Supplementary Materials for

Protecting ice from melting under sunlight via radiative cooling

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Supplementary Text 1 | A theoretical model of the energy transfer process of outdoor ice/iced-food under sunlight

The energy transfer process of outdoor ice/iced-food at low/middle latitudes (<60°N) consists of mid-infrared radiation, solar radiation, and non-radiative thermal flux in the form of convection and conduction. It can be expressed as the following equation (6, 17, 21-24, 49):

\[
P_{\text{net}}(T) = \left[ P_{\text{rad,ice}}(T) - \alpha_{\text{ice}} P_{\text{rad,amb}}(T_{\text{amb}}) \right] - \left( 1 - R_{\text{ice}} \right) P_{\text{sun}} - P_{\text{conv+cond}}(T, T_{\text{amb}})
\]  \hspace{1cm} (S1)

where \( P_{\text{net}} \) is the thermal load on the outdoor ice/iced-food, \( P_{\text{rad,ice}} \) is the mid-infrared radiation from the outdoor ice/iced-food, \( P_{\text{rad,amb}} \) is the mid-infrared radiation from the ambient air, \( P_{\text{sun}} \) is the incident solar radiation (sunlight), and \( P_{\text{conv+cond}} \) is the convective and conductive thermal flows. \( T \) and \( T_{\text{amb}} \) are the temperatures of the outdoor ice/iced-food and the ambient air, respectively. \( \alpha_{\text{ice}} \) and \( R_{\text{ice}} \) are the mid-infrared absorptivity and the solar reflectivity of the ice/iced-food.

The \( P_{\text{rad,ice}} \) is:

\[
P_{\text{rad,ice}} = \sigma T^{4} \int \varepsilon_{\text{ice}}(\lambda)P_{\text{b}}(\lambda) d\lambda
\]

in which \( \sigma \) is the Stefan-Boltzmann constant and \( \varepsilon_{\text{ice}}(\lambda) \) is the mid-infrared spectral emissivity of ice/iced-food. \( P_{\text{b}}(\lambda) \) is the spectral emissive power of a black body. \( P_{\text{b}}(\lambda) \) can be expressed as the Planck formula. Here, \( \varepsilon_{\text{ice}} \) is supposed to be 0.90 (based on our measurements in Fig. S1 and literatures (50, 51)) and is equivalent to the \( \alpha_{\text{ice}} \) according to the Kirchhoff’s radiation law.

The \( P_{\text{rad,amb}} \) can be expressed as:

\[
P_{\text{rad,amb}} = \sigma T_{\text{amb}}^{4} \int \varepsilon_{\text{amb}}(\lambda)P_{\text{b}}(\lambda) d\lambda
\]

where \( \varepsilon_{\text{amb}}(\lambda) \) is the mid-infrared spectral emissivity of ambient air. \( \varepsilon_{\text{amb}} \) is assumed to be 0.725 (47).
The $R_{\text{ice}}$ is:

$$R_{\text{ice}} = \frac{\int_{0.3}^{2.5} R_{\text{ice}}(\lambda)P_{\text{sun}}(\lambda)d\lambda}{\int_{0.3}^{2.5} P_{\text{sun}}(\lambda)d\lambda} \quad (S4)$$

in which $R_{\text{ice}}(\lambda)$ is the spectral solar reflectivity of the ice/iced-food. $P_{\text{sun}}$ denotes the spectral power of sunlight. In this calculation, $R_{\text{ice}}$ is assumed to be 0.40 (according to our measurements in Fig. S1 and literatures (52-54)).

The $P_{\text{conv+cond}}(T, T_{\text{amb}})$ is obtained by:

$$P_{\text{conv+cond}}(T, T_{\text{amb}}) = 2h_{c}(T_{\text{amb}} - T) \quad (S5)$$

in which $h_{c}$ is a combined non-radiative thermal transfer coefficient. It is assumed to be 1 W m$^{-2}$ K$^{-1}$ at a windless condition (55, 56).

