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# A dual-layer polymer-based film for all-day sub-ambient radiative sky cooling

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## **Credit Author Statement**

**Jie Liu:** Performed the experiments, Data curation, Formal analysis, Writing – original draft, Writing – review & editing; **Chengfeng Xu**: Performed the simulation and data analysis, Writing – review & editing; **Xianze Ao**: Data analysis, Writing – review & editing; **Kegui Lu**: Performed spectral testing; **Bin Zhao**: Project administration, Performed the experiments, Formal analysis, Writing – review & editing, Funding acquisition, conceived the idea and supervised the project; **Gang Pei**: Project administration, Writing – review & editing, conceived the idea and supervised the idea and supervised

## A dual-layer polymer-based film for all-day sub-ambient radiative sky cooling

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## Abstract

Radiative sky cooling (RSC) is a promising eco-friendly technique that requires no energy input for subambient cooling. A radiative cooler with high solar reflection and strong thermal emission is the key to achieving sub-ambient cooling effect. Recently, polymer-based coolers have attracted much attention due to their excellent radiative properties and flexibility. Herein, the parasitic absorption of functional groups is applied to select polymer materials for radiative cooling, and a dual-layer film consisting of ethylene-tetrafluoro-ethylene (ETFE) film and silver layer is fabricated for all-day sub-ambient RSC. Optical characterization shows that the fabricated ETFE cooler exhibits a high AM1.5 spectra-weighed solar reflectivity of 94% and has an average emissivity of nearly 0.83 in the atmospheric window (i.e.,8-13 μm). Besides, thermal performance tests reveal that the cooler's temperature is on average 3.0°C lower than ambient air during daytime in Hefei, and is approximately 1.6°C below ambient air even at noon. Additionally, the thermal performance prediction also indicates that the ETFE cooler is a good candidate for sub-ambient RSC. Keywords: Radiative sky cooling; Passive cooling; Polymer film; ETFE; Spectral selectivity

## **1. Introduction**

These days, global energy consumption has been surging, which requires widespread renewable energy as an alternative to traditional ones [1, 2]. As a passive cooling method, RSC has drawn great interest in academia [3-6]. Terrestrial objects can obtain sub-ambient cooling through thermal radiation through the atmospheric transparency window (i.e., 8-13 µm) [7-9].

Journal Pre-proof			
Nomenclature			
С	speed of light, $m \cdot s^{-1}$	ATR-FTIR	attenuated total reflectance
h	Planck's constant, J·s		Fourier transform infrared
Ι	spectral intensity, $W{\cdot}m^{-2}{\cdot}\mu m^{-1}{\cdot}sr^{-1}$	FTIR	Fourier transform infrared
$k_B$	Boltzmann constant, $J \cdot K^{-1}$	LDPE	low-density polyethylene
Р	heat flux, $W \cdot m^{-2}$	MCP	maximum cooling power
Т	temperature, K	MTD	maximum temperature difference
$h_c$	effective heat transfer coefficient,	PMMA	polymethyl methacrylate
	$W \cdot m^{-2} \cdot K^{-1}$	PVDF	polyvinylidene fluoride
G	solar irradiance, $W \cdot m^{-2}$	P(VDF-HFP)	poly(vinylidene fluoride
Greek letter			-hexafluoropropylene)
α	absorptivity	RSC	radiative sky cooling
З	emissivity	ТРХ	polymethyl pentene
t	transmittance	amb	ambient air
$\theta$	zenith angle, ra	atm	atmosphere
λ	wavelength, µm	BB	blackbody
${\it \Omega}$	solid angle, sr	net	net cooling
Abbreviation and subscripts		cond+conv	conduction and convection
ETFE	ethylene-tetra-fluoro-ethylene	rad	radiation

RSC was first investigated at night. High emissivity in the mid-infrared wavelength band, especially in the atmospheric window, is required for efficient nighttime passive cooling [5]. Harrison et al. realized a maximum temperature drop of 15°C at night by utilizing TiO<sub>2</sub> white paint whose emissivity in the 8-13  $\mu$ m region is approximately 92% [10]. Granqvist et al. fabricated a spectrally selective surface by evaporating silicon monoxide films onto a smooth Al substrate. They demonstrated a temperature drop of 14°C below the ambient temperature during a clear night [11].

