Energy Proceedings
Vol 50, 2025
ISSN 2004-2965

A Hierarchical Designed Superhydrophobic SiO_2/PVDF-HFP Nanofibrous Membrane for All-Day Radiative cooling[#]

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ABSTRACT

All-day passive radiative cooling materials, which are dedicated to cool objects by reflecting solar light and dissipating heat to the cold outer space, have received extensive attention in recent years. As a common radiative cooling material, poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) has high atmospheric window infrared emittance. However, the PVDF-HFP-based radiative cooler has low reflectance of sunlight and is prone to be contaminated, which would reduce the radiative cooling performance in outdoor applications. Therefore, in order to enhance the optical property and self-cleaning capability of the PVDF-HFP membrane, we herein prepared a hierarchical superhydrophobic SiO_2/PVDF-HFP nanofibrous membrane by electrospinning and electrostatic spraying technique; the radiative cooling performance of the as-prepared membrane is compared with that of the commercial PVDF-HFP membrane. The results demonstrate that the hierarchical superhydrophobic SiO_2/PVDF-HFP nanofibrous membrane consists of numerous stacked nanofibers and is uniformly distributed by SiO_2 particles, which enable the membrane to exhibit an average solar spectral reflectance of 97.8% and an average atmospheric window infrared emittance of 96.6% (both values are higher than those of the commercial PVDF-HFP membrane). The hierarchical SiO_2/PVDF-HFP membrane achieves sub-ambient temperature up to 11.5℃ under direct sunlight and 4.1℃ at night, demonstrating superior radiative cooling performance. Moreover, the hierarchical SiO_2/PVDF-HFP membrane possesses excellent self-cleaning property, remarkable flexibility, and mechanical stability, which endows the membrane with promising applications in cooling vehicles, buildings, large-scale equipment, etc.

Keywords: energy-free, all-day radiative cooling, hierarchical design, nanofibers, superhydrophobic

1. INTRODUCTION

Compressor-based cooling systems consume tremendous amounts of energy and release greenhouse gases into the environment, contributing to the energy crisis and the global warming (Biardeau et al., 2020; Munday, 2019). All day radiative cooling technique can cool objects to sub-ambient temperatures without any external energy input, which is an environmentally friendly and low-energy-loss strategy (Goldstein et al., 2017; Hu et al., 2020; Ürge-Vorsatz et al., 2015). To achieve all day radiative cooling, a radiator should have a high solar reflectance (0.3-2.5 μm) and be able to maximize the release of heat into outer space through atmospheric windows (8-13 μm) (Li et al., 2019; Zhao et al., 2019).

In recent years, polymer-based coolers based on creating light-scattering air voids have been investigated to achieve efficient all-day radiative cooling, especially during the daytime (Chae et al., 2020; Zhai et al., 2017; Zhang et al., 2020). For example, in 2018, Mandal et al. (Mandal et al., 2018) prepared a hierarchically porous poly (vinylidene fluoride-co-hexafluoropropene) [P(VdF-HFP) HP] coatings by phase inversion method. The micro- and nanopores in the coating can strongly scattering sunlight, allowing it to achieve a temperature drop of 6.3℃ and a cooling power of 96 $W \cdot m^{-2}$ under direct sunlight. Zhai et al. (Zhai et al., 2017) prepared a randomized glass-polymer hybrid metamaterial film by randomly distributing silica (SiO_2) particles into the transparent polymer polymethyl-pentene (TPX) and depositing a layer of silver (Ag) on the backside of the film. Due to the phonon-polariton resonance of the SiO_2 particles and the high solar reflectance of the Ag layer, the film exhibits high infrared emittance of more than 93% and high solar reflectance of 96%. Polymer-based radiative coolers are low cost, flexible, and scalable,

This is a paper for the 16th International Conference on Applied Energy (ICAE2024), Sep. 1-5, 2024, Niigata, Japan.

showing the potential to meet the increasing demand of practical applications (Bao et al., 2017; Drioli et al., 2015). However, it worth noting that equipment applied outdoors is susceptible to contamination by the build-up of rain or dust over time, which may degrade the solar reflectance and atmospheric window IR emittance of the materials, thereby adversely affecting the radiative cooling performance (Lu et al., 2015; Xu et al., 2013).