Via the above energy model, we calculated the heat fluxes of the outdoor ice/iced-food at 0 °C while exposed under the standard sunlight power of 1 kW m$^{-2}$ and the ambient temperature of 10 °C. The energy fluxes on the ice/iced-food in the forms of mid-infrared radiation, solar radiation, and non-radiative heat transfer are 46, 600, and 20 W m$^{-2}$, respectively.

Supplementary Text 2 | Relationship between melting rate of ice and net radiation power

We assume that a piece of spherical ice/iced-food is enclosed in a cubic air pocket (Fig. S2A). The air pocket is at a thermodynamic steady state. Its energy balance is

$$6a^2h_{\text{sa}}(T_{\text{amb}} - T_{\text{air}}) = a^2P_{\text{rad}} + 4\pi r^2h_{\text{ai}}(T_{\text{air}} - T_{\text{ice}}) \quad (S6)$$

where, $a$ and $r$ are the side length of the cubic and the radius of the sphere, respectively. $P_{\text{rad}}$ is the net radiation power, which denotes the net energy exchange between the air pocket and ambient in the form of radiation (including solar and mid-infrared). $h_{\text{sa}}$ and $h_{\text{ai}}$ are the convective thermal transfer coefficient between the air pocket and ambient, and between the air pocket and the ice/iced-food, respectively. $T_{\text{amb}}$, $T_{\text{air}}$ and $T_{\text{ice}}$ represent the temperatures of ambient, air pocket, and ice/iced-food. We suppose that they are constant because the air pocket is assumed to be at steady state and ice/iced-food melt is a phase change process.

Solving
\[ T_{\text{air}} = \frac{-a^2 P_{\text{rad}} + 6a^2 h_{\text{a}a} T_{\text{amb}} + 4\pi r^2 h_{\text{a}i} T_{\text{ice}}}{6a^2 h_{\text{a}a} + 4\pi r^2 h_{\text{a}i}} \]  

(S7)

Subsequently, we consider the energy transfer process of the ice/iced-food. The energy balance can be expressed as

\[ H_m \frac{dm}{dt} = 4\pi r^2 h_{\text{ai}} (T_{\text{air}} - T_{\text{ice}}) \]  

(S8)

in which, \( H_m \) is the enthalpy change of ice/iced-food melt. \( m \) is the mass of the ice/iced-food, \( t \) is time. \( \frac{dm}{dt} \) denotes the melting rate of the ice/iced-food, and is simplified as \( \dot{m} \).

Introducing \( T_{\text{air}} \) and solving

\[ \dot{m} = \frac{4\pi r^2 h_{\text{ai}}}{H_m} \left( \frac{-a^2 P_{\text{rad}} + 6a^2 h_{\text{a}a} (T_{\text{amb}} - T_{\text{ice}})}{6a^2 h_{\text{a}a} + 4\pi r^2 h_{\text{a}i}} \right) \]  

(S9)

This equation can be further rewritten as

\[ \dot{m} = \frac{24\pi r^2 a^2 h_{\text{a}a} (T_{\text{amb}} - T_{\text{ice}})}{H_m (6a^2 h_{\text{a}a} + 4\pi r^2 h_{\text{a}i})} = \frac{4\pi r^2 a^2 h_{\text{a}i}}{H_m (6a^2 h_{\text{a}a} + 4\pi r^2 h_{\text{a}i})} P_{\text{rad}} \]  

(S10)

Herein, we set

\[ A = \frac{24\pi r^2 a^2 h_{\text{a}a} (T_{\text{amb}} - T_{\text{ice}})}{H_m (6a^2 h_{\text{a}a} + 4\pi r^2 h_{\text{a}i})} \quad \text{and} \quad B = \frac{4\pi r^2 a^2 h_{\text{a}i}}{H_m (6a^2 h_{\text{a}a} + 4\pi r^2 h_{\text{a}i})} \]  

(S11)

Therefore, \( \dot{m} \) can be simplified as

\[ \dot{m} = A - BP_{\text{rad}} \]  

(S12)

