nature portfolio

Peer Review File

Self-adaptive and large-area sprayable thermal management coatings for energy saving

Corresponding Author: Professor Xinxing Zhang

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This work demonstrates a dual-mode thermal regulation material based on optical modulation for energy saving. The unique structure of amorphous calcium carbonate is utilized to achieve multistage scattering of incident light. The material exhibits not only exceptional optical properties but also large-area spraying feasibility. This work is novel and can overcome the overcooling of single-mode radiation cooling materials in the low-temperature environment with no energy consumption. While there is sufficient data to support the manuscript, it is essential to faithfully address the following comments:
（1）Could the authors provide more information about the experimental details related to the fabrication of CF? For example, the total amount of CCTM solution prepared for the fabrication of samples with a large area.（2）The CCTM film is prepared by vacuum filtration assembly and the CF is fabricated by spraying process. In practical applications, can it be used as a coating on other substrates?（3）PDRC materials have radiation ability to cool below the ambient temperature. The outdoor tests of this work have not given the ambient temperature, so it is impossible to judge whether it has the ability to reduce the temperature below the ambient temperature.（4）In Fig. 4f, it is obvious that net cooling power is related to heat transfer coefficients h. Please provide the heat transfer coefficients h of CCTM film.（5）The authors used a solar simulator for radiation cooling demonstration. This experiment is similar to the actual field PDRC performance demonstration under the sun. These two experiments may seem unnecessary.（6）It might be more intuitive to provide the color data in color space (such as CIE 1931) to represent the color change process of the material.

Reviewer #2

(Remarks to the Author)
The paper introduces a bio-based intelligent auto-switched dual-mode thermal management coating material. The solar heating/radiative cooling mode could be adaptively switched in different environment to save energy. The micro-heterostructures of amorphous calcium carbonate is very attractive and the formation process is interesting. This work provides a worthy radiative cooling design for dynamic thermal management materials through combining thermal sensitive phase change materials with PDRC. Therefore, it could be suitable for publication in Nature Communications if the issues listed below can be adequately revised.
1. The author should detail the quantitative method employed for characterizing fiber and particle sizes. This should encompass information regarding the number of samples characterized and averaged (not relative), as well as the specific software or methodologies employed in the analysis.
2. The authors claimed that the CCTM suspension exhibits long-term stability (more than one month). Details are required to justify whether this estimation is convincing.
3. Net cooling power of CCTM in white color is calculated. How about the net cooling power of CCTM in blue color?
4. More details are needed for the simulation of annual energy savings of CCTM.
5. The microstructure and size distribution of thermochromic micro-particles should be characterized alone, rather than in composites.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have carefully addressed all the raised issues in much details, and I would recommend its publication as it is.

Reviewer #2

(Remarks to the Author)
[Editor Note: Reviewer 2 made remarks to the Editor only and supports publication without any further changes]None

Point by Point Response to Reviewer Comments

To the Reviewer #1: This work demonstrates a dual-mode thermal regulation material based on optical modulation for energy saving. The unique structure of amorphous calcium carbonate is utilized to achieve multistage scattering of incident light. The material exhibits not only exceptional optical properties but also large-area spraying feasibility. This work is novel and can overcome the overcooling of single-mode radiation cooling materials in the low-temperature environment with no energy consumption. While there is sufficient data to support the manuscript, it is essential to faithfully address the following comments:

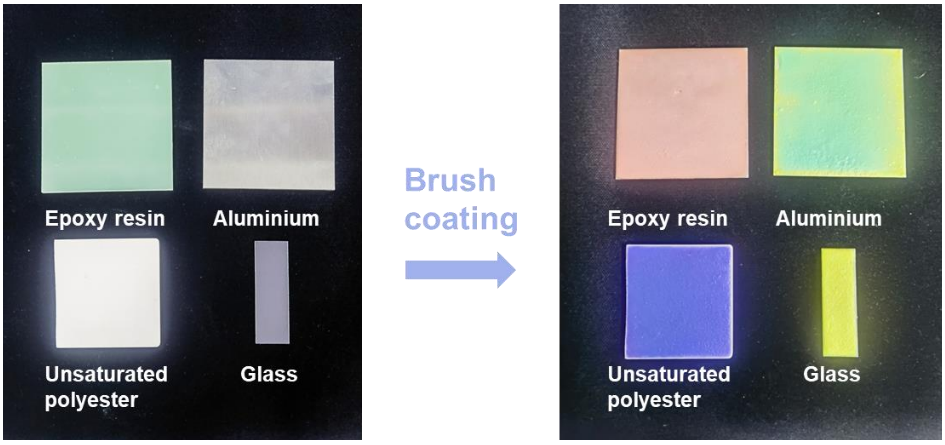
We appreciate your comments and suggestions, which are valuable for improving the quality of our manuscript. We have revised our manuscript in accordance with your instructive guidance and we believe the revised manuscript is a great improvement on the original version. Hopefully we have addressed all your concerns.

