ particles and controlling their concentration. The SiO₂ particles used in our experiments have sizes ranging from tens of nanometers to several micrometers (Figure S1). Figure 2e shows the infrared emissivity of the nanoporous PE-SiO₂ film measured using a Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet Nexus 670 FTIR) with a diffuse gold integrating sphere (PIKE Technologies). With increasing amount of SiO₂ particles added, the infrared emissivity in the wavelength region of 8–13 μm increases, reaching the maximum value of >90% at the SiO₂:PE weight ratio of 4:5. In the meantime, the addition of SiO₂ has little influence on the overall solar reflectance, only leading to a slight decrease in the ultraviolet region (Figure 2d). This indicates that the control over infrared emissivity can be separated from that of solar reflectance by engineering different components of the composites. This could add more flexibility in the material fabrication to achieve the targeted radiative cooling properties. Furthermore, there is no strict requirement on the size of the SiO₂ particles in this material design. With a suitable particle filling concentration and film thickness, random sized particles are sufficient to enable high mid-infrared emissivity,^{19,31–33} which have a lower cost to fabricate, unlike the previous study where a specified size of the SiO₂ particles is needed.¹⁷

Based on the optimized processing parameters, we fabricated an 840 μm-thick nanoporous PE-SiO₂ PMC film with a concentration gradient of SiO₂ particles. As illustrated in Figure 3a, the film contained fewer SiO₂ particles at the SiO₂:PE weight ratio of 0.5:5 in the top layer (280 μm thick), while a higher SiO₂:PE weight ratio of 4:5 was used for the

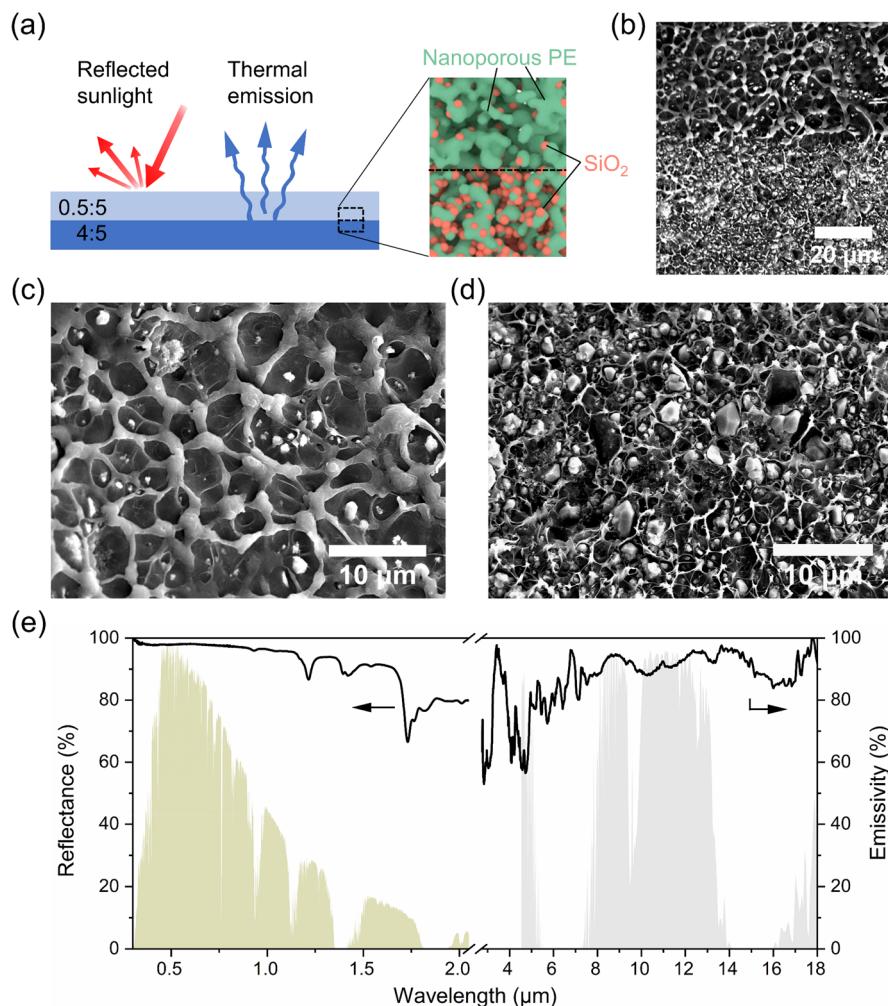


Figure 3. (a) Schematic of the nanoporous PMC film with the concentration gradient of the SiO₂ particles to achieve simultaneously high solar reflectivity and infrared emissivity, which eliminates the slight reflectance decrease in the ultraviolet region. The upper and lower layers correspond to the SiO₂:PE weight ratios of 0.5:5 and 4:5, respectively. SEM images showing the cross sections of (b) the nanoporous PMC film with the concentration gradient of SiO₂, (c) the upper layer at the weight ratio of SiO₂:PE = 0.5:5, and (d) the lower layer at the weight ratio of SiO₂:PE = 4:5. The upper and lower layers have thicknesses of 280 and 560 μm, respectively. (e) Solar reflectance and infrared emissivity of the nanoporous PMC film with the concentration gradient of the SiO₂ particles.