As \( A = 6h_{\text{a}a} (T_{\text{amb}} - T_{\text{ice}})B \)

\[ \dot{m} \] becomes

\[ \dot{m} = \left[ 6h_{\text{a}a} (T_{\text{amb}} - T_{\text{ice}}) - P_{\text{rad}} \right] B \]  

(S13)
We suppose a case where $h_{aa}$ is $1.5 \text{ W m}^{-2} \text{ K}^{-1}$ (44, 52) and $T_{amb} - T_{ice}$ is $10 \degree C$. The relationships between melting rate of ice/iced-food and net-radiation power is plotted in Fig. S2B. It is clear that the melting rate of ice/iced-food is significantly slowed down via increasing the net radiation power. For example, an increase of net radiation power from $70 \text{ W m}^{-2}$ to $110 \text{ W m}^{-2}$ is capable of preventing ice/iced-food from melting.

**Supplementary Text 3 | Optical modeling**

The optical simulation is based on Mie theory and Chandrasekhar radiative transfer theory (57, 58). In the calculation, we assume pores within the CA film as isotropic scatter, which is a good approximation for the purpose of understanding the pore size effect on reflectivity. We compute the reflectivity in the solar wavelength range from $0.3 \mu m$ to $2.5 \mu m$ by varying pore size, assuming the same material thickness and pore volume in the CA film. The calculation is shown in Fig. 2A. It can be seen that pores with size in the range of 0.5-3 μm give the best reflection performance. For pore with a diameter smaller than 500 nm, the near-infrared reflectivity drops, making it less ideal. For pore with a diameter larger than 3 μm, the reflectivity also drops as the number of pores decreases when the diameter increases for a given pore volume.

**Supplementary Text 4 | A theoretical model of the cooling performance of the hierarchically designed CA film**

The cooling power of the hierarchically designed CA film is written as (17, 20-24):

$$P_{cooling}(T) = \left[ P_{rad,CA}(T) - \alpha_{CA} P_{rad,amb}(T_{amb}) \right] - (1 - R_{CA}) P_{sun} - P_{conv+cond}(T,T_{amb})$$

(S14)

where $P_{rad,CA}$ and $P_{rad,amb}(T_{amb})$ is the mid-infrared emission from the hierarchically designed CA film and ambient air, respectively. $P_{sun}$ denotes sunlight power and $P_{conv+cond}(T,T_{amb})$ is power loss in the forms of convection and conduction, respectively. $T$ and $T_{amb}$ denote the temperatures of the hierarchically designed CA film and the ambient, respectively. $\alpha_{CA}$ and $R_{CA}$ is mid-infrared absorptivity and the solar reflectivity of the hierarchically designed CA film, respectively. The non-radiative thermal transfer coefficient for calculating $P_{conv+cond}(T,T_{amb})$ is set as $2.9 \text{ W m}^{-2} \text{ K}^{-1}$ (47, 59).
When $T$ equals to $T_{\text{amb}}$, the power $P_{\text{cooling}}(T = T_{\text{amb}})$ is the cooling power at the ambient air temperature. When $P_{\text{cooling}}(T)$ equals zero, we obtain the temperature of the hierarchically designed CA film at steady-state. The temperature difference $\Delta T = T_{\text{amb}} - T$ is defined as cooling temperature. We calculated the cooling power and cooling temperature of the hierarchically designed CA film under various ambient conditions (ambient temperature and sunlight power). The corresponding results are presented in Fig. S6 and Fig. S7, respectively. The theoretically predicted cooling power and the cooling temperature of the hierarchically designed CA film under the experimental conditions are ~125 W m$^{-2}$ and ~14 ℃, respectively, which is consistent with the measured values of ~110 W m$^{-2}$ and ~12 ℃, respectively. Meanwhile, the theoretical analysis suggests that a better cooling performance can be realized with optimized test conditions, as lower ambient humidity and better thermal isolation of the test device.