(1) Could the authors provide more information about the experimental details related to the fabrication of CF? For example, the total amount of CCTM solution prepared for the fabrication of samples with a large area.

√Thank you for your kind advice. To be specific, blue CCTM was stirred for 30 minutes before being sprayed on the original 0.9 m × 0.9 m fabric. In order to get a uniform fabric, a series of parameters were selected on purpose, including nozzle size of 3 mm, spray distance of 20 cm, spray time of about 2 min to paint the whole fabric and finally two times of sprays fore even coverage. About 400 ml CCTM suspension (1 wt.%) was consumed during the process of spraying.

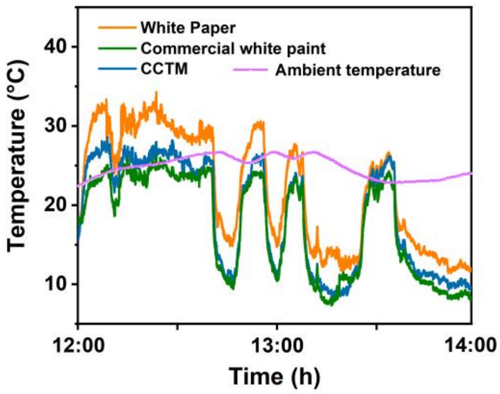
(2) The CCTM film is prepared by vacuum filtration assembly and the CF is fabricated by spraying process. In practical applications, can it be used as a coating on other substrates?

√Thank you very much for the kind suggestion. We have assembled the CCTM with different colors on different substrates, such as epoxy resin, aluminum, unsaturated polyester and glass via brush coating. The result shows that CCTM has excellent adhesion on these substrates.



(3) PDRC materials have radiation ability to cool below the ambient temperature. The outdoor tests of this work have not given the ambient temperature, so it is impossible to judge whether it has the ability to reduce the temperature below the ambient temperature.

√According to the suggestion of the reviewer, we conducted another outdoor experiment to record the surface temperature of white paper, commercial white paint, CCTM and ambient temperature on Feb. 10, 2025. The surface temperature of CCTM is higher than the ambient temperature under direct sunlight (12:00-12:40). While the surface temperature of CCTM is lower than the ambient temperature when the sun was covered by clouds (12:40-14:00). This result illustrates that CCTM can effectively switch between the heating mode and radiative cooling mode in cool environment.



(4) In Fig. 4f, it is obvious that net cooling power is related to heat transfer coefficients h. Please provide the heat transfer coefficients h of CCTM film.

√We conducted experiments accordingly based on the reviewer's suggestion. The thermal conductivity of TMCP is 0.45 W m^{-1} K^{-1}. Thank you for your kind suggestion.

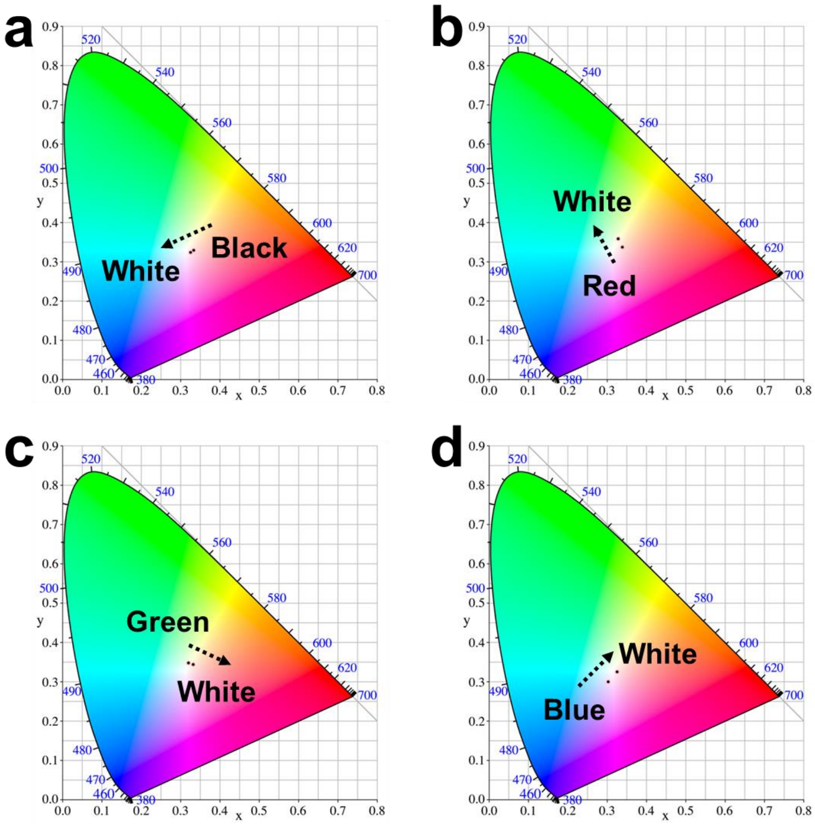
(5) The authors used a solar simulator for radiation cooling demonstration. This experiment is similar to the actual field PDRC performance demonstration under the sun. These two experiments may seem unnecessary.