Herein, we fabricated a hierarchical superhydrophobic polymer-based radiative cooler, which consisted of PVDF-HFP nanofiber membrane and SiO_2 nanoparticles developed by electrospinning and electrostatic spraying. Due to the combined effect of the PVDF-HFP nanofiber membrane and the uniformly distributed SiO_2 particles on the surface, the cooler exhibits a high average solar reflectance of 97.8% and a high average atmospheric window infrared emittance of 96.6%. In addition, the uniform distribution of SiO_2 on the surface endows the membrane excellent self-cleaning property, while the special bead (SiO_2 nanoparticles)-on-string (nanofibers) structure increases the durability of the membrane.

2. MATERIAL AND METHODS

2.1 Fabrication of the hierarchical superhydrophobic SiO_2/PVDF-HFP nanofiber membrane

Electrostatic spinning and electrostatic spraying techniques are used to prepare the typical sample (Fig. 1). Acetone and N, N-dimethylacetamide (DMAC) were mixed in a mass ratio of 7:3 as the solvent (Acetone/DMAC) and 0.06 g of lithium chloride (LiCl) was added to improve the electrical conductivity. The spinning solution was obtained by adding 9 g of PVDF-HFP 51 g of the Acetone/DMAC solution and magnetically stirring at 70℃ for 12 h. 20 g of spinning solution was loaded into a 20 mL syringe and held at a distance of 20 cm from the receiving roller. The spinning solution was electrospun (SS-2535H, Ucalery, Beijing, China) at an ambient temperature of 25°C and a humidity of 45%, with a positive and negative voltage of 21 KV and 2.5 KV respectively and an injection speed of 0.15 mm/min. After 10 h of spinning, the PVDF-HFP nanofiber membrane with a thickness of ~0.5 mm as dried at 80℃ for 30 min.

The SiO_2 nanoparticles were attached to the PVDF-HFP nanofiber membrane by electrostatic spraying. Firstly, the PVDF-HFP and SiO_2 nanoparticles, both with a mass fraction of 4wt% to the solution, were mixed into 4.2 g of Acetone/DMAC and stirred thoroughly for 3 h at room temperature and then ultrasonic vibrated for 1 h. The PVDF-HFP nanofiber membrane (300 mm long and 80 mm wide) was fixed on the receiving end as the substrate and the injection speed were the same as spinning. After spraying SiO_2 at a positive voltage of 23.8 KV and a negative voltage of 2.3 KV for 4 hours, the hierarchical membrane was dried at 80℃ for 30 min. Then the membrane was immersed in a silane solution consisting of 10 µL of 1H,1H,2H,2H-perfluorooctyl trichlorosilane and 20 mL of n-hexane for 30 min for fluorination modification. After drying at 60°C for 2 h, the hierarchical superhydrophobic SiO_2/PVDF-HFP nanofiber membrane (labeled as SHPo-SP NFM) was obtained. Commercial PVDF-HFP membrane (labeled as PVDF-HFP CM, thickness ~0.7 mm) was purchased from Shanghai Shengli Industrial Co., Ltd (China).

2.2 Characterization

The micro and nanoscale morphology of the membrane surface was detected by a field emission scanning electron microscopy (FEI Nova Nano SEM 450, USA) and the size distribution of nanofibers, SiO_2 nanoparticles and micropores were measured by ImageJ software. The reflectance spectral (0.3-2.5 µm) were recorded using a UV−VIS−NIR spectrophotometer (SolidSpec-3700, Shimadzu) and the spectral infrared emittance (5-25 µm) were measured using a Fourier transformed infrared (FT-IR) spectrometer (Bruker VERTEX 80). The values for the water contact angles (CA) and sliding angles (SA) were obtained by averaging the data from 5 different points on each sample using a contact angle goniometer (Ram é-hart 290-U1, USA).

2.3 Radiative cooling performance measurement

All Samples was placed on a self-designed apparatus, which consisted of 2 polystyrene (PS) foam blocks measuring 20 cm×20 cm×12 cm with an air chamber measuring 7 cm×6 cm×1.2 cm at the top of each block. The foam blocks were wrapped in aluminium (Al) foil to reduce solar heat and the opening of the chambers were sealed with polypropylene (PE) film. The real-time temperatures of the samples were measured by thermocouples fixed to the back of each sample and the temperatures of the ambient circumstance were monitored by fixing the thermocouple in the air chamber. An 8-channel temperature logger (EX-6000, Yili Technology corp, China) was used to recorded the temperatures during the test every 5 s and a solar power (TES-1333R, TES electric electronics corp. Taiwan, China) were used to recorded irradiance. The ambient relative humidity was measured by a hygrometer (GSP-8, Elitech corp, China).