Supplementary Text 5| Changes in thermal load on outdoor ice/iced-food while wrapped by different materials

To quantitatively reflect the changes in thermal load on the outdoor ice/iced-food while it is wrapped by different packing materials, we assume that the temperature of the ice/iced-food keeps constant (does not vary with the changes in the thermal load). In this scenario, the non-radiative thermal fluxes of convection and conduction are kept constant. In addition, the temperatures of the packing materials are assumed to be the same as the ice/iced-food (efficient thermal transfer).

The system solar reflectivity of ice/iced-food with the hierarchically designed CA film, white paper, PET-Al-PE, and Al film are calculated to be around 0.974, 0.813, 0.692, and 0.880, respectively. Here, as the solar transmissivity of the white paper is 0.129, the first reflection on the ice/iced food for the permeable sunlight is considered. For the other three cases, this part of the energy is ignored due to their low solar transmissivity (<0.1). The system mid-infrared emissivity of ice/iced-food with the hierarchically designed CA film, white paper, PET-Al-PE, and Al film are calculated to be around 0.92, 0.89, 0.62, and 0.05, respectively. These values are verified to be reasonable, by our measurements with ice-cream (at solid-state, with a temperature lower than 0 ℃) as an example in Fig. S9 (0.93, 0.91, 0.60, 0.03, respectively).

Based on the above optical analysis, we obtain that the power of energy flows in the forms of sunlight, convection, and mid-infrared emission are 26, 20, and -47 W m$^{-2}$, respectively, for the
case of applying the hierarchically designed CA film. The net thermal load on the ice/iced-food with the hierarchically designed CA film is -1 W m$^{-2}$.

The utilization of the hierarchically designed CA film enables 161, 282, and 94 W m$^{-2}$ reductions in solar energy input; while 1, 15, and 44 W m$^{-2}$ increase in mid-infrared emission, compared with using white paper, PET-Al-PE, and Al film, respectively. As a result, the hierarchically designed CA film lowers the thermal load on the outdoor ice/iced-food under sunlight by 155, 297, and 138 W m$^{-2}$ compared with employing white paper, PET-Al-PE, and Al film, respectively.

**Supplementary Text 6 | Iceberg Model**

An iceberg with a size of dozens of square kilometers (has been observed off Baffin Island) in the summer season (June, July and August) at high latitudes (>70.5°N) is studied. The surface energy balance of it is governed by:

$$LA\frac{dH}{dt} = \left[ (1-R)(1-i_o)P_s - (P_d - \alpha P_b) + P_h + P_{le} + F_c \right]A$$

(S15)

where, $L$ is the thickness change of the iceberg, $A$ is the area of the iceberg, $H$ is the energy used to melt a unit volume of a summer iceberg, and $t$ is time. $R$ and $i_o$ denote the surface reflectivity and transmittance of the iceberg for sunlight, respectively. $\alpha$ is the surface absorptivity for mid-infrared light. The $P_s$, $P_d$, $P_b$, $P_h$, $P_{le}$, $F_c$ are powers of incident sunlight, incoming mid-infrared, mid-infrared emission, sensible heat, latent heat, and conduction, respectively.

The value of $H$ is assumed to be 2.31\times10^5 \text{kJ m}^{-3}, the average value of first-year and multiyear sea ice at high latitudes (60). The duration of calculation ($t$) is presumed as two months of round-the-clock daytime due to polar day at high latitudes. The surface sunlight reflectivity, mid-infrared emissivity/absorptivity when the iceberg is covered by the hierarchically designed CA film depends on the optical properties of the CA film, while are set as 0.5 and 0.98 for the intrinsic iceberg surface, respectively (61). The mean $P_s$ is assumed to be 200 W m$^{-2}$ according to satellite data (62). We presume that sunlight always interacts with the iceberg on the surface and therefore $i_o$ equals zero.