bottom layer (560 μm thick). This design is beneficial for avoiding the slight decrease of the solar reflectance at the ultraviolet region with a high concentration of SiO₂ particles, while the high infrared emissivity can be simultaneously achieved. Besides, the PE to oil ratio was kept constant at 1 g to 5 mL for fabrication, which enabled the whole film to maintain the interconnected nanoporous structure. The cross-sectional morphology of the as-fabricated sample is shown by the scanning electron microscopy (SEM, Hitachi S4700) images in Figure 3b–d. It is evident that the upper layer has a lower concentration of SiO₂ and the lower layer is filled with a higher concentration of SiO₂. In each layer, the SiO₂ particles are uniformly dispersed in the nanoporous polymer matrix without any agglomeration. The pore sizes are mainly distributed in the range of 200 nm–2 μm, which are comparable to the wavelengths of ultraviolet, visible, and near-infrared lights to induce strong Mie scattering effects.³⁴ Characterization results in Figure 3e demonstrate that the solar reflectance in the wavelength of 0.3–2 μm and infrared emissivity in the wavelength of 8–13 μm for this nanoporous PE-SiO₂ PMC film reach high values of 96.2% and >90%,

respectively, which is comparable to the state-of-the-art radiative cooling materials.^{4,10,17,21,25,27}

Finally, the radiative cooling performance of nanoporous PE-SiO₂ PMC was tested on clear summer days in Champaign, Illinois (40.12° N, 88.24° W). The measurement setup is shown in Figure 4a,b, which was placed on the roof of a three-story building and facing the sky directly to record the subambient temperature drop and cooling power in real time. In the setup, convective/conductive heat transfer from the environment is minimized by the polyethylene film and the foam, while the radiative heat exchange between the nanoporous PMC film and the sky is not hindered owing to the transparency of the polyethylene film. As shown in Figure 4c, the nanoporous PMC radiative cooling film achieved an average temperature drop of 6.1 °C below the ambient temperature under a solar irradiance of 747 W/m² and wind velocity of 6 km/h. This temperature drop test corresponds to the condition when the net cooling power is zero. For the cooling power measurement, which corresponds to a zero subcooling temperature, a feedback-controlled electrical heater was used on the backside to keep the radiative cooling film