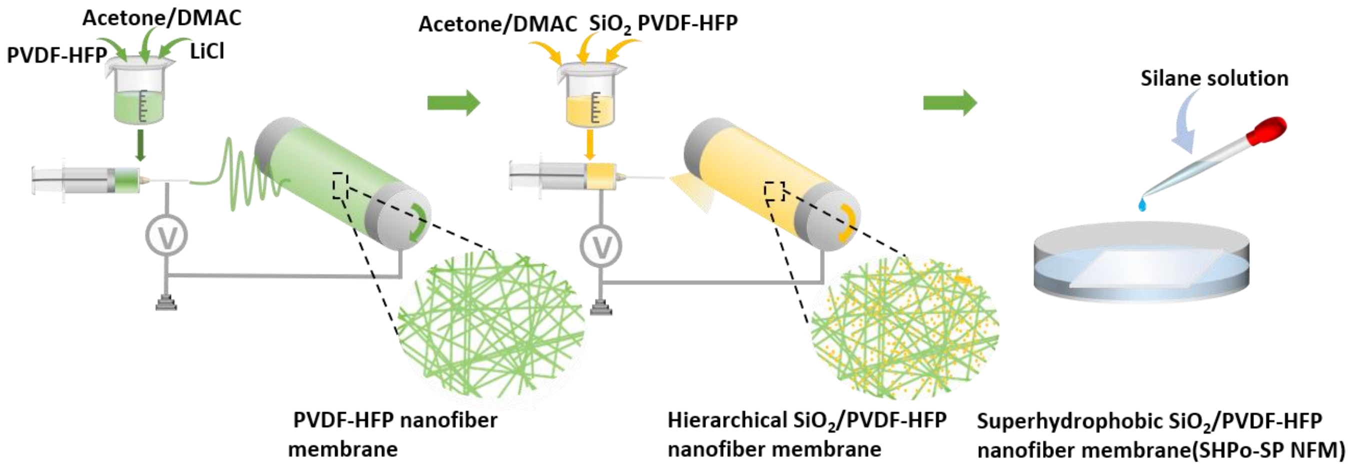

Fig. 1 Schematic diagram of the preparation of the hierarchical superhydrophobic SiO_2/PVDF-HFP nanofiber membrane (SHPo-SP NFM).

3. RESULTS AND DISCUSSION

3.1 Morphology, superhydrophobic and optical properties

Fig. 2a shows the morphology of the SHPo-SP NFM, it can be seen that the underlayer of the membrane consists of a large number of interlaced nanofibers and the top is decorated with SiO_2 nanoparticles. The high magnification SEM image shows the SiO_2 nanoparticles are connected by many nanofibers, forming a special bead (SiO_2 nanoparticles)-on-string (nanofibers) structure, which improves the adhesion of SiO_2 to the nanofiber membranes. The formation of this structure is attributed to the appropriate addition of PVDF-HFP to the electrostatic spraying solution, which improves the interaction between the polymer chains and creates a continuous jet under the electrostatic field(Ge et al., 2018). The uniformly distributed SiO_2 nanoparticles improve the roughness of the membrane surface and endow the membrane remarkable superhydrophobicity with CA > 164° and SA < 2.8° (inset of Fig. 2a) after surface modification. The PVDF-HFP CM is a dense polymer membrane with a thickness of ~0.7 mm (Fig. 2b).

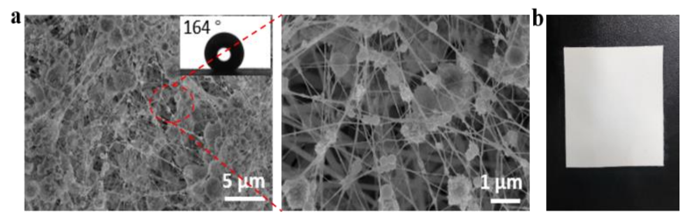

Fig. 2 (a) SEM images of the PVDF-HFP nanofiber membrane (PVDF-HFP NFM) and (b) photograph of the PVDF-HFP commercial membrane (PVDF-HFP CM).