The sensible heat exchange between the iceberg and ambient is realized via convection, and the thermal transfer coefficient ($h$) is assumed to be 21 W m$^{-2}$ K$^{-1}$ ($h = 1 + 6\times V^{0.75}$, the mean wind speed ($V$) is assumed to be 5 m s$^{-1}$) (56, 63). The latent heat and conduction heat exchanges are
The temperature of the iceberg is assumed to be -0.8 °C based on the averaged value from field observations (60) and the ambient temperature is 0.4 °C, with a projected 2 °C warming of atmosphere in summer from nowadays value of -1.6 °C in the scope of the Paris Agreement (64). The equation S15 is solved for both scenarios of the intrinsic iceberg surface and the iceberg surface with the hierarchically designed CA film to obtain the thickness changes of the iceberg due to top surface energy exchange.

Supplementary Text 7 | Climate model for verifying the cooling effects of the hierarchically designed CA film at high latitudes

We use the Community Earth System Model Version 2 (CESM2) to simulate the large-scale effect of the hierarchically designed CA film over sea ice at high latitudes (>70.5°N). CESM2 is a community-developed, fully coupled earth system model, which consists of atmosphere, land, land-ice, ocean, and sea ice models that exchange states and fluxes via a coupler (65). CESM2 uses CICE Version 5.1.2 (66) as its sea ice component, and the solar reflectivity of the sea ice is calculated from sea ice optical and thermal properties by the delta Eddington (DE) solar parameterization in CICE (67). The atmosphere and land models run on a 0.9°×1.25° grid, while the ocean and sea ice model use a nominal 1° grid. To verify the cooling effects of the hierarchically designed CA film over sea ice at high latitudes, we follow Ref. (68) to increase the global sea ice albedo by perturbing snow tuning parameters in the DE parameterization. What is noteworthy is that we presume that the hierarchically designed CA film works only in summer (June, July, and August), when the snowfall intensity is minimum in the year, minimizing the potential compromise to the optical properties. The highest solar reflectivity of the sea ice nearly reaches 0.96, which is close to 0.974, the solar reflectivity of the hierarchically designed CA film. The mid-infrared emissivity of sea ice is kept as the default value (0.95), close to the one of the CA film (0.92), because most global climate models including CESM2 do not include proper and consistent treatments for surface spectral emissivity across model components (69) and the deviation from such an approximation is almost negligible (Table 1). Both experiments with and without the impacts of the hierarchically designed CA film start in 2000 and continue for 10 years. The 10-year annual average is used for Fig. 4 and Fig. S22 to show the overall cooling effect of the hierarchically designed CA film. The July average is used for Fig. 1B and Table 1 to represent the high latitudes surface under solar radiation, when the solar radiation is dominant and has the largest thermal load in the year.
The impact of mid-infrared emission on the cooling effects at high latitudes

