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Article

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Abstract:

Passive radiative cooling provides a promising way to reduce energy consumption for cooling. However, it always requires stringent materials designs or manipulations, which are neither cost-effective nor widely adaptable. Here, we report a fast, inexpensive, and scalable UV-curing method to fabricate porous polymer coatings via photopolymerization-induced phase separation. This coating with hierarchical pore structure, has a superior long-wave infrared emittance of 0.98 and strong solar reflectance of 0.96, resulting in sub-ambient temperature drops of ~ 9.8 °C during the night and ~ 5.7 °C under solar intensity of ~ 960 W m⁻² in the metropolitan area in summer. Moreover, the UV-cured coating is highly crosslinked and superhydrophobic without any treatment, showing excellent durability after long-term UV irradiation, thermal aging, or immersion in corrosive chemicals. The paint-like simplicity and remarkable weather resistance are vital for promoting practical applications of cooling coatings.

Keywords: Hierarchical pores, intrinsic emitter, photopolymerization, phase separation, sub-ambient cooling

Introduction

Traditional cooling and refrigeration technologies that rely on vapor compression and liquid transportation occupy ~15% of the global electricity consumption and speed the depletion of fossil fuels.¹ These systems also cause huge greenhouse gas emissions and exacerbate the urban heat island effect, threatening human health and economic development.^{2,3} To address these adverse effects, an alternative technique of passive daytime radiative cooling (PDRC) has attracted much attention.⁴⁻¹⁰ PDRC can spontaneously transmit heat to the cold outer space through the atmospheric long-wave infrared (LWIR) transmission window (8-13 μm) and reflect sunlight (0.3-2.5 μm) simultaneously. The temperature of a surface towards the sky will drop effectively when the surface exhibits both high solar reflectance ($\bar{R}_{sun}$) and high LWIR thermal emittance ($\bar{\epsilon}_{LWIR}$).^{4,9} Thus, the electricity-free PDRC is a promising green cooling solution to mitigate energy and environment problem.

Various approaches have been proposed to achieve PDRC in the last decade, including using multilayer dielectrics,^{4,11,12} wavelength-selective metamaterials,^{13,14} photonic films,^{15,16} inorganic/polymer composites,^{5,17,18} and porous polymers.^{6,19,20} Preparation methods such as electron beam evaporation,^{4,11,13} roll-to-roll extrusion,⁵ electrospinning,^{17,21,22} templating,^{15,16,19} and phase separation^{6,20,23} have been developed. Among these coolers, solution processable polymer coatings are preferable for practical utilization owing to their paint-like simplicity and large-scale production.^{6,18,24} To obtain a high $\bar{R}_{sun}$, a silver layer behind the coating or sufficient refractive index difference within the coating are always required.^{4,5,8,25-27} However, coating silver layer needs sophisticated devices and increases the cost. Inorganic particles with high refractive index, like titanium dioxide (TiO_2) and zinc oxide (ZnO), have been used as additives yet inevitably absorb UV light (occupying ~8% of solar

energy), resulting in an unsatisfied cooling effect. In contrast, creating air pores in the coating can scatter light from ultraviolet to mid-infrared spectrum, which is more cost-effective than employing silver layer and inorganic particles.⁶ Considering the long-term service of PDRC coatings in the outdoor environment, the coating durability is critical for the practical application but has rarely been concerned.⁸ Therefore, developing a cost-effective method for preparation of highly efficient radiative cooling coatings with long-term reliability remains a challenge.

Herein, we present a photopolymerization-induced phase separation (PIPS) strategy to fabricate porous and crosslinked polymer coatings with excellent $\bar{R}_{sun}$ and $\bar{\epsilon}_{LWIR}$. This PIPS process is based on UV light triggered free radical polymerization of commercial resins in solvents. Because of the poor miscibility of the generated polymers in the solvents, an opaque gel layer will be left after polymerization, and porous coating can be obtained after drying. Using trimethylolpropane triacrylate (TMPTA) and vinyltriethoxysilane (VTES) as a formulation, the obtained poly(TMPTA-VTES) coating has a hierarchical pore structure, and exhibits high $\bar{R}_{sun}$ (0.96) and $\bar{\epsilon}_{LWIR}$ (0.98), resulting in an excellent passive all-day radiative cooling capability. Average sub-ambient temperature reduction (ΔT_{cool}) of ~ 9.8 °C during the night and ~ 5.7 °C at midday under a solar intensity (I_{sun}) of ~ 960 W m⁻², have been achieved in a metropolitan area in summer. The coating also shows good performance under unfavourable weather conditions. Different from previously reported materials, our coating has crosslinked thermoset networks that intrinsically own decent weather resistance, and is automatically superhydrophobic without post treatment. This UV-curing approach provides insights into design and large-scale preparation of high performance all-day radiative cooling coating with long-term reliability.