The efficiency of radiative cooling depends heavily on solar reflectance and atmospheric window infrared emittance. Fig. 3a shows the comparison of the optical properties of SHPo-SF NFM and PVDF-HFP CM. The solar reflectance of the SHPo-SP NFM is much higher than that of PVDF-HFP CM, with an average reflectance of 97.8% (PVDF-HFP CM only 75.1%) (Fig. 3b). According to Kirchhoff's law, the infrared emittance (ε) of an object can be calculated by equation $\varepsilon=1-t-r$, where r is the infrared reflectance and t is the infrared transmittance. The average atmospheric window emittance was calculated to be 96.6% and 94.4% for the SHPo-SP NFM and PVDF-HFP CM, respectively. The high optical properties of the SHPo-SP NFM should be ascribed to the hierarchical structure consisting of stacked nanofibers and SiO_2 nanoparticles and the pores formed by the interlaced nanofibers. Fig. 3c shows the size distributions of fibers, pores and particles. Firstly, the fiber diameters are mostly distributed in the range of 0.1-0.7 µm, which can effectively reflect sunlight. Second, the agglomerated SiO_2 nanoparticles of 0.5-3.5 µm caused a refractive index mismatch between the interlaced nanofibers and the micropores in the base membrane, which severely scattered sunlight in the spectral region(Huang et al., 2020; Zhao et al., 2019). Furthermore, the phonon polarization resonance of the Si-O bond confers the SiO_2 nanoparticles high emittance (Chen et al., 2021; Wang et al., 2021). Third, most of the spectrum of sunlight can be reflected by micropores of ~5 μm and the short wavelength can be further scattered by micropores of ~0.5 μm, which are all formed by interlacing stacks of nanofibers (Mandal et al., 2018). In summary, owing to the unique structure, the SHPo-SP NFM has more superior optical properties, suggesting greater potential for all-day radiative cooling.