However, achieving sub-ambient cooling under direct sunlight is more attractive since the peak cooling demand mainly concentrates on the daytime. Compared with the previously reported coolers for night RSC, the solar absorption of daytime radiative coolers needs to be maximally suppressed and their thermal emissivity should be simultaneously enhanced. In recent years, spectral selectivity has been successfully achieved by advanced optical materials and structures, including stacks of dielectric materials [3],

metamaterials [12-15], paint [16], and polymer-based coatings [17-19]. In 2014, Raman et al. [3] firstly demonstrated the sub-ambient RSC during the daytime through experiment tests based on a multilayer photonic cooler that contains alternative HfO<sub>2</sub> and SiO<sub>2</sub> layers on top of a 200-nm-thick Ag layer. The cooler can reflect 97% solar irradiance and has an average emissivity of approximately 0.7 in the atmospheric window, which demonstrates the cooling effect of nearly 5°C below the ambient temperature and a maximum cooling power of 40.1 W/m<sup>2</sup>. Since that, photonic coolers became a widely-used base for designing high-performance radiative coolers. Dongwoo et al. [20] proposed an optimized photonic cooler consisting of simple multilayer inorganic materials including Al<sub>2</sub>O<sub>3</sub>, Si<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub>, and silver. The proposed cooler exhibits high emission of 87% in the 8-13 µm region and its average absorptivity in the solar band is 5.2%. The photonic radiative cooler can achieve the RSC performance of 8.2°C below ambient temperature during the daytime.

Although photonic coolers have excellent spectral selectivity, the fabrication of complicated structures (e.g., pyramids and gratings) is based on the precise process (e.g., etching method), which is not available for large-scale production. Thus, polymer materials with the potential for large-scale fabrication became alternatives for the next-generation radiative cooler. To achieve efficient sub-ambient RSC based on polymer materials, the polymer materials need to fulfill the following requirements. First, they should be optically lossless to minimize solar absorption. Second, the extinction coefficient of polymer materials should be high in the thermal radiation band to enlarge radiation exchange with outer space. Following the above requirements, various polymer-based coolers have been developed, including transparent polymer/highly reflective silver layer and micro/nanostructure-based polymer with strong solar scattering. Zhai et al. [21] embedded micron-sized resonant polar dielectric SiO<sub>2</sub> spheres randomly in a TPX matrix, resulting in an infrared emissivity greater than 0.93 across the atmospheric window. The metamaterial can reflect 96% of solar irradiance and generate a noontime radiative cooling power of 93 W/m<sup>2</sup> when backed with silver coating. Mandal et al. [22] proposed hierarchically porous PVDF-HFP coatings fabricated via phase-inversion-based method. Attributing to the role of backscattering sunlight and enhancing thermal emittance played by propersize nanopores, the coatings possessed solar reflectivity of 96% and emittance of 97% in the 8-13µm region without silver coating. This optical property enabled the coatings to achieve a sub-ambient temperature drop

of 6°C and cooling powers of 96  $W/m^2$  under solar intensities of 890  $W/m^2$  and 750  $W/m^2$ .

The excellent radiative properties and flexibility of polymer-based coolers make it vital to explore the mechanism of the polymer materials' strong thermal emission. Moreover, it can be a practical guide for the selection and fabrication of polymer-based radiative coolers without complex top-down fabrication. Aili et al. [19] demonstrated the selection of applicable polymer materials for RSC through functional groups. They proposed that the specific functional groups including C–O, C–Cl, C–F, and C–N (6.7-16.7 µm) could identify potential polymer candidates with strong emission in the atmospheric window. Thus, they chose two common polymers-PVDF and PMMA films, and successfully demonstrated sub-ambient radiative cooling of water in all-day outdoor experiments.