Results and discussion

The formation of poly(TMPTA-VTES) coating

UV curable resins have been widely used in furniture coatings, dental materials, printing inks and integrated circuits due to the advantages of fast polymerization, low energy consumption, mild temperature requirement, superior durability and so on.^{28,29} Here, poly(TMPTA-VTES) coatings were fabricated by a UV-curing free radical polymerization of commercial resins containing TMPTA, VTES (typically with a mass ratio of 1:4) and photoinitiator. The homogeneous mixtures coated on the substrate turned opaque immediately when exposed to UV light, due to the phase separation into polymer and porogen (solvent) phases upon the copolymerization of TMPTA and VTES. After dried in air to evaporate the residual VTES (Supplementary Fig. 1a), the phase separation structure was remained (Fig. 1a). The obtained poly(TMPTA-VTES) coating exhibits a matt white and uniform appearance (Fig. 1b). SEM images show a sub-micro structure of interconnected globules-aggregates, separated by numerous pores (Fig. 1c-d). The coating has a porosity of ~ 0.67 with a bimodal pore size distribution (Fig. 1e). Rapidly curing process and connected “strings of pearls” topography indicate that the phase separation has a feature of spinodal decomposition, delivering a bicontinuous structure arrested by the polymerization.^{30,31} The fast PIPS process, with a gelation transition time of ~ 2 s (Fig. 1f), is conducive to anchor the porous structure at an early stage of the phase separation, and thereby avoids structure coarsening and collapsing.

Fig. 1 The formation and characterization of poly(TMPTA-VTES) coating. (a) Schematic depiction of preparation of the porous coating by photopolymerization-induced phase separation. (b) Photograph of the coating (20 cm × 20 cm in size). SEM images of (c) the cross-section and (d) the top views of the coating. (e) Pore size distribution of the coating. (f) Photorheology characterization of the photopolymerization kinetics. The change of shear storage modulus (G') with time shows that the gelation transition time is ~2 s. (g) Conversion of the vinyl groups as a function of illumination time for the homopolymerization of TMPTA, and for the copolymerization of TMPTA and VTES, respectively. (h) Thermogravimetric analysis (TGA) curves of poly(TMPTA-VTES) and poly(TMPTA).

Herein, VTES acted as both monomer and porogen (Supplementary Fig. 1-3 and discussion). The vinyl group of VTES has a poor reactivity³² and usually cannot undergo polymerization on its own, but it can copolymerize with TMPTA (Fig. 1g). The percentage of VTES involved in poly(TMPTA-VTES) is ~23wt% (Supplementary Fig. 1 and discussion). The TGA curves also confirm the composition of poly(TMPTA-VTES), which leaves ~7.6% residual at 600 °C due to the formation of silica from VTES, whereas nothing is left for poly(TMPTA) (Fig. 1h). As a porogen, VTES showed poor miscibility with poly(TMPTA-VTES), leading to phase separation once

polymerization occurred. Evaporation of the residue VTES resulted in the formation of porous and white poly(TMPTA-VTES) coating, compared to the dense and transparent poly(TMPTA) coating obtained under a similar UV curing process without phase separation (Supplementary Fig. 3).

The copolymerization of TMPTA with VTES also plays an important role to get a defect-free coating. TMPTA is a trifunctional acrylate monomer with a high reactivity (Fig. 1c, see poly(TMPTA) line). The high crosslinking density of poly(TMPTA) makes the network so rigid that cracks always appear after the coating formation (Supplementary Fig. 4a).³³ When copolymerized with the monofunctional VTES, the crosslinking density could be reduced. The appearance of the resulting coatings (VTES ranging from 0~90wt%) are summarized in Supplementary Fig. 4 and Table S1. Cracks formed on the coatings when the percentage of VTES in the resins was less than 60wt% or larger than 80wt%. Therefore, enough VTES is needed to decrease the rigidity of the as-formed polymer networks to get a crack-free coating, but excessive VTES makes the network not robust enough, leading to the formation of cracks again. In control experiments, when using other non-reactive porogens to replace VTES, phase separation could occur. However, the crosslinking density was too high that cracks appeared on the resultant coatings (Supplementary Fig. 5).

This mild and fast PIPS technique is compatible with a wide variety of UV curable resins. For example, a three-component formulation containing TMPTA, butyl acrylate (BA, monofunctional monomer to reduce the crosslinking density), and ethanol (porogen) was used and the resulted poly(TMPTA-BA) coating also displayed a white and crack-free appearance, porous topology and excellent optical performance (Supplementary Fig. 6). The two-component formulation of TMPTA and VTES is

preferable for practical application since it is easy to realize the reuse of VTES. Therefore, exploiting the suitable reactive diluents and porogens to regulate the film-forming ability is essential for fabrication of porous and white coatings via UV-curing.

Optical properties of poly(TMPTA-VTES) coating

Fig. 2 Optical properties of poly(TMPTA-VTES) coating. (a) Spectral reflectance of a ~ 370 μm thick coating along with the normalized ASTM G173 Global solar spectrum and the LWIR atmospheric transmission window. Relationship between reflectance (normalized intensity) and receiver angle for the coating and the white board at 550 nm (b) and 1500 nm (c), respectively. (d) LWIR absorption spectrum of the coating with the corresponding characteristic groups. (e) Variation in $\bar{R}_{sun}$ and $\bar{\epsilon}_{LWIR}$ with the coating thickness.