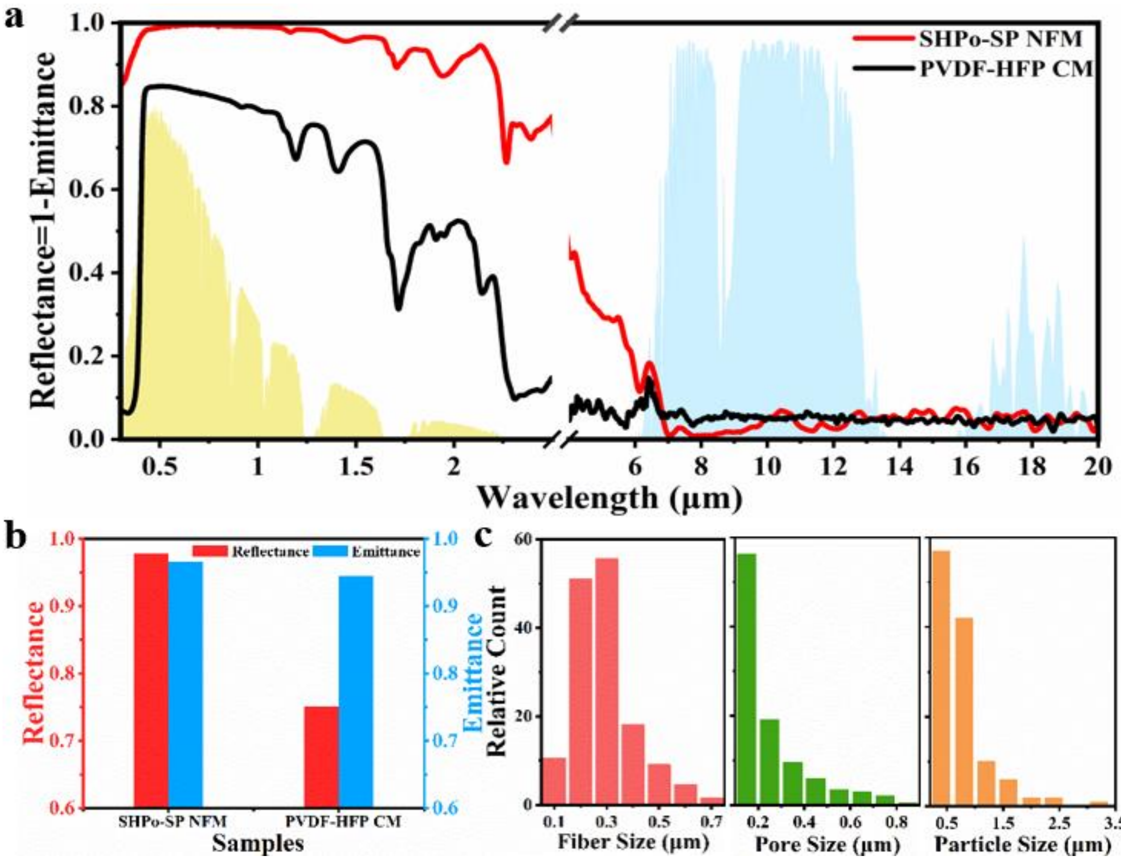

Fig. 3 (a) Spectra reflectance (R=1-E) of the SHPo-SP NFM and the PVDF-HFP CM displayed with the AM1.5 solar spectrum (shaded yellow color) and atmospheric transparency window (shade blue color) as background. (b) Average solar reflectance and average atmospheric window emittance of the samples in (a). (c) The size distribution of nanofibers, particles and pores of the SHPo-SP NFM.

3.2 Cooling performance and practical applications

Outdoor experiments were conducted on the roof of Nanjing University of Science and Technology (N32°01′, E118°51′, Jiangsu, China) to demonstrate the cooling performance of the SHPo-SP NFM. A self-designed experimental apparatus was placed on a 1 m high platform to reduce the effect of heat radiation from the roof (Fig. 4a). As the sample was placed in the foam chamber and the opening was covered with PE film, the temperatures of the sample were affected by the air inside the chamber and therefore the air inside the chamber was a better environment for the film than the outside air. Daytime and nighttime temperatures of SHPo-SP NFM were measured compared to the temperatures of PVDF-HFP CM and ambient (PE covered air). As shown in Fig. 4b, the SHPo-SP NFM exhibits a much lower average temperature of 31.8℃ under direct solar intensity of up to 806 $W \cdot m^{-2}$, reaching a temperature drop (ΔT) of 11.5℃ relative to the ambient. The intensity of sunlight decreased continuously during the period from 13:00 PM to 15:00 PM, while the temperature of the SHPo-SP NFM still increased, probably due to the excellent insulation of the foam chamber, which prevented the membrane from dissipating heat, and the higher air temperature inside the chamber which transferred heat to the membrane, causing the temperature of the membrane to increase. During the nighttime, the SHPo-SP NFM radiated heat into outer space through the atmospheric window, exhibiting the lowest temperature, which is 4.1℃ lower than the ambient temperature, which can meet the need of nighttime radiation cooling. In the outdoor experiments, the absolute error of the thermocouple used to measure the real-time temperatures was ±0.5℃, the average relative error of the temperature of SHPo-SP NFM was calculated to be less than 2%, which is negligible.