√Thank you for your kind advice. To assess the PDRC performance of the CCTM film, a solar simulator is used to irradiate the sample vertically. In this experiment, solar simulator can provide an approximate spectrum specification of AM1.5G and a relatively stable power irradiation. As can be seen from the curve in Fig.4i, the three samples showed different heating behavior under relatively low light, which is conducive to the quantitative evaluation of the self-adaptive radiative cooling ability of CCTM.

On the other hand, the actual field PDRC performance demonstration is necessary for further practical application, since environmental conditions such as cloud cover, wind blow etc. should be taken into account. In addition, the solar flux (~850 W m^{-2}) is much higher than that of the simulation experiment in the actual measurement process. Thus, solar simulator demonstration and actual field PDRC performance demonstration are both necessary.

(6) It might be more intuitive to provide the color data in color space (such as CIE 1931) to represent the color change process of the material.

√Thank you for your useful advice. The Commission Internationale de l’ Eclairage (CIE) chromaticity coordinates of black, red, green, blue samples and their white states have been added as follow. The results show that the x and y coordinates visibly shift between two different color state.



To the Reviewer # 2: The paper introduces a bio-based intelligent auto-switched dual-mode thermal management coating material. The solar heating/radiative cooling mode could be adaptively switched in different environment to save energy. The micro-heterostructures of amorphous calcium carbonate is very attractive and the formation process is interesting. This work provides a worthy radiative cooling design for dynamic thermal management materials through combining thermal sensitive phase change materials with PDRC. Therefore, it could be suitable for publication in Nature Communications if the issues listed below can be adequately revised.

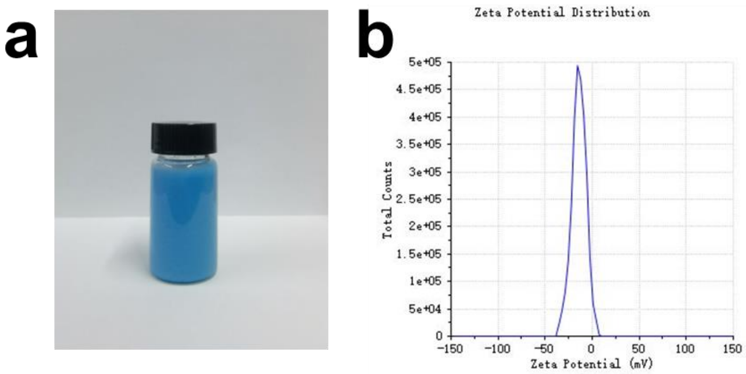
We acknowledge your comments and suggestions. We have revised our manuscript in accordance with your instructive guidance. Hopefully, we have addressed your concerns. Thank you very much.

1. The author should detail the quantitative method employed for characterizing fiber and particle sizes. This should encompass information regarding the number of samples characterized and averaged (not relative), as well as the specific software or methodologies employed in the analysis.

√Thank you for your kind question. Nano Measure 1.2 was used for quantitative size statistics. More than 100 samples (both ACC and TMP) were randomly selected from SEM images for data statistics. The size distributions of ACC and TMP were obtained by the ratio of the number of ACC/TMP to the total number of the samples.