Poly(TMPTA-VTES) coating, with a thickness of ~ 370 μm , presents high $\bar{R}_{sun}$ of 0.96 and $\bar{\epsilon}_{LWIR}$ of 0.98 (Fig. 2a). The scattering behaviour is similar to a standard white board at 550 and 1500 nm, respectively (Fig. 2b-c). This implies that hemispherical solar reflectance of the coating is angle-independent even at large incidence angles, which ensures effective reflection of sunlight. Compared with the reported coolers, $\bar{R}_{sun}$ and $\bar{\epsilon}_{LWIR}$ of our coating are high enough to satisfy the requirement for radiative cooling without the deposition of silver or adding of pigments.

The excellent $\bar{R}_{sun}$ and the angle-independent reflectance can be ascribed to the hierarchical porous structure. First, the moderate porosity and the refractive index (n) difference between polymer matrix ($n \approx 1.5$) and air voids ($n=1$), both provide an efficient light scattering ability.^{34,35} Second, the continuous nano- to microscale pores ranging from ~ 200 nm to ~ 8 μ m (Fig. 1e), leads to multiple reflection via a dramatically prolonged dissipation route.³⁶ It is worth noting that Mie scattering occurs when the size of the scatterer is comparable to the wavelength of incident light.³⁷ Thereby the incorporation of pores with different sizes can strongly scatter the sunlight ($0.3 \sim 2.5$ μ m). Third, the unoriented morphology of the coating is in favour of an angle-independent $\bar{R}_{sun}$.

The high $\bar{\epsilon}_{LWIR}$ can be predominantly ascribed to the composition. Generally, extinction peaks of poly(TMPTA-VTES) in the infrared region are embodied in the molecular vibrational absorptions of FTIR spectrum (Fig. 2d), which are caused by typical bond vibrations, including -C-H ($3020\text{--}2810$ cm^{-1}), C=O (1735 cm^{-1}), C-O-C (1256 , 1109 , and 990 cm^{-1}), C-Si-O-C-C (1163 , $1100\text{--}1000$, and 960 cm^{-1}), and C=C (810 , 780 cm^{-1}). Some bonds vibrating between 770 and 1250 cm^{-1} ($8\text{--}13$ μ m), have great potential to provide strong LWIR emission because the emittance is often enhanced across the transmission window by the broadening of the absorption peaks.⁶ As a result, poly(TMPTA) ($\bar{\epsilon}_{LWIR} \sim 0.95$) and poly(TMPTA-VTES) ($\bar{\epsilon}_{LWIR} \sim 0.98$) both exhibit strong thermal emittances in the LWIR window (Supplementary Fig. 7). The higher $\bar{\epsilon}_{LWIR}$ of poly(TMPTA-VTES) than that of poly(TMPTA) is due to: the introduction of silicon increases the infrared absorption (band of C-Si-O-C-C), the hierarchical pore structure increases the infrared absorption by multiple diffuse reflection¹⁹ and benefits the emitted radiation, and the porous structure also provides a

gradual refractive index transition across the coating-air interface, thus decreasing the surface reflectance of LWIR wavelengths.

High $\bar{R}_{sun}$ means keeping the energy received from sunlight to a minimum, which is the foundation to achieve sufficiently cooling effect. We investigated the influence of the porous structures on the sunlight scattering performance. Poly(TMPTA-VTES) coatings obtained from resins containing VTES of 60, 70, and 80 wt% have an average globule diameter of 389, 476, 480 nm, a porosity of 0.49, 0.62, and 0.67, and $\bar{R}_{sun}$ of 92.7%, 96.1%, and 96.4%, respectively (Supplementary Fig. 8). It can be found that the coating from 80 wt% VTES has the best scattering ability. Note that the coating from 70 wt% and 80 wt% VTES show the similar morphology both with bimodal pore size distribution ranging from nanoscale to microscale (Supplementary Fig. 9). However, the 60 wt% VTES sample only has nanoscale pores centred at ~ 120 nm, so the coating shows strong scattering ability in the visible spectrum but poor reflectance in the near-infrared region (Supplementary Fig. 8). These results demonstrate that a broad pore size distribution from nano to micrometres can enhance $\bar{R}_{sun}$, which is in accordance with the findings of Yang *et al.*^{6,34} In addition, $\bar{R}_{sun}$ and $\bar{\epsilon}_{LWIR}$ both increase with coating thickness (Fig. 2e and Supplementary Fig. 10). Because the morphology did not change with the thickness (Supplementary Fig. 11), the thicker porous coating endows more effectively backscattering of the sunlight and broadens the absorption peaks in the mid-infrared region. Therefore, a thickness of ~ 370 μm was used to balance the optical performance and material cost.