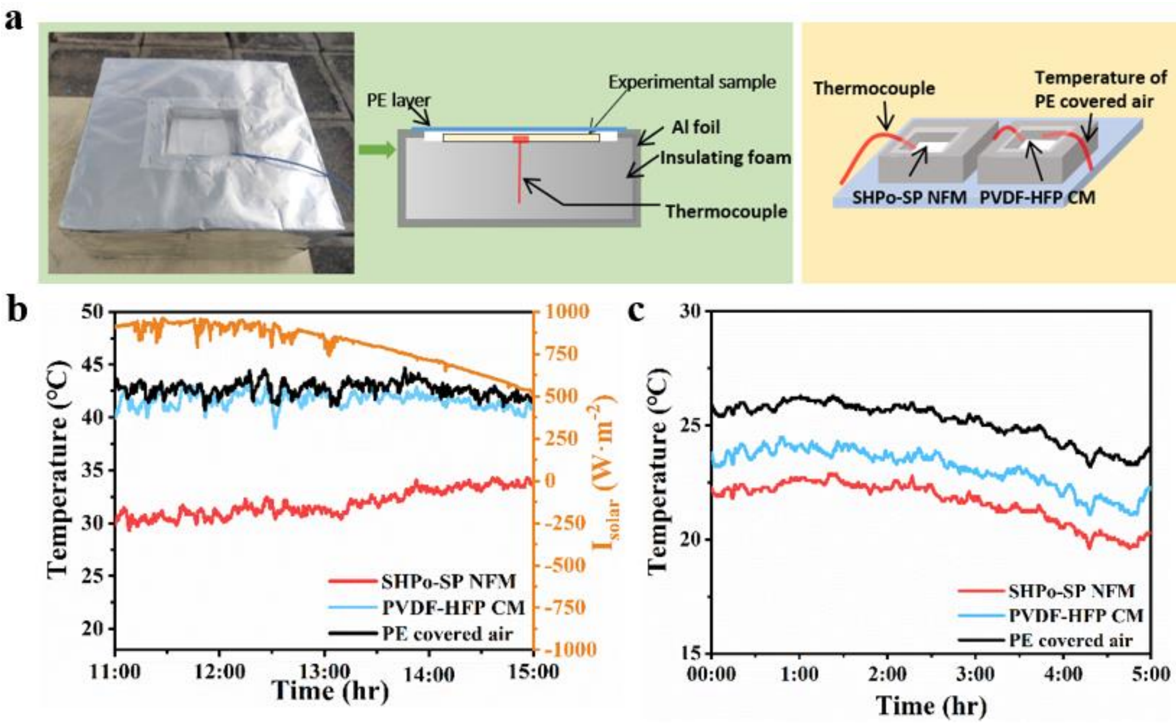

Fig. 4 (a) Photograph and schematics of the apparatus used to test the real time radiative cooling performance of the samples. (b) Real-time temperatures of the SHPo-SP NFM, PVDF-HFP CM and ambient circumstance (PE covered air) under direct sunlight. (c) Nighttime temperatures of the SHPo-SP NFM, PVDF-HFP CM and ambient circumstance (PE covered air).

In order to demonstrate the cooling performance of the SHPo-SP NFM in practical applications, car models and house models were used for testing. As shown in Fig. 5a, two car models covered by SHPo-SP NFM and PVDF-HFP CM, respectively, and one bar car model are placed on the ground for testing at midday with strong sunlight. The infrared (IR) image shows that the car model covered with SHPo-SP NFM displayed the lowest temperature of 38.8℃, while the temperature of the bare car model was as high as 55.7℃. In addition, the real-time temperatures of three car models were measured by fixing the thermocouples between the models and the membranes. Fig. 5c reveals that the SHPo-SP NFM-covered car model exhibits an average temperature of 40.3℃ in strong sunlight, which is lower than that of the PVDF-HFP CM-covered cart model (45.7℃) and even reaches the temperature difference of 12℃ with the bar car model. Furthermore, the SHPo-SP NFM can also be applied as a roof shade for indoor cooling (Fig. 5d). The real-time temperatures of one bare house model and two-house models covered by the SHPo-SP NFM and PVDF-HFP CM were recorded for comparison (Fig. 5e). The SHPo-SP NFM-covered house model shows the lowest average indoor temperature (33.9℃), which is 4.2℃ lower than the bare house model. Accordingly, the temperature drops of the models covered by the SHPo-SP NFM indicates the potential of this membrane in practical applications such as vehicles, buildings, and large-scale equipment, etc.

3.3 Self-cleaning property and stability of the SHPo-SP NFM

Long-term application of outdoor coolers is usually impacted by raindrop washing, dust accumulation and acid/alkali-base corrosion, resulting in reduced cooling performance (Chu et al., 2012) The synergistic cooperation of nanofibers and SiO2 endows the SHPo-SP NFM excellent flexibility, as the membrane can be twisted and bent at will (Fig 6a). In addition, the sample surface also shows favorable superhydrophobicity, which allows the membrane to be self-cleaning without contamination (Fig 6b). As shown in Fig 6c, carbon black powders were sprinkled on the SHPo-SP NFM surface to simulate dust contamination, and when water is dripped