Taking the above-mentioned consideration into account, the parasitic absorption of functional groups is applied to select polymer materials for radiative cooling in this work. Through the absorption peaks generated by the characteristic vibrations of specific functional groups in the infrared band, we chose the polymer materials with specific functional groups- C—F and C—H from the vast variety of polymer materials. Besides, the solar absorption of the polymer materials was also considered during the cooler design. The higher transmittance the polymer materials have, the higher solar reflectivity the polymer-based coolers have after being combined with the highly reflective layer. Based on the above analysis, we applied the ethylene-tetra-fluoro-ethylene (ETFE) film with good light transmittance and high thermal emission to the design of a polymer-based daytime radiative cooler for the first time.

In this paper, a dual-layer ETFE/Ag cooler (i.e., ETFE cooler) is proposed and fabricated for all-day subambient RSC. Spectral properties of the ETFE cooler are measured to confirm its high solar reflection and strong thermal emission. Outdoor experiments are performed in Hefei, China (31.86°N, 117.27°E) and Beijing, China (39.92°N, 116.46°E) to evaluate the radiative cooling performance of ETFE cooler. Moreover, a preliminary parametric analysis is conducted to reveal the radiative cooling performance of the ETFE cooler under different conditions.

## 2. Experiment section

## 2.1 Fabrication and characterization

The ETFE cooler consists of an optically transparent ETFE film, an silver (Ag) layer, and a silica (SiO<sub>2</sub>) layer. The transparent ETFE film provides high infrared emission due to its functional groups' vibrations induced electromagnetic wave absorption. For polymer material, thicknesses from tens of microns to 100 microns have been widely applied for high infrared emission. Herein, ETFE film with a thickness of 25 µm is selected due to that it can produce strong infrared emission while maintaining high light transmittance. If thicker ETFE film is used, the parasitic solar absorption of the cooler will increase, which will counteract the radiative cooling effect. Ag layer coated below the ETFE film can reflect sunlight. A thin Ag layer will transmit some light, while a 200 nm thick Ag layer is enough to reflect visible and infrared light. Notably, a 200-nm-thick Ag layer is commonly used as a solar reflector for efficient radiative coolers [3, 20, 21]. We simulate the spectral transmittance of Ag with different thicknesses in the wavelength range of 300-1500 nm and the results are shown in Fig. 1. The transmittance of the Ag layer gradually decreases as its thickness increases and the 200-nm-thick Ag layer is almost opaque to sunlight and can be used for daytime radiative cooling. Moreover, the SiO<sub>2</sub> layer is used to protect the Ag layer from being oxidated.



**Fig. 1.** The spectral transmittance of the Ag layer with different thicknesses in the wavelength range of 300-1500 nm. During the fabrication, the ETFE cooler (Fig. 2) is fabricated by depositing a 200-nm-thick Ag layer on

the 25- $\mu$ m-thick ETFE film (Daikin Fluorochemicals(China)Co., Ltd) using electron beam evaporation (Lesker LAB18, Kurl J Lesker Company). The background vacuum during evaporation is less than 10<sup>-8</sup> Torr. The deposition rate of the Ag is 2 Å/s to ensure the uniform surface of the Ag layer. Besides, a 60-nm-thick silica layer is then deposited on the Ag layer at a rate of 0.6 Å/s.



**Fig. 2.** Photo and schematic of the ETFE cooler. The left object is a 1-mm-thick Al film that is provided for comparison. The ETFE cooler is composed of a 25-µm-thick ETFE film, a 200-nm-Ag layer, and a 60-nm-thick silica layer.

The solar spectral reflectivity of the ETFE cooler is measured by a UV-Vis-NIR spectrometer (SolidSpec-3700, Shimadzu) equipped with a barium sulfate-coated integrated sphere. The spectral emissivity of the ETFE cooler in the mid-infrared wavelength region is obtained by a Fourier transform infrared (FTIR) spectrometer (Nicolet iS 10, Thermo Fisher Scientific) equipped with a gold-coated integrated sphere, combining the energy balance law and Kirchhoff's law [23].