Passive all-day radiative cooling performance of poly(TMPTA-VTES) coating

Fig. 3 Passive all-day radiative cooling performance of poly(TMPTA-VTES) coating. (a) Schematic of the test equipment and photographs of the equipment on the roof of a building in downtown Beijing. Sub-ambient temperature drops with solar intensity (I_{sun} at noon) and relative humidity recorded at (b) hot sunny day (I_{sun} of $\sim 960 \text{ W m}^{-2}$), (c) sunny day (I_{sun} of $\sim 800 \text{ W m}^{-2}$), (d) sunny day with haze (I_{sun} of $\sim 750 \text{ W m}^{-2}$), (e) clear to cloudy day (I_{sun} of $\sim 720 \text{ W m}^{-2}$), (f) overcast day (I_{sun} of $\sim 200 \text{ W m}^{-2}$).

The high $\bar{R}_{sun}$ and $\bar{\epsilon}_{LWIR}$ allow coatings to achieve outstanding all-day sub-ambient cooling under different climate conditions in the urban area of Beijing (40.00 °N, 116.34 °E, altitude 46 m; continental monsoon climate). The radiative cooling efficiency of poly(TMPTA-VTES) coating was measured using a self-made apparatus (Fig. 3a, details in Methods). A whole day test was conducted in a hot sunny day in summer (from 19:30 on 19 Jun. to 19:30 on 20 Jun. 2021), and a remarkable ΔT_{cool} of $\sim 5.7 \text{ }^{\circ}\text{C}$ at a dry midday was achieved under intense I_{sun} of $\sim 960 \text{ W m}^{-2}$ and the negative influence of the heat radiation from the surrounding high buildings (Fig. 3b). Moreover, the coating can achieve an impressive ΔT_{cool} of $\sim 9.8 \text{ }^{\circ}\text{C}$ during the night (between 19:30 and 5:00), which demonstrates an excellent radiative cooling capability.

Passive radiative cooling efficiency is essentially affected by the weather conditions including solar intensity, wind speed, and atmospheric transmittance which are determined by relative humidity (RH), degree of cloudiness, air quality, and so on.³⁸ As shown in Fig. 3c-f, under different weather conditions (listed in Supplementary Table S2) like sunny, sunny with haze (RH of ~46% and PM_{2.5} of 105, O₃ of 101), clear to cloudy (RH of ~47%), and overcast (RH of ~58%), the coatings can achieve a ΔT_{cool} of ~8.4, ~4.9, ~4.0, and ~4.2 °C at noontime, respectively. Compared with ΔT_{cool} ~5.7 °C measured under I_{sun} of ~960 W m⁻² (Fig. 3b), ΔT_{cool} ~8.4 °C was obtained under ~800 W m⁻² (Fig. 3c), showing that I_{sun} indeed has a profound influence on the cooling effect. In addition, the reduction of ΔT_{cool} (from ~8.4 to ~4.9 °C, Fig. 3d) was measured on the sunny day with haze, because the haze decreased the transmittance in both the 1st and 2nd atmospheric transmission window for the thermal radiation to the universe. Similarly, cloud also reduced atmospheric transmittance, resulting in a declining cooling effect (Fig. 3e-f). Nocturnal cooling efficiency was also measured to verify the effect of atmospheric transmittance when excluding the influence of sunlight. In this case, ΔT_{cool} is ~9.0 °C (RH of ~60%, between 22:30 and 5:30 of next day, clear, Supplementary Fig. 12), ~7.2 °C (RH of ~75% between 0:00 and 6:00, clear to cloudy, Figure 3e), and ~6.5 °C (RH of ~70% between 18:00 and 6:00 of next day, overcast, Figure 3f), showing a decreased ΔT_{cool} with deterioration of atmospheric transmittance. These results demonstrate that poly(TMPTA-VTES) coating provides an encouraging multi-climatic all-day cooling efficiency, which have not been reported yet.

To further investigate the cooling capability of poly(TMPTA-VTES) coating, we adopted a feedback-controlled heating system to measure its cooling power (P_{cool}) all day. The measured average P_{cool} was ~92 W m⁻² at night (RH of ~77% between 0:00 and 6:00, Fig. 4a). The data represents the radiative cooling power of the coating when

excluding the effect of sunlight. In the daytime (between 12:00 and 14:00, Fig. 4b), the coating attained an average P_{cool} of $\sim 67 \text{ W m}^{-2}$ under solar intensity of $\sim 780 \text{ W m}^{-2}$. The cooling capability is remarkable considering the relatively low atmospheric transmittance, high RH and adverse air quality (RH of $\sim 45\%$ and O_3 of 82, Supplementary Table S3).

The calculated net cooling power ($P_{net,cal}$) with different conductive-convective heat transfer coefficients (h_c) is present (Fig. 4c-d) during the nighttime and daytime (details of theoretical model are given in the Methods). A theoretical maximum of $P_{net,cal}$ of 116 W m^{-2} can be achieved, exhibiting the ideal radiative cooling capability of poly(TMPTA-VTES) in the urban area of low altitude. For daytime, the maximum $P_{net,cal}$ is 95 W m^{-2} under adiabatic conditions and a calculated ΔT_{cool} of $8.0 \text{ }^\circ\text{C}$ in a normal conductive and convective environment (h_c of $10 \text{ W m}^{-2} \text{ K}^{-1}$) were achieved. The calculated ΔT_{cool} is comparable to the measurements of ΔT_{cool} on the sunny day. In addition to heat gain coefficient, a more significant external factor is the atmospheric transmittance. As seen in Fig. 4e-f, $P_{net,cal}$ during the night and daytime decreases from 139 to 93 W m^{-2} and from 122 to 68 W m^{-2} , respectively, as the atmospheric transmittance decreases from 90% to 60%. The measured P_{cool} in Fig. 4b is in good accordance with the $P_{net,cal}$ of 68 W m^{-2} due to the unfavourable atmospheric transmittance.