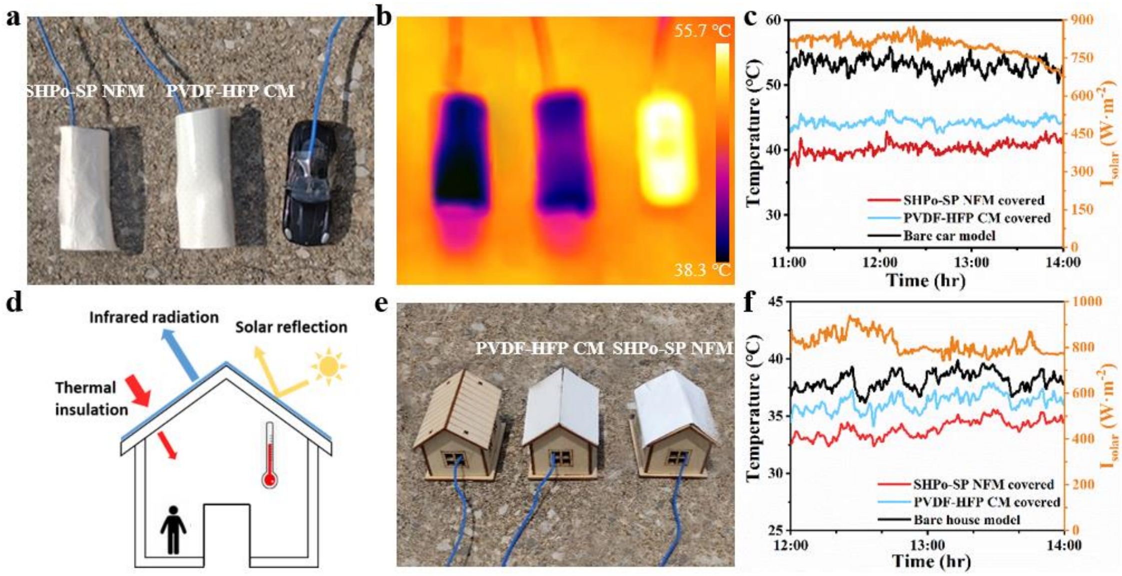

Fig. 5 Cooling performance of the SHPo-SP NFM on car model and house model. (a) Photographs of a bare car model and the other two car models covered by SHPo-SP NFM and PVDF-HFP CM respectively. (b) IR picture of (a). (c) Real-time temperatures of the car models in (a) under direct sunlight. (d) SHPo-SP NFM with high solar reflectance and infrared emittance of atmospheric windows utilized in building roof cooling devices. (e) Photographs of a bare house model and the other two models covered by SHPo-SP NFM and PVDF-HFP CM respectively. (f) Real time temperatures inside the three house models under direct sunlight.

onto the membrane, the water droplets can flow down smoothly and carry away the carbon black along the way without leaving any traces. After the membrane has been completely cleaned by water flow, the surface still exhibits comparable CA and SA to the pristine sample after being immersed in the aqueous solutions of PH=1and PH=14 for 72 h (Fig 7a). Considering the necessity of mechanical stability of the SHPo-SP NFM, membrane surface was touched by finger for 80 cycles, after which the surface remained superhydrophobic CA of 153° and SA of 6° (Fig 7b), demonstrating the contribution of bead-on-string structure to SiO_2 adhesion. In addition, the durability of the SHPo-SP NFM under long-time sunlight was tested. The sample were left outdoors for 40 days and guaranteed to be exposed to direct sunlight, after which the optical properties were tested. As shown in Fig 7c-d, compared to the original sample, the solar reflectance after outdoor exposure exhibits minimal decrease in solar reflectance, while the infrared emittance in the atmospheric window remained largely unchanged. Meanwhile, the membrane exhibits a CA of 160° and a SA of 4.2° after 40 days of outdoor exposure. The sample retains excellent optical properties and superhydrophobicity after prolonged exposure to direct sunlight, which indicates the potential of the sample for long-term outdoor applications.

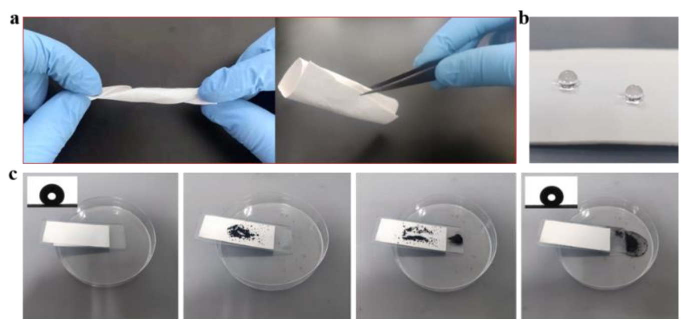

Fig. 6 (a) Photographs of the SHPo-SP NFM after twisting and curling, showing excellent flexibility. (b) Photograph of the SHPo-SP NFM with droplets of water. (c) Photograph of the self-cleaning process of the membrane.