Generally, there are two types of mid-infrared emissivity spectra for radiative cooling materials: 1) highly emissive across the whole mid-infrared band (broadband emissivity) and 2) highly emissive only at the atmospheric window (selective emissivity). A radiative-convective column model built upon an open-source modeling framework CLIMLAB (70) is used to assess the impacts of the two types of mid-infrared emissivity on the cooling effect of the radiative cooling materials on the sea ice at high latitudes. The column model includes the RRTMG radiation scheme and dry adiabatic convective adjustment process and assumes a time-fixed relative humidity vertical profile. The surface emissivity is set to 1 in each mid-infrared emissivity band for the broadband radiative cooling material. For the selective radiative cooling material, the surface emissivity is set to 1 only within the atmospheric window band of 8.5-12.2 μm (as used by Ref.S70) and 0 at other mid-infrared emission bands. The surface reflectivity is set to 0.2. Both simulations start from the same temperature and relative humidity profile, which come from the climatological (1981-2010) global mean of the ERA5 reanalysis (63), and run towards equilibrium. Fig. S23 shows that the selective mid-infrared emissivity leads to a temperature increase at each layer and above 6 °C increase at surface compared with the broadband mid-infrared emissivity. As is shown in Table S1, the temperature increase in the experiment with a selective mid-infrared emissivity mainly results from the less mid-infrared emission at surface in the non-atmospheric-window band, where the surface generally emits more energy than it receives from the atmosphere. Therefore, the high mid-infrared emissivity of the hierarchically designed CA materials across broadbands is important and beneficial for maximizing the mid-infrared emission (better cooling).
Fig. S1. Optical spectra of ice/iced-food with transparent (both at the solar and mid-infrared bands) PE film. A and B Solar reflectivity spectra of ice and iced-cream with PE, respectively. C and D, Mid-infrared emissivity spectra of ice and ice-cream with PE, respectively. The average solar reflectivity and mid-infrared emissivity of ice/ice-cream are estimated to be ~0.4 and ~0.9, respectively. Here, common ice frozen in refrigerator and the ice frozen in liquid nitrogen (enabling higher solar reflection by preventing the escape of air in water and making many cracks, abbreviated as Ice-N₂) were used as examples of ice. Three kinds of randomly selected commercialized ice-creams were utilized as instances for iced-food. The thickness of the ice/iced-food sample is 1.5 cm, which is also the upper size limit of the device we used to measure the optical spectrum. Transparent PE was adopted to prevent contamination for optical instruments.
**Fig. S2| Relationship between melting rate of ice/iced-food and net radiation power.** A, A schematic shows the energy transfer process between ice/iced-food, air pocket, and ambient (detailed in Supplementary Text 2). B, Relationship between melting rate of ice/iced-food and net radiation power. The melting rate is normalized by the case where there is no net radiation power ($P_{\text{rad}}=P=0$). It is clear that an increasing net radiation power can effectively slow down the melt of ice/iced food, even to the un-melted region.
Fig. S3 | Fabrication of the hierarchically designed CA film. A photograph of the custom-made roll-to-roll electrospinning device for fabricating the hierarchically designed CA film. Multi-needles increase the output of the CA fibers and accelerate the production of the hierarchically designed CA film.
Fig. S4 | Porosity characterizations of the hierarchically designed CA film by the mercury intrusion porosimetry. The (A) mercury intrusion/extrusion curves and the corresponding (B) pore size distribution. The pores within the hierarchically designed CA film have a broad distribution, ranging from hundreds of nanometers to several micrometers.
**Fig. S5** FTIR spectrum of CA. The multiple molecular vibration modes of CA endow the hierarchically designed CA film with a high mid-infrared emissivity across broadband, especially at the atmospheric transparent window (8-13 μm).
Fig. S6| The theoretical cooling power of the hierarchically designed CA film under various ambient conditions. $T_{\text{amb}}$ and $P_{\text{sun}}$ denote the ambient temperature and incident sunlight power, respectively. The unit of the color bar is W m$^{-2}$. 
Fig. S7 | The theoretical cooling temperature of the hierarchically designed CA film under various ambient conditions. $T_{\text{amb}}$ and $P_{\text{sun}}$ denote the ambient temperature and incident sunlight power, respectively. The unit of the color bar is K/$^\circ$C.
**Fig. S8** Solar reflectivity spectra of various commercialized Al film. The solid line shows the solar reflectivity spectrum of the Al film that we used as a control in the main text.
Fig. S9 | Mid-infrared emissivity spectra of ice-creams with different packing materials.