Fig. 4 Measured and calculated net radiative cooling power of poly(TMPTA-VTES) coating. Continuous measurement of the cooling power (P_{cool}) at night (a) and noon (b), with the temperature of the ambient air (T_a) and the coating (T_c) with I_{sun} and relative humidity recorded. Calculated net cooling power ($P_{net,cal}$) as a function of the temperature drop ($T_a - T_c$) with different conductive-convective heat transfer coefficients (0-20 W m⁻² K⁻¹) during the nighttime (c) and during the daytime (d); with different atmospheric transmittance (50-90%) during the nighttime (e) and during the daytime (f).

Substrate-adaptability and durability of poly(TMPTA-VTES) coating

The substrate-adaptability and durability of the coating play a pivotal role for practical application. Thanks to the solution-based process, poly(TMPTA-VTES)

coating can be easily applied to various substrates, and the temperature can be reduced 12-23 °C (Fig. 5a). Interestingly, the coating is superhydrophobic without any post treatment, exemplified by a water contact angle (CA) of $158 \pm 2^\circ$ and sliding angle of $\sim 4^\circ$ (Fig. 5b and Supplementary Fig. 13). The excellent water repellence stems from the low surface energy of methyl and methylene groups of the crosslinked polymer, and the consistently rough topography across the coating (Supplementary Fig. 14).⁴⁷

The crosslinked poly(TMPTA-VTES) shows excellent resistance to long-term exposure to UV, high temperature, or corrosive chemicals. The UV and moisture exposure test (365 nm, $\sim 2.0 \text{ mW cm}^{-2}$, RH $\sim 70\%$) conducted up to 50 days did not cause any appearance and microstructure changes, whereas the “coating” written on glass by a marking pen had been faded (Fig. 5c-d). Moreover, the coating retained a CA above 150° (Fig. 5b) in this harsh environment due to the integrity of the rough surface and the persistence of chemical composition (Supplementary Fig. 15). The reflectance and emissivity spectra of the coating showed slight fluctuations after the 50 days accelerated weathering treatment of UV and moisture (Supplementary Fig. 16). Meantime, $\bar{R}_{sun}$ changed a little when the coating was conducted the accelerated thermal aging test at 80 °C for 20 days, or immersed in hydrochloric acid solution (pH=1) or potassium hydroxide solution (pH=13) for 7 days (Fig. 5e). The crosslinked chemical structures and porous morphology across the coating contribute to the superior durability compared with the most of reported counterparts (Supplementary Table S4). Finally, poly(TMPTA-VTES) coating presented self-cleaning ability and contaminants on the surface could be easily removed to recover its solar reflectance (Fig. 5f and Supplementary Fig. 17). Our coating with impressive weather resistance, large-scale versatility and substrate independency, promises the practical application of radiative cooling materials.

Fig. 5 Substrate-adaptability and durability of poly(TMPTA-VTES) coating. (a) Optical and thermal images of the coating on various substrates. (b) Changes on water CA of the coating after UV and moisture exposure for different periods. Inset is a water droplet profile with a CA of $158 \pm 2^\circ$. (c) Optical and (d) SEM images of the coating before (top) and after (down) UV and moisture exposure for 50 days. The coating is still superhydrophobic but the marked word “coating” has been disappeared after the UV irradiation. (e) $\bar{R}_{sun}$ of the coating after suffering from various harsh environmental treatment. (f) Snapshots showing the self-cleaning ability of the coating.

We summarize the recently reported radiative cooling coatings or films in Supplementary Table S4, taking the self-cleaning ability and weather resistance into account. Through the comparison, the remarkable cooling efficiency, the fast and

straightforward fabrication process and the excellent durability of the crosslinked poly(TMPTA-VTES) coating make it stand out and very suitable for large-scale applications.

In summary, we developed a UV-curing approach for the preparation of porous polymer coatings for highly efficient passive all-day sub-ambient radiative cooling in various weather conditions. The coating features high $\bar{R}_{sun}$ (0.96) and $\bar{\epsilon}_{LWIR}$ (0.98), and realizes a ΔT_{cool} of ~ 5.7 °C at midday under I_{sun} of ~ 960 W m⁻² and as high as ~ 9.8 °C during the night in a metropolitan area. Even in high relative humidity and air polluted weather, the coating presents considerable cooling capability. The thermoset nature of the crosslinked coating and its intrinsic superhydrophobicity endow the coating excellent durability. This approach is solution-based, rapidly operating, and formulation-expandable, promising the practical application of passive all-day radiative cooling.