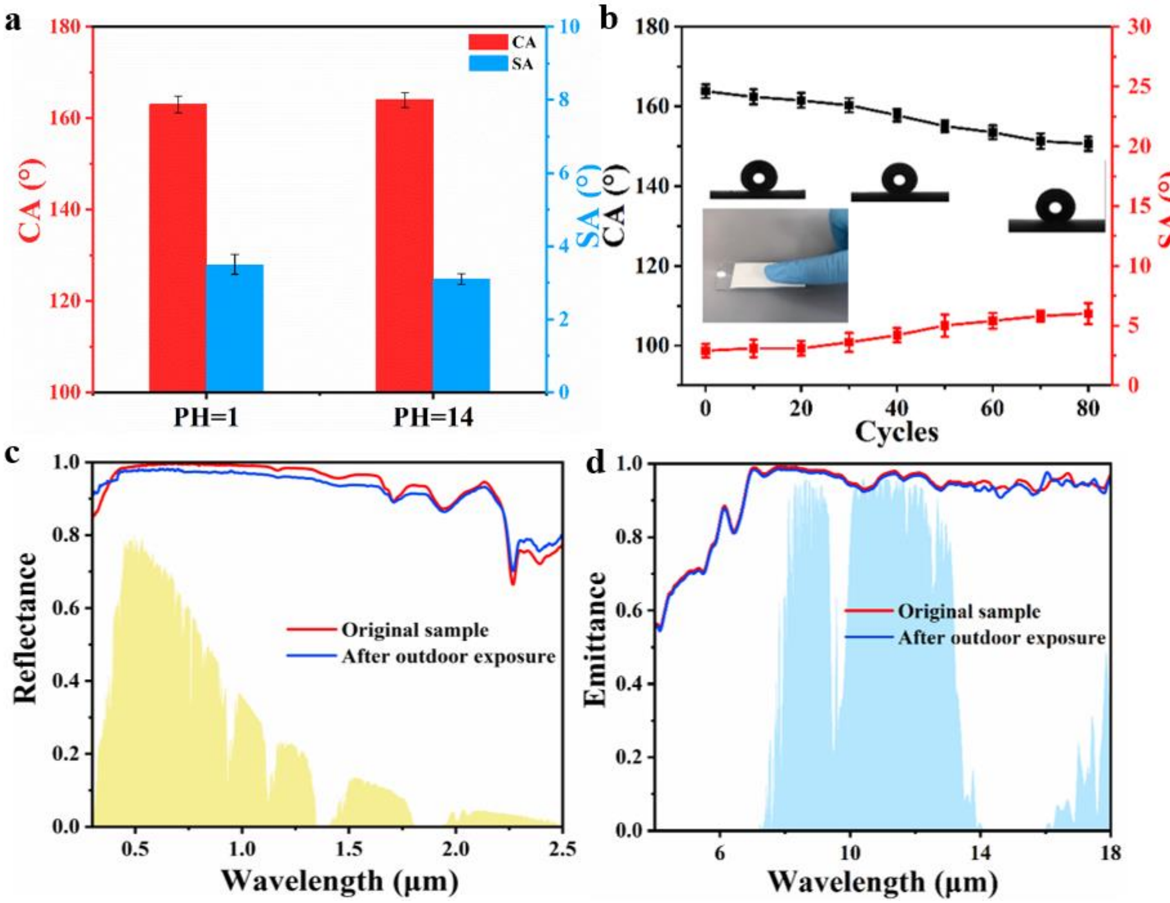

Fig. 7 (a) Water droplet CA and SA of the SHPo-SP NFM after being immersed in the aqueous solutions of PH=1 and PH=14 for 72 h. (b) The CAs/SAs of the SHPo-SP NFM after multiple finger touch test. The comparison of (c) spectral solar reflectance, and (d) spectral infrared emittance of SHPo-SP NFM before and after outdoor exposure.

4. CONCLUSIONS

In summary, the hierarchical SHPo-SP NFM for radiative cooling was prepared by facile electrospinning and electrostatic spraying method. The membrane exhibits excellent optical properties as a result of the hierarchical structure and the phonon-polarized resonance of SiO_2 nanoparticles, achieving superior radiative cooling performance compared to the PVDF-HFP CM with a temperature drop of 11.5℃ and 4.1℃ relative to ambient during the day and night, respectively. Meanwhile, the SHPo-SP NFM exhibits remarkable flexibility, self-cleaning ability, and stable chemical/mechanical properties. This work demonstrated a promising method to improve surface designs for functional radiative cooling applications.

ACKNOWLEDGEMENT

The authors acknowledge the financial support from the National Natural Science Foundation of China (52276071 and U2241252).

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