As shown in Fig. 3, the ETFE cooler exhibits high solar reflectivity with a weighted solar reflection of 94%, which is greater than the commercial reflective Al film (80.6%). Besides, it can be seen from Fig. 4 that the ETFE cooler has a strong thermal emission in the mid-infrared wavelength region. The weighted thermal emissivity in the atmospheric window is approximately 0.83. The above spectral properties of the ETFE cooler indicate that ETFE is a potential candidate for efficient RSC.



**Fig. 3.** The measured solar reflectivity of the ETFE cooler and the Al film in the wavelength range of 0.3-2.5 µm. The red part represents a normalized AM1.5 solar spectrum.



Fig. 4. The measured thermal emissivity of the ETFE cooler and the Al film in the wavelength range of  $2.5-15 \mu m$ . The light blue part represents the atmospheric transmittance of mid-latitude winter obtained from the MODTRAN model [24].

The exhibited strong emissivity in the atmospheric window is because the ETFE film has functional groups whose vibrations contribute to absorption peaks in this band. The attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet iN10MX, Thermo Fisher) is used to characterize the infrared absorbance spectrum of the ETFE film, which reveals structural information of organic components

on the surface of the ETFE film can be obtained. According to the energy level transition caused by the molecular vibration after absorbing the radiation energy, the obtained infrared absorption spectrum (Fig. 5) shows two absorption peaks resulting from the antisymmetric (1164 cm<sup>-1</sup>) and symmetric (1249 cm<sup>-1</sup>) stretching vibration of C—F. In addition to C—F, there exists another functional group C—H which corresponds to several different characteristic vibrations in ETFE film, including twisting vibration (1040 cm<sup>-1</sup>), scissoring vibration (1453 cm<sup>-1</sup>), and wagging vibration (970 cm<sup>-1</sup>). All the above-mentioned vibrations contribute to the certain absorption of the ETFE film in the mid-infrared bands. These characteristic absorption peaks form the critical basis for us to choose ETFE film for RSC.



**Fig. 5.** Absorbance spectrum of the ETFE film attributing to different vibrations of functional groups (C–F and C–H) in the wavelength region from 6 to 13  $\mu$ m. The specific vibrations of the two functional groups have been marked in the figure.

## 2.2 Experimental setup

Outdoor tests are performed to investigate the RSC performance of the ETFE cooler under realistic conditions. The schematic and photograph of the experimental setup are presented in Fig. 6. The transparent acrylic sheets form the sample compartment and decouple the sample from ambient air to reduce the parasitic cooling loss. A thin low-density polyethylene (LDPE) film with high transmittance over almost the entire wavelength band covers the ETFE cooler to shield it from the wind and minimize non-radiative heat losses.

The plastic foam is used to thermally insulate the bottom surface of the ETFE cooler.

During the experimental test, the real-time temperatures of the ETFE cooler and ambient air are measured by T-type thermocouples (OMEGA, America) with an uncertainty of 0.5°C. The ambient temperatures are tested by a thermocouple in the louver box with an uncertainty of 0.5°C. The solar irradiance is measured by a pyranometer (TBQ-2, Jinzhou Sunshine Technology Co.Ltd.) with an uncertainty of 2%. All the abovemeasured data are recorded by a data logger (LR8400, HOIKI).



Fig. 6. (a) Schematic and (b) photograph of the outdoor experimental setup.

## 2.3 Field experiment demonstration

Outdoor experiments are conducted in Hefei, China (31.86°N, 117.27°E), on January 1-2, 2021, and in Beijing, China (39.92°N, 116.46°E), on April 18-19, 2021. The ambient temperatures, solar irradiance, and samples' temperature are measured and presented in Fig. 7 and Fig. 8, respectively. During the tests, a highly reflective Al film is applied as a reference and the corresponding temperature is also plotted in the figures.



Fig. 7. Measured ambient temperature, the temperature of ETFE cooler and Al, and solar irradiance in Hefei.