Methods

Fabrication of poly(TMPTA-VTES) coatings. TMPTA and VTES were mixed with a mass ratio of 1:4, and then the photoinitiator (TPO) was added (0.75wt% of the mixture). The mixture was shaking until a homogeneous phase was resulted. To turn the coating thickness well, a simple set-up was assembled, which consists of a PET film coated glass as an anti-adhesion layer, two PET films as spacers, and the desired substrates (e.g., glass, metal, plastics, etc.). After dropping certain amount of liquid paints in the set-up, the substrate was exposed under UV light (LED UV lamp, distance ~ 10 cm) for 300 s. Subsequently, the taken-out coating was dried in air to remove the residual solvent.

Measurements of cooling temperature and cooling power. The radiative cooling performance was carried out in the downtown Beijing (40.00 °N, 116.34 °E, altitude 46 m) from late June to mid-October. Solar irradiance, relative humidity and wind speed were recorded in real time or obtained from the local weather bureau. The solar irradiance was recorded by a datalogging solar power meter (TES132, TES Electrical Electronic corp. Taiwan, China), and the relative humidity was recorded by a hygrometer (TH20R-EX, Inste Technology Co., Ltd., China). They tracked the data every 60 s automatically. The air quality conditions (values of PM_{2.5}, PM₁₀, or O₃) were accessible on website (<https://aqicn.org>). Temperature was measured by the thermocouples (JY-DAM-PT08) and recorded by computer via a self-designed program. Sub-ambient temperature drop (ΔT_{cool}) of copper plate coated with poly(TMPTA-VTES) was detected using the apparatus shown in Fig. 3a (in this case, the Kapton heater was removed), with a thermocouple outside the box to detect the ambient temperature. The box was made from polystyrene foam and wrapped with Al foil outside, and a 20- μ m-thick liner low density polyethylene (LLDPE) film was covered on the top. The box was elevated 1.0 meter over the roof and was surrounded by polyurethane board as sunshine shield. When turned on Kapton heater, the apparatus can be used to measure cooling power (P_{cool}) of poly(TMPTA-VTES) though a feedback control program to keep the temperature of copper plate consistent with ambient temperature. Thus, the heating power is approximately equal to the radiative cooling power at night or the net cooling power in the daytime excluding the influence of heat conduction and convection. Poly(TMPTA-VTES) coatings applied for cooling measurements have a thickness of ~ 370 μ m and an effective size of 18 cm $\times$ 18 cm.

Theoretical model of the radiative cooling performance of the emitter.

The average solar reflectance $\bar{R}_{sun}(\theta)$ is defined as:

$$\bar{R}_{sun}(\theta) = \frac{\int_0^\infty I_{sun}(\lambda) R_{sun}(\theta, \lambda) d\lambda}{\int_0^\infty I_{sun}(\lambda) d\lambda} \quad (1).$$

Where θ is the incident angle from the surface normal, λ is the wavelength in the range of 0.3-2.5 μm , $I_{sun}(\lambda)$ is the AM 1.5 solar spectrum, and $R_{sun}(\theta, \lambda)$ is the surface angular spectral reflectance. Because the scattering behaviour of poly(TMPTA-VTES) coating is similar to a standard white board (Fig. 2b-c), here $\bar{R}_{sun}$ is assumed to be equivalent to $\bar{R}_{sun}(\theta)$ when ignoring the effect of incident angle on the reflectivity.

The average LWIR emittance of the coating can be calculated by:

$$\bar{\varepsilon}_{LWIR} = \frac{\int_{8\mu\text{m}}^{13\mu\text{m}} I_B(T, \lambda) \varepsilon(T, \lambda) d\lambda}{\int_{8\mu\text{m}}^{13\mu\text{m}} I_B(T, \lambda) d\lambda} \quad (2).$$

Where $I_B(T, \lambda) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/(\lambda k_B T)} - 1}$ is the spectral radiance of an ideal blackbody calculated according to Planck's law (h is Planck's constant, k_B is the Boltzmann constant, and c is the speed of light. Here T is assumed to be 298.15 K, unless otherwise stated), and $\varepsilon(T, \lambda)$ is the surface spectral thermal emittance in the range of 8-13 μm .

When poly(TMPTA-VTES) coating towards the sky in an open environment, its surface temperature is influenced by self-radiative ability, solar irradiance, atmospheric downward thermal radiation (atmospheric inverse radiation), and heat conduction and convection with the surroundings. Thus, the net cooling power per unit area can be expressed as:

$$P_{cool,cal}(T) = P_{rad}(T) - P_{atm}(T_{atm}) - P_{sun} - P_{cond+conv}(T_{atm}, T) \quad (3).$$

Here T is the surface temperature of the coating and T_{atm} refers to the ambient temperature. $P_{rad}(T)$ is the radiation power emitted by the poly(TMPTA-VTES)

coating, $P_{atm}(T_{atm})$ is the downward thermal radiation power from the atmosphere, P_{sun} is the solar irradiation power from the absorption of the coating and $P_{cond+conv}(T_{atm}, T)$ is the convective and conductive power.