Fig. S10 | The experimental setup used to measure the temperature of the ice-cream wrapped by different materials. A, A photograph of the experimental setup. A piece of thick foam (~10 cm), as a thermal insulator, was used to develop the setup. The cover material of Al foil (with a solar reflectivity of ~0.88) and the lining material of PVDF film (with a solar reflectivity of >0.95) are adopted to minimize the impacts of the environment. Ice-crams were placed in the container during experiments. (B) A photograph shows that different wrapping films were left as the only windows to exchange heat with ambient. The temperatures were real-time monitored by thermocouples. The scale bars are 5 cm.
Fig. S11 | The environmental conditions while measuring the temperatures of ice-creams.
Fig. S12 | Melting behaviors of the ice protected by different packing materials with the same thermal contact. A, A schematic of the control experiments. The air gap between the cooling material and the ice is controlled to enable poor thermal contact (large thermal resistance). The foam isolates the experimental system from the surroundings, but leaves the packing materials as windows to exchange heat with the ambient. B, Comparison of ice protection performance after 6 hours of sunlight exposure. The area and initial mass of ice are 65.61 cm$^2$ and 110 g, respectively. The solar reflectivity of the Al foil and white paint are 0.88 and 0.83, respectively. The larger remaining mass (smaller melting mass) of ice subjacent the hierarchically designed CA film confirms that it is the optical properties (or thermal load) rather than thermal resistance that dominates the performance of ice protection.
The experimental setup used to compare the melt of ice-cream wrapped by different materials. A and B, Photograph of the experimental setup. Identical commercially available ice-creams were enclosed in the portable bags made from the hierarchically designed CA film, white paper, Al film, and PET-Al-PE film, and exposed under outdoor sunlight. The scale bares are 5 cm. A transparent portable bag in (B) is used to show the inner conditions of the experiments. The Al mirror and PVDF film with solar reflectivity of >0.95 were used to minimize the impact of sunlight irradiated on the lining material, especially considering the packing material white paper with ~13% transmission for sunlight. The foam with Al foil was adopted to minimize the impact from ambient as well. C and D, Solar reflectivity spectra of the PVDF film and Al mirror, respectively.
Fig. S14 | First comparisons between the hierarchically designed CA film and current commercial cooling materials. A, A photograph of the hierarchically designed CA film and current commercial cooling materials, including polished Al and Al-Foam. The scale bars are 5 cm. B and C, Solar reflectivity and mid-infrared emissivity spectra of the samples, respectively. D, A photograph shows the setup used for monitoring the temperatures of samples under sunlight. The Al film and foam are used for minimizing the impacts from surroundings. The temperatures of samples were measured via thermocouples. E, Temperatures of samples. The temperature of the hierarchically designed CA film is ~5 °C lower than that of polished Al, and is ~10 °C lower than that of Al-Foam. F, Comparison in the melt of ice. The experimental setup is similar to the one used in D), in which the cooling materials are placed above the ice. The area and initial mass of ice are
38.43 cm$^2$ and 50 g, respectively. With the protection of hierarchically designed CA film, ice has the largest remains after ~3 hours of sunlight exposure, and therefore lowest melt accordingly.
Fig. S15 | Second comparisons between the hierarchically designed CA film and current commercial cooling materials. A, A photograph of the hierarchically designed CA film and current commercial cooling materials, including another Al-foam and white paint. The scale bares are 5 cm. B, Solar reflectivity of the samples. C, Solar reflectivity spectra of many commercialized white paints (which were bought randomly online). The one with the highest solar reflectivity (purple line with rhombic symbol) was used as the control in (B). The average solar reflectivity of it (~0.83) is according with the summarized value reported in literature of ~0.85 (Ref. (21) and Ref. (10)). Admittedly, there may exist whiter paints (for example, in Ref. (21) and Ref. (25)) that we do not refer. We have discussed these super-white paints in the introduction part of our main text. D, Mid-infrared emissivity spectra of the samples. E, Temperatures of samples under sunlight...
exposure. The temperature of the hierarchically designed CA film is \(^{\sim}8 \, ^{\circ}C\) lower than that of the Al-Foam, and is \(^{\sim}6 \, ^{\circ}C\) lower than that of white paint. F, Comparison in the melt of ice. The area and initial mass of ice are 65.61 cm\(^2\) and 110 g, respectively. With the protection of hierarchically designed CA film, ice has the largest remains after \(^{\sim}6\) hours of sunlight exposure, and therefore lowest melt accordingly.