An all-day sub-ambient RSC phenomenon based on the ETFE cooler has been demonstrated in Hefei (Fig. 8). During the two days in Hefei, the ETFE cooler can achieve on average  $1.6^{\circ}$ C and  $1.5^{\circ}$ C below ambient temperature from 10:00-14:00 when the solar irradiance exceeds 500 W/m<sup>2</sup>. The temperature of the ETFE cooler is average  $3.0^{\circ}$ C lower than ambient air from 6:00-18:00. Besides, the maximum value of temperature differences between the ambient air and the ETFE cooler is  $6.0^{\circ}$ C on the first day (10:00-14:00) and  $5.1^{\circ}$ C on the second day (10:00-14:00). Such temperature differences achieved in humid Hefei show a good radiative cooling performance, which can be used for various applications related to energy-saving and thermal management, such as decreasing a part of the cooling load for buildings and saving electricity. Compared with the ETFE cooler, the temperature of the Al film is always higher than the ambient temperature due to the solar absorption during the two days. The sky condition on the first day is better than that on the second day since there are a lot of fluctuations in the solar irradiance curve and this may be caused by the clouds [25]. During the two nights (21:00-6:00), the average temperature of the ETFE cooler is  $5.8^{\circ}$ C and  $5.2^{\circ}$ C lower than ambient temperature, respectively, while Al film maintains almost the same temperature as the ambient temperature. Moreover, the maximum value of temperature difference between ambient air and the ETFE cooler is nearly 7.1^{\circ}C and  $6.7^{\circ}$ C on these two nights, respectively.



Fig. 8. Measured ambient temperature, the temperature of ETFE cooler and Al, and solar irradiance in Beijing.

During the two days in Beijing (Fig. 8), the measured solar irradiance is larger than that in Hefei and the peak exceeds 910 W/m<sup>2</sup>. The strong solar radiation will weaken the radiative cooling performance of the ETFE cooler. In the periods (10:00-14:00) when the sun shines the most in two days, the ETFE cooler's temperature is almost equivalent to the ambient temperature without being heated. In contrast, Al's temperature in the same period is 16.5°C and 15.4°C higher than ambient temperature. During the two nights (23:00-6:00), the ETFE cooler's temperature is reduced by 8.3°C and 7.4°C on average compared to ambient temperatures, while Al film's temperature is reduced by 3.2°C on average. Moreover, the maximum value of temperature differences between ambient air and the ETFE cooler is nearly 8.9°C and 8.3°C on these two nights, respectively. The RSC performance in the different places shows that, although solar radiation and atmospheric conditions have a great impact on radiative cooling performance, the proposed ETFE cooler can still achieve a stable RSC performance.

The ETFE cooler consists of the ETFE film and Ag layer. Therefore, the lifecycle of the ETFE cooler is closely related to these two parts. Strong bonds within ETFE film prevent material degradation with respect to weather and ultraviolet radiation conditions. For this reason, ETFE foil does not deteriorate, discolor, or

hardness during its lifetime [26]. Moreover, ETFE foils have chemical resistance to acids and alkali and nonstick properties. In terms of durability, ETFE foil is reported to be excellent resistant to weathering with no remarkable reduction in performance and life expectancy above 30 years [27]. The radiative cooling films based on glass-polymer hybrid metamaterial [21] containing Ag coating have an eight-year warranty. In addition, the ETFE cooler with a similar structure to the above radiative cooling film has a SiO<sub>2</sub> layer to prevent oxidation of the Ag layer, indicating that the ETFE cooler can achieve a similar life cycle.

## **3.** Theoretical analysis

## **3.1 Theoretical model**

Considering the ETFE cooler with a temperature of *T* is exposed to the sky directly, the net cooling power of the cooler can be calculated by:

$$P_{net}(T) = P_{rad}(T) - P_{sun} - P_{atm}(T_{amb}) - P_{cond+conv}$$

$$\tag{1}$$

here,  $P_{rad}(T)$  is the total power radiated by the ETFE cooler, which can be given by:

$$P_{rad}(T) = \int d\Omega \cdot \cos\theta \int_0^\infty d\lambda \cdot I_{BB}(T,\lambda) \cdot \varepsilon(\lambda,\Omega)$$
(2)