In the above equation, these parameters can be calculated as follows:

$$P_{rad}(T) = \int_0^\infty d\lambda \int d\Omega I_B(T, \lambda) \varepsilon(\theta, \lambda) \cos\theta \quad (4)$$

$$P_{atm}(T_{atm}, T) = \int_0^\infty d\lambda \int d\Omega I_B(T_{atm}, \lambda) \varepsilon(\theta, \lambda) \varepsilon_{atm}(\theta, \lambda) \cos\theta \quad (5)$$

$$P_{sun} = \int_0^\infty d\lambda I_{sun}(\lambda) \varepsilon(\theta_{sun}, \lambda) \approx I_{sun}(1 - \bar{R}_{sun}) \quad (6)$$

$$P_{cond+conv}(T_{atm}, T) = h_c(T_{atm} - T) \quad (7).$$

Where $\int d\Omega = 2\pi \int_0^{\pi/2} d\theta \sin\theta$ represents the angular hemisphere integral, $\varepsilon_{atm}(\theta, \lambda)$ is the emissivity of the atmosphere, which is given by $\varepsilon_{atm}(\theta, \lambda) = 1 - \tau_{atm}(\lambda)^{1/\cos\theta}$ (τ_{atm} represents the transmittance of the atmosphere), and h_c is heat coefficient combining the effect of conductive and convective.

To simulate the weather condition in experiment (Table S2 and Table S3), the power of solar radiation in the simulation section is set to be 1000 for simplicity, and the ambient air temperature is assumed to be 308.15 K in the daytime and 298.15 K at night. Different values of h_c (0-20 W m⁻² K⁻¹) and τ_{atm} (50-90%) have been varied to imitate different weather conditions (Fig. 4c-f). In Fig. 4c-d, the atmospheric transmittance was stipulated to be equal with the average transmittance in Beijing (mid-latitude, continental monsoon climate, low altitude, visibility of clear: ~75%) according to MODTRAN.¹⁷ In Fig. 4e-f, h_c is set to be 10 W m⁻² K⁻¹ for a natural convection condition. The temperature reduction of the thermal radiation reaches a steady state when the net cooling power is zero.

Data availability

The data that support the findings in the paper are presented in the manuscript text or the Supplementary Information. Additional data may be requested from the corresponding author.

References

1. Goldstein, E. A., Raman, A. P. & Fan, S. Sub-ambient non-evaporative fluid cooling with the sky. *Nat. Energy* **2**, 17143 (2017).
2. Chu, S. & Majumdar, A. Opportunities and challenges for a sustainable energy future. *Nature* **488**, 294-303 (2012).
3. Qin, Y. A review on the development of cool pavements to mitigate urban heat island effect. *Renewable Sustainable Energy Rev.* **52**, 445-459 (2015).
4. Raman, A. P., Anoma, M. A., Zhu, L., Rephaeli, E. & Fan, S. Passive radiative cooling below ambient air temperature under direct sunlight. *Nature* **515**, 540-544 (2014).
5. Zhai, Y. *et al.* Scalable-manufactured randomized glass-polymer hybrid metamaterial for daytime radiative cooling. *Science* **355**, 1062-1066 (2017).
6. Mandal, J. *et al.* Hierarchically porous polymer coatings for highly efficient passive daytime radiative cooling. *Science* **362**, 315-319 (2018).
7. Li, T. *et al.* A radiative cooling structural material. *Science* **364**, 760-763 (2019).
8. Zhao, D. *et al.* Radiative sky cooling: fundamental principles, materials, and applications. *Appl. Phys. Rev.* **6**, 021306 (2019).
9. Yin, X., Yang, R., Tan, G. & Fan, S. Terrestrial radiative cooling: using the cold universe as a renewable and sustainable energy source. *Science* **370**, 786-791 (2020).
10. Zeng, S. *et al.* Hierarchical-morphology metafabric for scalable passive daytime radiative cooling. *Science* **373**, 692-696 (2021).
11. Zou, C. *et al.* Metal-loaded dielectric resonator metasurfaces for radiative cooling. *Adv. Opt. Mater.* **5**, 1700460 (2017).
12. Ma, H. *et al.* Multilayered SiO₂/Si₃N₄ photonic emitter to achieve high-performance all-day radiative cooling. *Sol. Energy Mater. Sol. Cells* **212**, 110584 (2020).
13. Hossain, M. M., Jia, B. & Gu, M. A metamaterial emitter for highly efficient radiative cooling. *Adv. Opt. Mater.* **3**, 1047-1051 (2015).
14. Chae, D., Son, S., Liu, Y., Lim, H. & Lee, H. High-performance daytime radiative cooler and near-ideal selective emitter enabled by transparent sapphire substrate. *Adv. Sci.* **7**, 2001577 (2020).
15. Zhang, H. *et al.* Biologically inspired flexible photonic films for efficient passive radiative cooling. *Proc. Natl. Acad. Sci. U. S. A.* **117**, 14657-14666 (2020).
16. Liu, X. *et al.* Biomimetic photonic multiform composite for high-performance radiative cooling. *Adv. Opt. Mater.* **9**, 2101151 (2021).
17. Wang, X. *et al.* Scalable flexible hybrid membranes with photonic structures for daytime radiative cooling. *Adv. Funct. Mater.* **30**, 190756 (2019).
18. Xue, X. *et al.* Creating an eco-friendly building coating with smart subambient radiative cooling. *Adv. Mater.* **32**, e1906751 (2020).