**Fig. S16** | **A photograph of the experimental setup for ice protection under sunlight.** This setup is mainly consisted by a refrigerator, a temperature recorder, and a temperature controller. The refrigerator with a temperature controller is used to obtain an ambient temperature (in the refrigerator chamber) close to the air temperature at high latitudes under sunlight of 0-8 °C. The chamber of the refrigerator is isolated from the surroundings with a temperature of ~30 °C by a PE film and a foam with sunlight reflector (which was removed when taking the photo to show the inner structure of the device). The Al film serves as a reflector for the incoming sunlight to reduce the heating on the refrigerator. The thermal stabilizer assists the refrigerator in maintaining a relatively stable temperature under sunlight. The temperatures of ice and ambient are real-time measured by thermocouples and a temperature recorder.
Fig. S17 | Power of outdoor sunlight over 5 days (6:00 am to 13:00 pm every day) for the experiments of ice protection.
Fig. S18 | The photograph shows the initial state of the experiments of outdoor snow protection under sunlight. The (A) bare snow and (B) the piece of snow with the protection of the hierarchically designed CA materials. The two pieces of snow were controlled to have the same shape and mass.
Fig. S19 | Power of outdoor sunlight over 20 days for the experiments of outdoor snow protection.
Fig. S20| The photograph shows the remains of snow after 20 days of outdoor sunlight exposure. After 20 days, the piece of (A) bare snow shows clear melt compared with (B) the one with the CA materials. This indicates that the hierarchically designed CA materials effectively slow the melt of snow.
Fig. S21 | Photographs captured while the field test of glacier protection in Tianshan Glacier No. 1. A and B. Photographs show the initial and after 20-day states of the protected glaciers, respectively. Due to the effective radiative cooling of our film, the melt of the glaciers below the radiative cooling film reduces by ~0.7 m, compared with the adjacent untreated scenario.
Fig. S22 | The difference between the thicknesses of sea ice with and without the hierarchically designed CA film. A-C, The CA film is applied over the sea ice (A) within the Beaufort Gyre region, (B) the annulus between 70.5°N and 80.5°N, and (C) the north of 70.5°N, respectively. These areas are marked by black dash lines. Owing to the passive protection of the hierarchically designed CA film, sea ice is thicker than the untreated scenario.
Fig. S23] The impact of mid-infrared emission on the cooling effects. A. The vertical temperature profiles for radiative cooling materials with the broadband and selective mid-infrared emissivity covering the surface. The pressure drop of the vertical axis denotes the rising of elevation. B. The vertical profile of the temperature difference between the two curves shown in (A). The radiative cooling material with a broadband mid-infrared emissivity enables a temperature decrease at each atmospheric layer compared with the one with a selective mid-infrared emissivity. The results suggest that a high mid-infrared emissivity across broadbands for a radiative cooling material is essential for maximizing the radiative energy output of large-scale applications.
Fig. S24 | The biodegradability tests under moist soil of CA and the mainly reported polymers for developing radiative cooling materials. CA shows the best biodegradability. The scale bar is 2 cm.
Fig. S25 | The setup used to measure the cooling temperature of the hierarchically designed CA film. A, A photograph of the experimental setup (bird’s view). The foam, sunlight reflector and PE film are used to reduce the impacts from ambient on the hierarchically designed CA film. B, A sectional (D-D in (A)) schematic of the setup.
Fig. S26| A photograph of the experimental setups for measuring the cooling power of the hierarchically designed CA film. They are composed of a power meter, a temperature controller, the hierarchically designed CA film with wind shelters coupled with sunlight reflectors, a computer, and thermocouples. The measuring method is consistent with previous studies (21, 22, 24).
Fig. S27 | Optical spectra of an ice-cream. A and B, sunlight and mid-infrared transmission spectra of an ice-cream, respectively. No matter sunlight or mid-infrared light hardly pass the ice-cream.
Supplementary Table

Table S1 | The surface radiation at equilibrium state for a radiative cooling material with a broadband or selective mid-infrared emissivity. The unit is W m\(^{-2}\). The arrows denote the directions of energy transfer referring to the ground: ↓ downward and ↑ upward.

|                   | Broadband | Selective | Difference |
|-------------------|-----------|-----------|------------|
| Solar net ↓       | 184.81    | 179.58    | -5.23      |
| Mid-infrared net ↑| 105.58    | 71.97     | -33.61     |
| Mid-infrared Net ↑(window band) | 72.46 | 71.97 | -0.49 |
| Mid-infrared Net ↑(non-window band) | 33.12 | 0 | -33.12 |
| Surface Net ↓     | 79.23     | 107.61    | 28.38      |
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