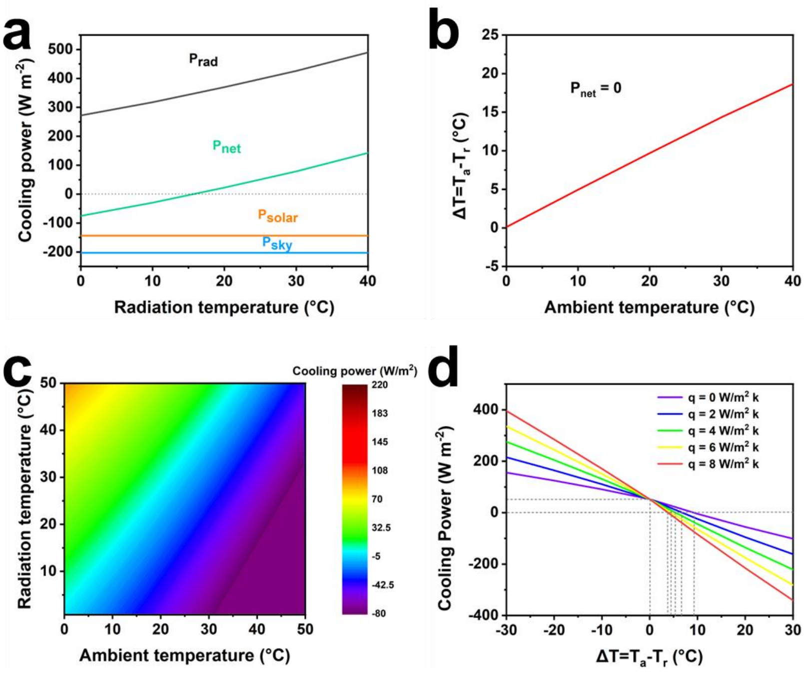
2. The authors claimed that the CCTM suspension exhibits long-term stability (more than one month). Details are required to justify whether this estimation is convincing.

√Thank you for the valuable suggestion. Photograph of CCTM suspension shows that CCTM is stable over a period of more than one month. We further conducted the Zeta characterization to quantitatively evaluated the suspension stability of CCTM. The result shows that the Zeta potential of CCTM suspension is -19.2 mV, proving that CCTM suspension has strong electrostatic repulsion. Besides, the volume effect among C-CNFs endows CCTM with long-term stability.



3. Net cooling power of CCTM in white color is calculated. How about the net cooling power of CCTM in blue color?

√Thank you for your constructive suggestion. Net cooling power (P_{net}) of the blue CCTM is further calculated. It can be seen that the P_{net} is about 20 W/m^2 with a 20 °C radiation temperature, while the P_{net} is 142 W/m^2 with a 40 °C radiation temperature. When the P_{net} is zero, maximum temperature drop (ΔT) can reach 17 °C with a 40 °C radiation temperature. However, the cooling power of the blue CCTM is much lower than that of white CCTM due to the strong absorption of sunlight in colored state. Consequently, blue CCTM can achieve a temperature drop about 3.8 °C under the condition of quite high conductive−convective heat transfer, which is much lower than that of CCTM in white state.



4. More details are needed for the simulation of annual energy savings of CCTM.

√Thank you for your constructive suggestion. Weather data for different cities are obtained from the official EnergyPlus weather database. As shown in Supplementary Fig. S11, building model constructed in Openstudio software has eight rooms on two floors. The indoor air temperature is established at 24 °C throughout the year, and all cooling and heating capacities are automatically adjusted. The parameters for the external building materials of the original building are as follows:

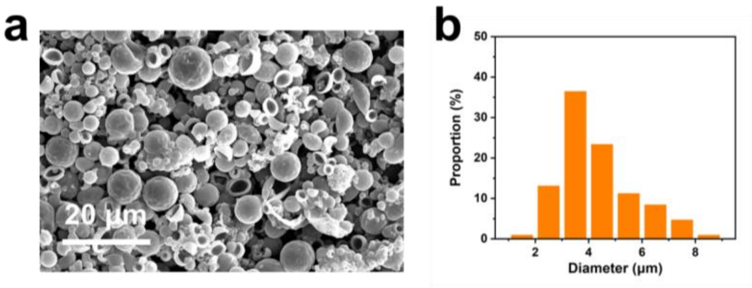
CCTM (Solar absorptance = 0.08, thermal emissivity = 0.93) compared to white paper (Solar absorptance = 0.48, thermal emissivity = 0.9) in summer.

CCTM (Solar absorptance = 0.28, thermal emissivity = 0.9) compared to commercial white paint (Solar absorptance = 0.07, thermal emissivity = 0.94) in winter.

5. The microstructure and size distribution of thermochromic micro-particles should be characterized alone, rather than in composites.

√According to the reviewer's suggestion, we have characterized the microstructure and size distribution of thermochromic micro-particles using scanning electron microscopy (SEM). The

SEM image shows that the particle sizes is predominantly about 4 μm, most of which are spherical and a small part of them are collapsed. Thank you for your valuable advice.



Thank you very much for your assistance in this review process. The manuscript has been resubmitted to your journal. We look forward to your response. If there is something else needed, please do not hesitate to contact me directly by email listed below, and I will answer you as soon as possible.

With best regards,

Sincerely yours,

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