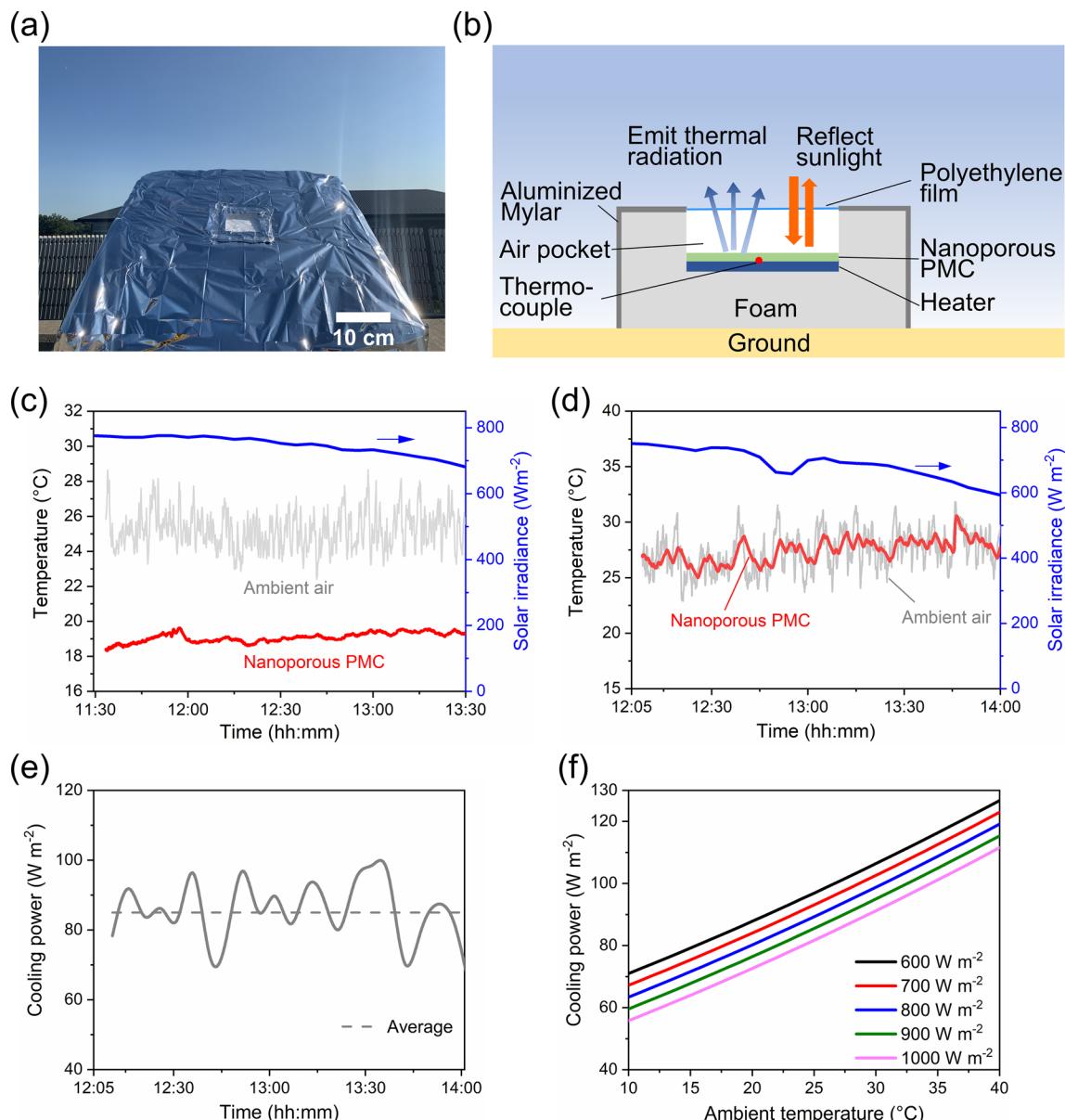


Figure 4. (a) Photograph and (b) schematic of the experimental setup for testing the daytime radiative cooling performance. (c) Measurement of the subambient temperature drop for the nanoporous PMC film. (d) Temperature tracking during (e) the measurement of cooling power. Both measurements were performed in Champaign, Illinois, on sunny days. (f) Simulated cooling power as a function of the ambient temperature with different solar irradiation intensities. The spectral properties used in the simulation were obtained from experimental measurements.

temperature the same as the ambient temperature, while the heating power was adjusted based on the real-time temperature difference between the film and the environment. Throughout the cooling power test period, the film temperature closely tracked the ambient temperature fluctuation (Figure 4d), validating the effectiveness of our feedback-controlled testing setup. The tested cooling power in Figure 4e attained an average value of 85 W/m^2 , which matched very well with the simulation results in Figure 4f. Here, the cooling power simulation is based on a theoretical heat transfer model (more details are in the Supporting Information) and performed by home-developed codes using the characterized solar reflectance and infrared emissivity of the nanoporous PMC film. Given its high performance of 6.1°C subambient cooling and 85 W/m^2 cooling power that is comparable with those of the state-of-the-art radiative cooling materials, this nanoporous

PMC material shows promising potential for radiative cooling applications.

In summary, we developed a novel nanoporous polymer matrix composite for radiative cooling using nanoporous PE as the solar reflective polymer matrix and SiO_2 particles as the thermal emitting fillers. It has the key advantage of simple, scalable, and cost-effective fabrication using molding, extrusion, or 3D-printing techniques. By optimizing the processing parameters, the fabricated nanoporous PMC samples achieved a high solar reflectance of 96.2% in the wavelength of $0.3\text{--}2 \mu\text{m}$ and infrared emissivity $>90\%$ in the atmospheric transparency window of $8\text{--}13 \mu\text{m}$, enabling a passive radiative cooling capability under direct sunlight with a subambient temperature drop of 6.1°C and cooling power of 85 W/m^2 , which is on par with the performance of state-of-the-art designs. The feasibility of using 3D printing for fabricating

daytime radiative cooling materials provides a new prospect of deploying radiative cooling strategies for energy savings and reduced emissions.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.0c04810>.

Simulation model and SEM images of SiO₂ particles ([PDF](#))

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Author Contributions

L.C. conceived the study. K.Z. carried out the material synthesis, SEM characterization, UV–vis measurement, and thermal measurement. W.L. and S.F. helped with the FTIR characterization. B.P., Y.C., and Y.D. led the 3D printing experiments. R.T. assisted with material synthesis and 3D printing. K.Z. and L.C. analyzed the data and wrote the manuscript. All authors discussed the results and commented on the paper.

Notes

The authors declare no competing financial interest.

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