19. Wang, T. *et al.* A structural polymer for highly efficient all-day passive radiative cooling. *Nat. Commun.* **12**, 365 (2021).
20. Yang, M. *et al.* Bioinspired "skin" with cooperative thermo-optical effect for daytime radiative cooling. *ACS Appl. Mater. Interfaces* **12**, 25286-25293 (2020).
21. Li, D. *et al.* Scalable and hierarchically designed polymer film as a selective thermal emitter for high-performance all-day radiative cooling. *Nat. Nanotechnol.* **16**, 153-158 (2021).
22. Zhong, H. *et al.* Hierarchically hollow microfibers as a scalable and effective thermal insulating cooler for buildings. *ACS Nano* **15**, 10076-10083 (2021).
23. Xiang, B. *et al.* 3D porous polymer film with designed pore architecture and auto-deposited SiO₂ for highly efficient passive radiative cooling. *Nano Energy* **81**, 105600 (2021).
24. Huang, W. *et al.* Scalable aqueous processing-based passive daytime radiative cooling coatings. *Adv. Funct. Mater.* **31**, 2010334 (2021).
25. Sun, K. *et al.* Metasurface optical solar reflectors using AZO transparent conducting oxides for radiative cooling of spacecraft. *ACS Photonics* **5**, 495-501 (2018).
26. Mandal, J., Yang, Y., Yu, N. & Raman, A. P. Paints as a scalable and effective radiative cooling technology for buildings. *Joule* **4**, 1350-1356 (2020).
27. Chen, J. & Lu, L. Development of radiative cooling and its integration with buildings: a comprehensive review. *Solar Energy* **212**, 125-151 (2020).
28. Blasco, E., Wegener, M. & Barner-Kowollik, C. Photochemically driven polymeric network formation: synthesis and applications. *Adv. Mater.* **29**, 1604005 (2017).
29. Corrigan, N., Yeow, J., Judzewitsch, P., Xu, J. & Boyer, C. Seeing the light: advancing materials chemistry through photopolymerization. *Angew. Chem., Int. Ed.* **58**, 5170-5189 (2019).
30. Guenther, A. J., Hess, D. M. & Cash, J. J., Dimensional stability of sparse network microstructures formed by photopolymerization-induced phase separation. *J. Polym. Sci., Part B: Polym. Phys.* **48**, 396-410 (2010).
31. Moore, D. G., Barbera, L., Masania, K. & Studart, A. R. Three-dimensional printing of multicomponent glasses using phase-separating resins. *Nat. Mater.* **19**, 212-217 (2020).
32. Bauer, F. *et al.* UV curing of nanoparticle reinforced acrylates. *Nucl. Instrum. Methods Phys. Res., Sect. B* **265**, 87-91 (2007).
33. Ngai, K. L. & Roland, C. M. Chemical-structure and intermolecular cooperativity-dielectric-relaxation results. *Macromolecules* **26**, 6824-6830 (1993).
34. Chen, M. *et al.* Designing mesoporous photonic structures for high-performance passive daytime radiative cooling. *Nano Lett.* **21**, 1412-1418 (2021).
35. Yoon, J., Lee, J. H., Lee, J. B. & Lee, J. H. Highly scattering hierarchical porous polymer microspheres with a high-refractive index inorganic surface for a soft-focus effect. *Polymers* **12**, 2418 (2020).
36. Liu, C. & Liao, X., Collagen fiber/Fe₃O₄/polypyrrole nanocomposites for absorption-type electromagnetic interference shielding and radar stealth. *ACS Appl. Nano Mater.* **3**, 11906-11915 (2020).
37. Mie, G. Articles on the optical characteristics of turbid tubes, especially colloidal

metal solutions. *Ann. Phys.* **25**, 377-445 (1908).

38. Lin, K. T. *et al.* Radiative cooling: fundamental physics, atmospheric influences, materials and structural engineering, applications and beyond. *Nano Energy* **80**, 105517 (2021).

39. Luo, H., Yang, M., Li, D., Wang, Q., Zou, W., Xu, J., Zhao, N. Transparent super-repellent surfaces with low haze and high jet impact resistance. *ACS Appl. Mater. Interfaces* **13**, 13813-13821 (2021).

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Author contributions

H. L. and N. Z. conceived the idea and designed the research. H. L., M. Y. and W. Z. performed the experiments. H.L. and J. G. analysed the data. H. L. and N. Z. wrote the manuscript. N. Z. and J. X. supervised the study. All authors commented on the paper.

Competing interests

There are no conflicts to declare.

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