where  $\int d\Omega = \int_{0}^{\pi/2} d\theta \sin \theta \int_{0}^{2\pi} d\phi$  is the hemispherical angle integral,  $I_{BB}(T,\lambda) = (2hc^2/\lambda^5)/(e^{hc/\lambda k_B T} - 1)$  is the spectral radiance of a blackbody defined by Planck's law at any temperature *T*, where *h* is Planck's constant,  $k_B$  is the Boltzmann constant, *c* is the speed of light in vacuum, and  $\lambda$  is the wavelength. In Eq.(2),  $\varepsilon(\lambda, \Omega)$  is the spectral and angular emissivity of the ETFE cooler. According to Kirchhoff's law, the spectral absorptivity of the ETFE cooler is equal to its spectral emissivity. In Eq.(1),  $P_{sun}$  is the absorbed incident solar radiation, which can be calculated by:

$$P_{sun} = G\alpha \tag{3}$$

where G is the total solar irradiance and  $\alpha$  is the AM1.5 weighted solar absorptivity of the ETFE cooler.

In Eq.(1),  $P_{atm}(T_{amb})$  is the absorbed incident atmospheric radiation, which can be described by:

$$P_{\rm atm}(T_{\rm amb}) = \int d\Omega \cdot \cos\theta \int_0^\infty d\lambda \cdot I_{\rm BB}(T,\lambda) \cdot \varepsilon(\lambda,\Omega) \cdot \varepsilon_{\rm atm}(\lambda,\Omega)$$
(4)

where  $\varepsilon_{atm}(\lambda, \theta) = 1 - t(\lambda)^{1/\cos\theta}$  is atmospheric emissivity,  $t(\lambda)$  is atmospheric transmittance in the zenith direction [28]. The transmittance of different latitudes and different climates can be obtained from the MODTRAN model [24].

In Eq.(1),  $P_{cond+conv}$  is the non-radiative cooling loss power of the ETFE cooler and can be described by

$$P_{cond+conv} = h_{c} \left( T - T_{amb} \right) \tag{5}$$

where  $h_c$  is the effective heat transfer coefficient between the ETFE cooler and ambient air, which includes the effect of heat convection and conduction.

The aforementioned thermal model can predict the cooling performance of the ETFE cooler under the given parameters. According to the thermodynamic equilibrium equation of the radiative cooler, the maximum cooling power (MCP) of the cooler occurs when the cooler temperature is equal to the ambient temperature. The MCP is an important indicator for evaluating the cooling capacity of radiative coolers. Moreover, the stagnation temperature that the ETFE cooler can reach under specific parameters can also intuitively quantify the cooling performance of the ETFE cooler. Thus, the maximum temperature difference (MTD) between ambient air and the cooler is used to describe the cooling performance of the ETFE cooler.

## 3.2 Thermal simulation

As the main heat input to the radiative cooler, solar radiation should be suppressed as much as possible to improve the cooling effect. Moreover, the atmospheric condition is another key factor in determining the performance of RSC. Therefore, a thermal simulation study is conducted to further investigate the ETFE cooler's performance under a wider variety of working conditions. During simulation, the atmospheric transmittance profile of mid-latitude summer and winter are considered, and the spectral transmittance from 4.5  $\mu$ m to 25.0  $\mu$ m can be obtained from MODTRAN, as shown in Fig. 9. The absorbed incident atmospheric radiation in the aforementioned thermal analysis model can be calculated numerically by combing the spectral atmospheric transmittance and the emissivity of the ETFE cooler in the corresponding band. The solar irradiance is set as 900 W/m<sup>2</sup>, and the absorbed incident solar radiation can be obtained according to the

AM1.5 spectra-weighted reflectivity of the ETFE cooler. Besides, the non-radiative heat transfer coefficient is  $6.9 \text{ W/(m^2 \cdot K)}$  [3].



**Fig. 9.** Schematic of atmospheric transmittance of mid-latitude winter and summer. The average transmittance of mid-latitude winter and summer in the atmospheric window band (8-13µm) is 81.63% and another is 45.07%.

First, the MCP of the ETFE cooler under different ambient temperatures is investigated. During calculation, the atmospheric transmittance of the mid-latitude winter is adopted as the atmospheric condition parameter, and ambient temperature varies from 0°C to 40°C. The predicted MCP of the ETFE at day and night is presented in Figs. 10 and 11. During the day (Fig. 10), the MCP of the ETFE cooler increases when the ambient temperature increases. For example, when the temperature varies from 0°C to 40°C, the MCP of the ETFE cooler increases from 6.8 W/m<sup>2</sup> to 63.7 W/m<sup>2</sup>. In contrast, the MCP of the Al film is negative, which means the Al film is heated up by sunlight. The ETFE cooler can reflect most of the sunlight and produce a certain amount of cooling power, while natural materials like Al films do not have this ability. At night (Fig. 11), the MCP of the ETFE cooler is greatly improved due to the absence of sunlight, while Al film produces a lower cooling power than the former one by an order of magnitude due to the low mid-infrared emissivity.



Fig. 10. Simulated MCP of the ETFE cooler during the day.



Fig. 11. Simulated MCP of the ETFE cooler at night.

Second, the effect of the atmospheric condition on radiative cooling performance of the ETFE is also investigated. During calculation, the MTD between the ambient air and the ETFE cooler under mid-latitude summer and winter conditions is calculated and presented in Figs. 12 and 13.



Fig. 12. The MTD between the ambient air and the two samples during the daytime.



Fig. 13. The MTD between the ambient air and the two samples during the night.

During the day in the mid-latitude winter, the ETFE cooler can still achieve sub-ambient cooling. The MTD between the ambient air and the ETFE cooler is 0.7°C to 5.7°C when the ambient temperature changes from 0°C to 40°C, while Al film is always higher than the ambient temperature by more than 22°C. During the daytime in the mid-latitude summer whose atmospheric transmittance is relatively low, the performance of the proposed ETFE cooler is affected and it is slightly heated by the sunlight. The above results reveal that

the two samples' cooling performance under mid-latitude winter is better than that under mid-latitude summer, and this is because of the decrease in the atmospheric transmittance from winter to summer. Besides, similar conclusions are found in the night condition. It is worth mentioning that the ETFE cooler possessed the potential to achieve the deep-cooling effect of being 10 degrees lower than the ambient temperature at night under the influence of non-radiative heat transfer.

## 4. Conclusion

In this paper, the ETFE material is selected for sub-ambient RSC since it has C—F and C—H functional groups whose vibrations contribute to thermal absorption peaks in the mid-infrared bands. Then, a reflective Ag film is deposited below the transparent ETFE film to form a dual-layer polymer-based radiative cooler, where the optically transparent ETFE film enhances thermal emission and the Ag layer reflects the sunlight. Outdoor experiments and thermal simulations are conducted to investigate the performance of the ETFE cooler, which reveal that:

(1) The solar reflectivity and atmospheric thermal emissivity of the ETFE cooler are 94% and 83%, which indicates the ETFE cooler is a good candidate for all-day RSC.

(2) The temperature of the cooler is on average 3.0°C lower than ambient air during daytime in Hefei, and is approximately 1.5°C below ambient air even at noon, which means the all-day sub-ambient cooling effect is successfully achieved.

(3) An all-day sub-ambient radiative cooling under sunlight is predicted to be possible for the ETFE cooler and a temperature drop of nearly 10°C could be obtained at night.

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## **Highlights**

- 1. Parasitic absorption of functional groups is applied to select polymer materials.
- 2. A dual-layer ETFE/Ag film is fabricated for sub-ambient radiative cooling.
- 3. The cooler reflects 94% solar radiation and emits strongly in the mid-infrared.
- 4. Temperature of ETFE cooler is average 3.0°C below ambient air during daytime.
- 5. ETFE is a good candidate of materials for sub-ambeint radiative sky cooling.

## **Declaration of interests**

 $\boxtimes$  The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: