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(54) **RECYCLABLE, SELF-CLEANING CELLULOSE-FIBER COMPOSITES**

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(57) **ABSTRACT**

Disclosed are composite paper materials comprising hydrophobic fluorocarbons. Also disclosed are passive cooling materials comprising the composite paper materials. Further disclosed are methods of making the composite paper materials.

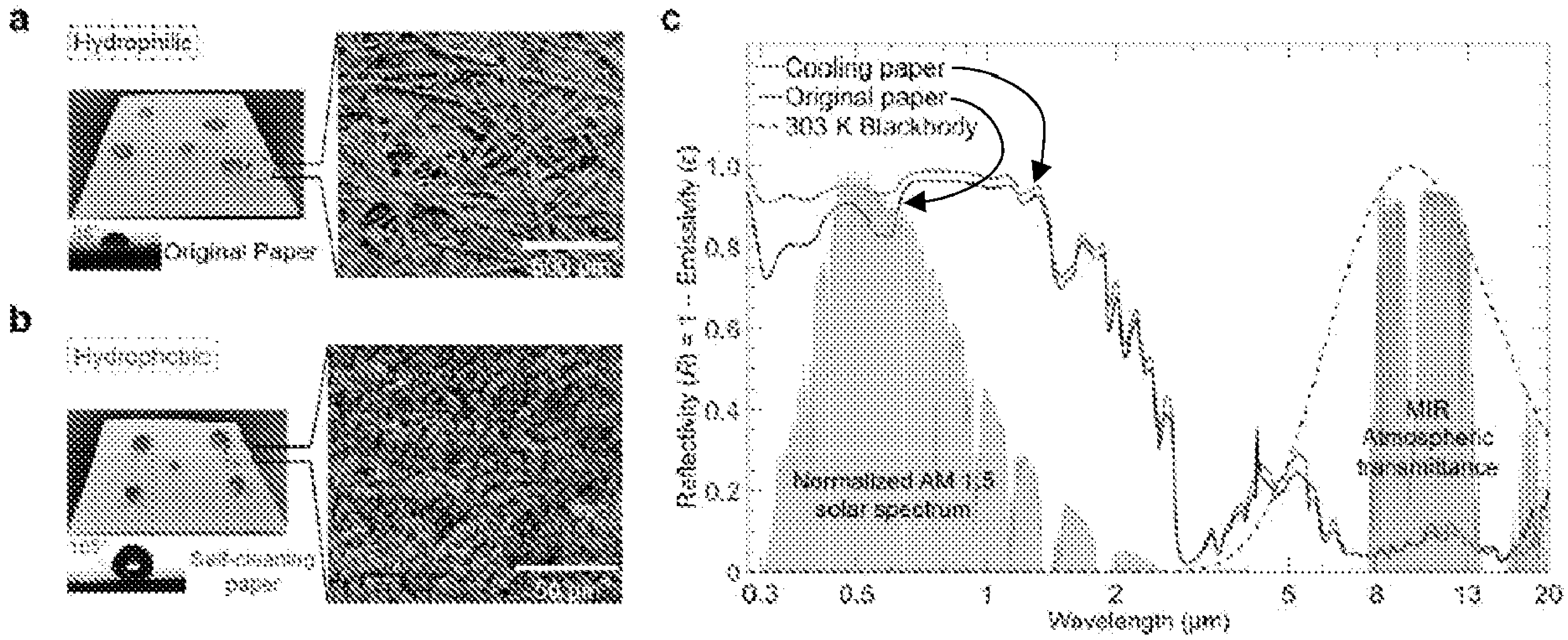


FIG. 1

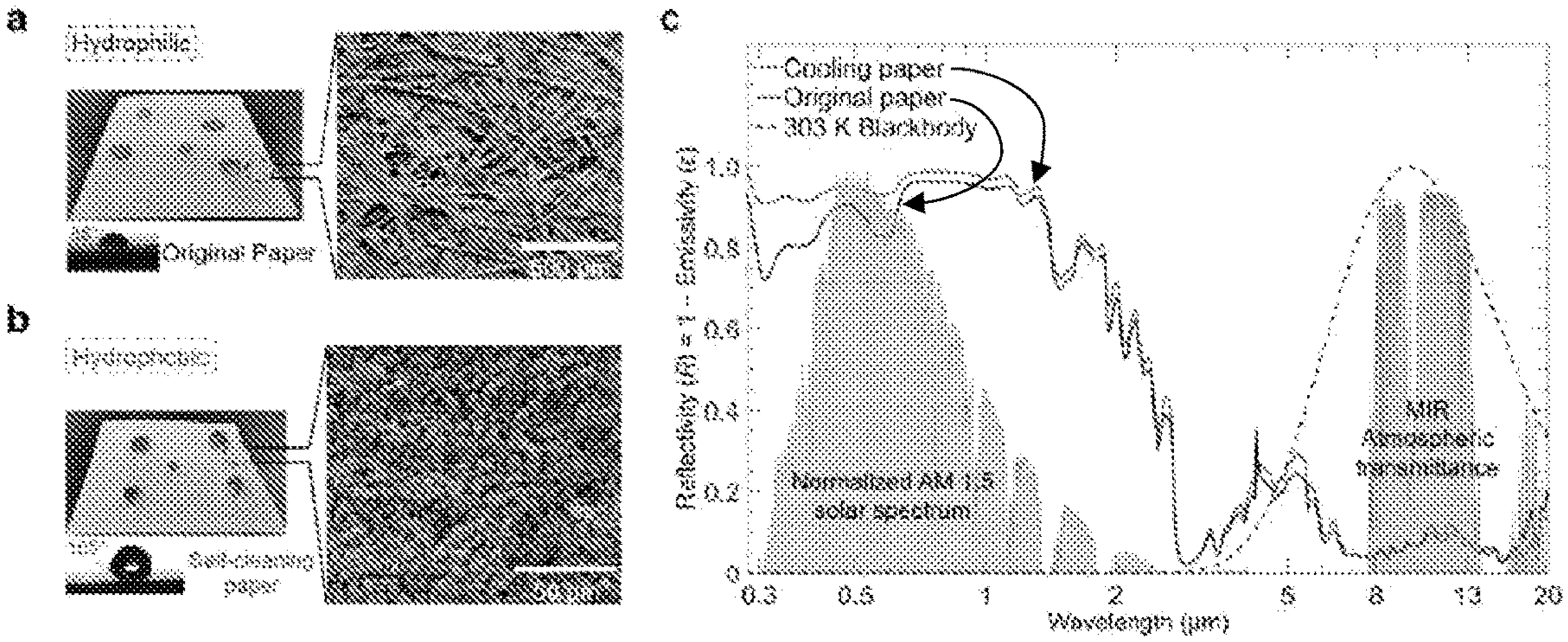

a
Hydrophilic
Original Paper
b
Hydrophobic
Self-cleaning paper
50 μm
c
Cooling paper
Original paper
303 K Blackbody
Reflectivity (R) = 1 − Emissivity (ε)
1.0
0.8
0.6
0.4
0.2
0
Normalized AM 1.5 solar spectrum
MIR Atmospheric transmittance
0.3
0.5
1
2
5
8
13
20
Wavelength (μm)

FIG. 2

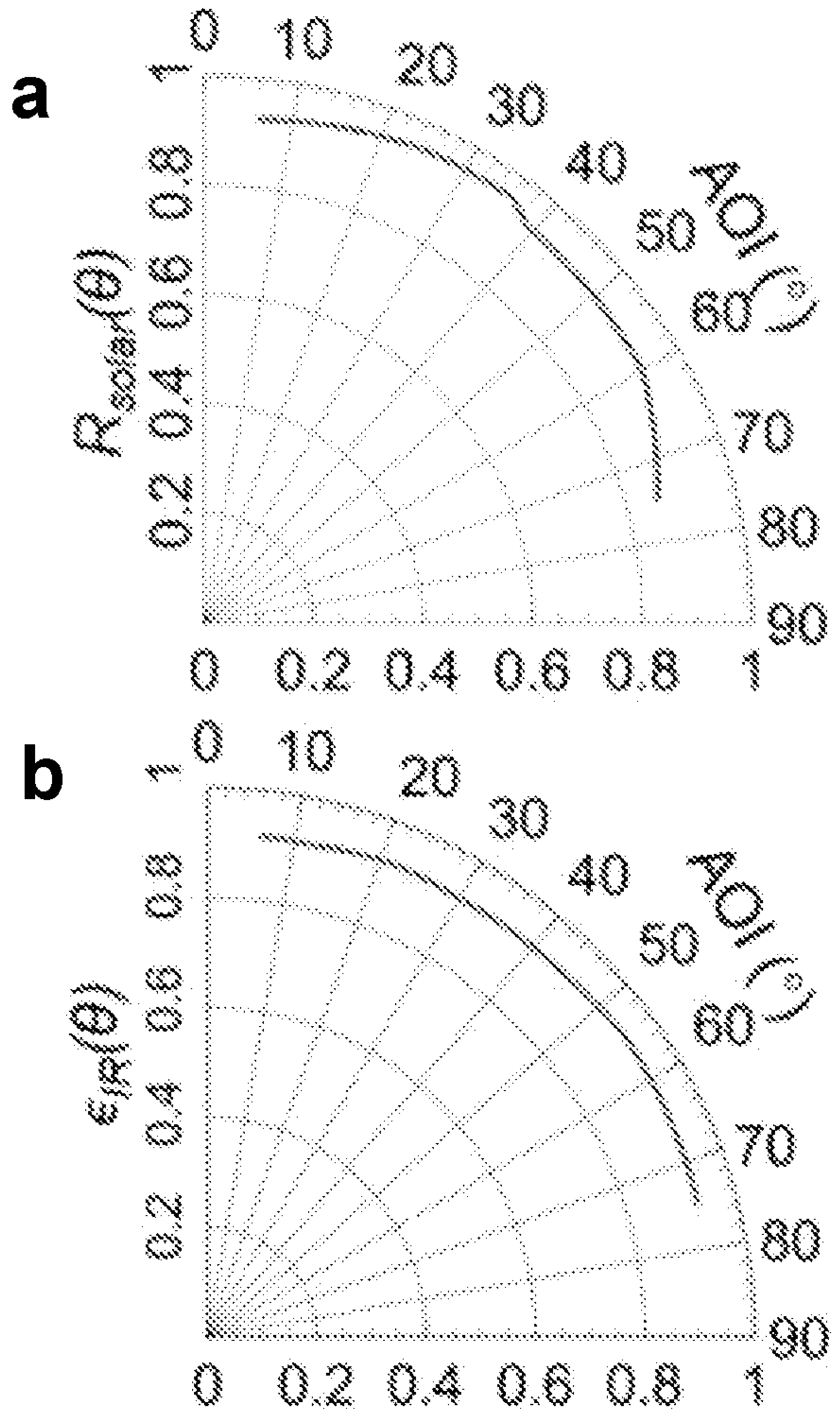

a
$R_{solar}(\theta)$
AOI (°)
0
10
20
30
40
50
60
70
80
90
0.2
0.4
0.6
0.8
1
0
0.2
0.4
0.6
0.8
1
b
$\epsilon_{IR}(\theta)$
AOI (°)
0
10
20
30
40
50
60
70
80
90
0.2
0.4
0.6
0.8
1
0
0.2
0.4
0.6
0.8
1

FIG. 3

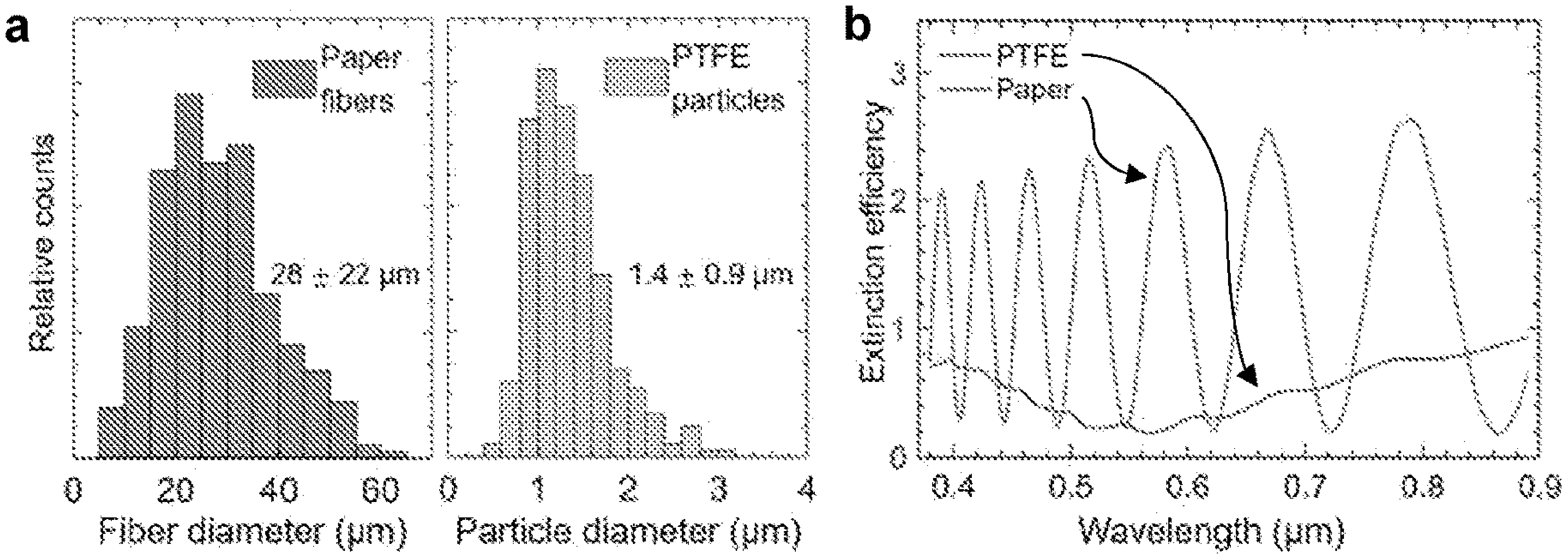

a
Relative counts
Paper fibers
28 ± 22 µm
0
20
40
60
Fiber diameter (µm)
PTFE particles
1.4 ± 0.9 µm
0
1
2
3
4
Particle diameter (µm)
b
Extinction efficiency
PTFE
Paper
0
1
2
3
0.4
0.5
0.6
0.7
0.8
0.9
Wavelength (µm)

FIG. 4

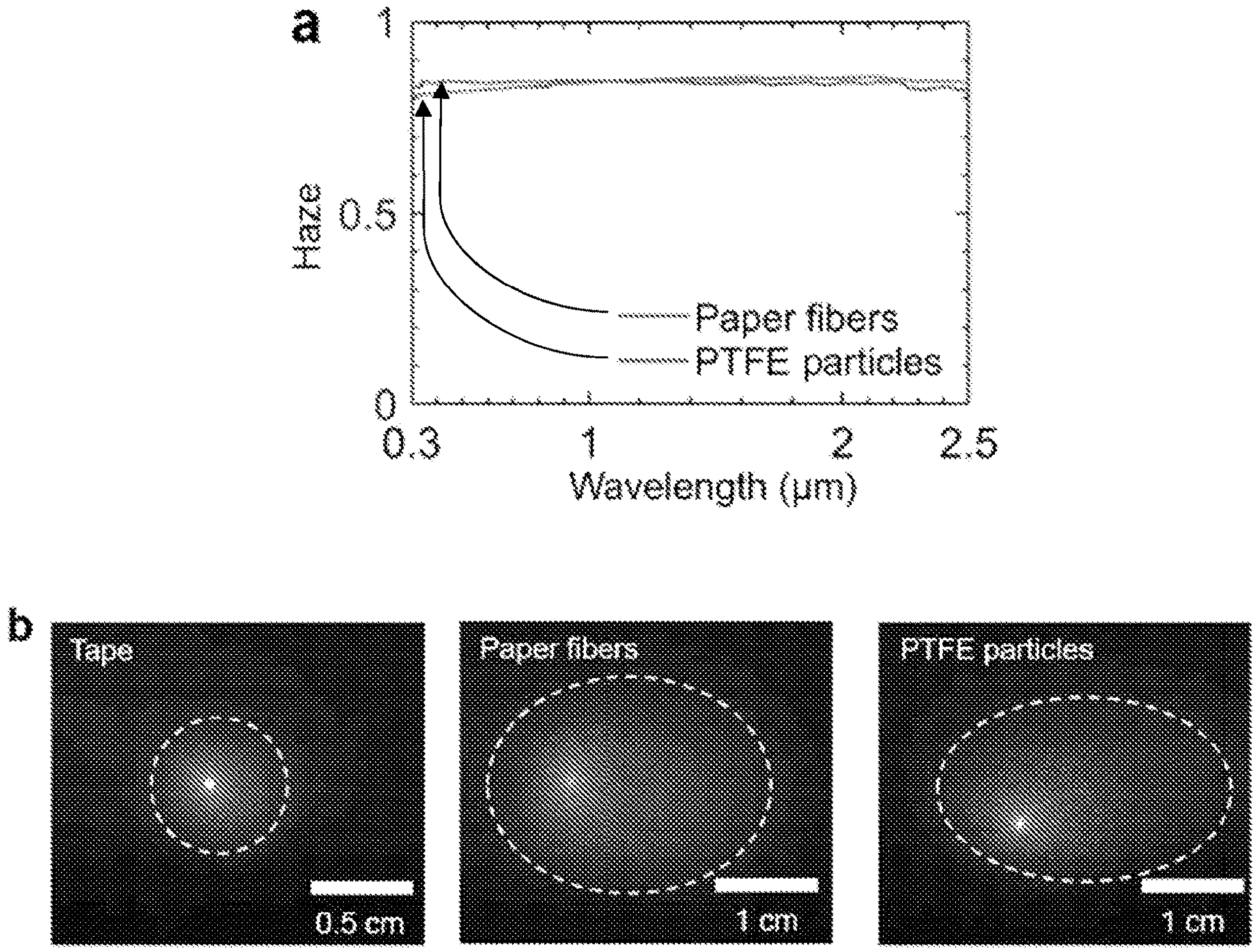

a
1
0.5
0
Haze
0.3
1
2
2.5
Wavelength (μm)
Paper fibers
PTFE particles
b
Tape
0.5 cm
Paper fibers
1 cm
PTFE particles
1 cm

FIG. 5

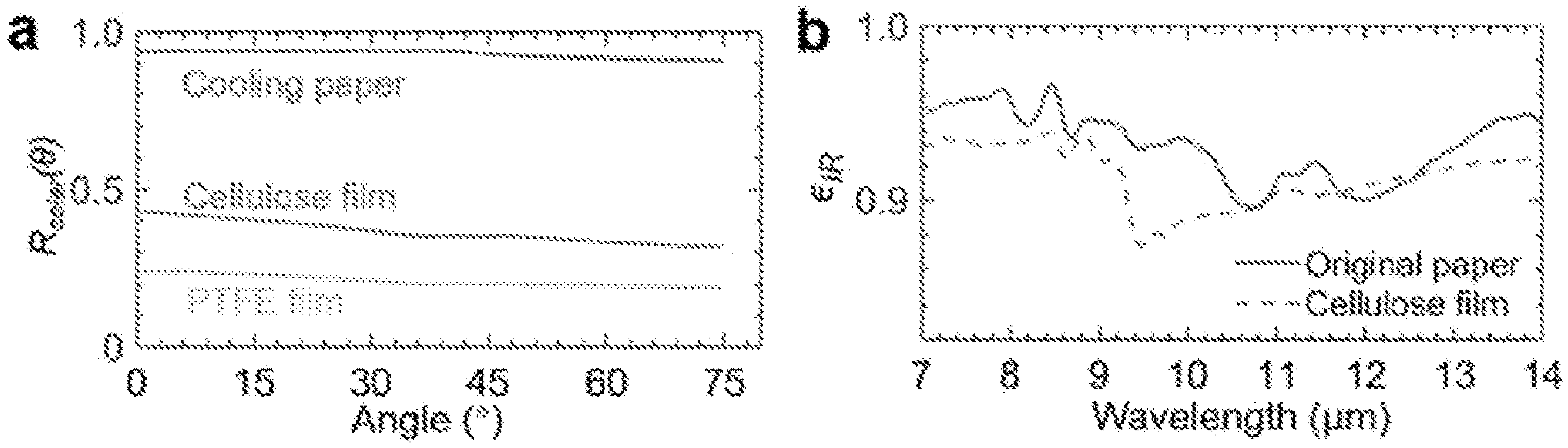

a
b
$R_{solar}(\theta)$
1.0
0.5
0
Cooling paper
Cellulose film
PTFE film
0
15
30
45
60
75
Angle (°)
ϵ_{IR}
1.0
0.9
Original paper
Cellulose film
7
8
9
10
11
12
13
14
Wavelength (μm)

FIG. 6

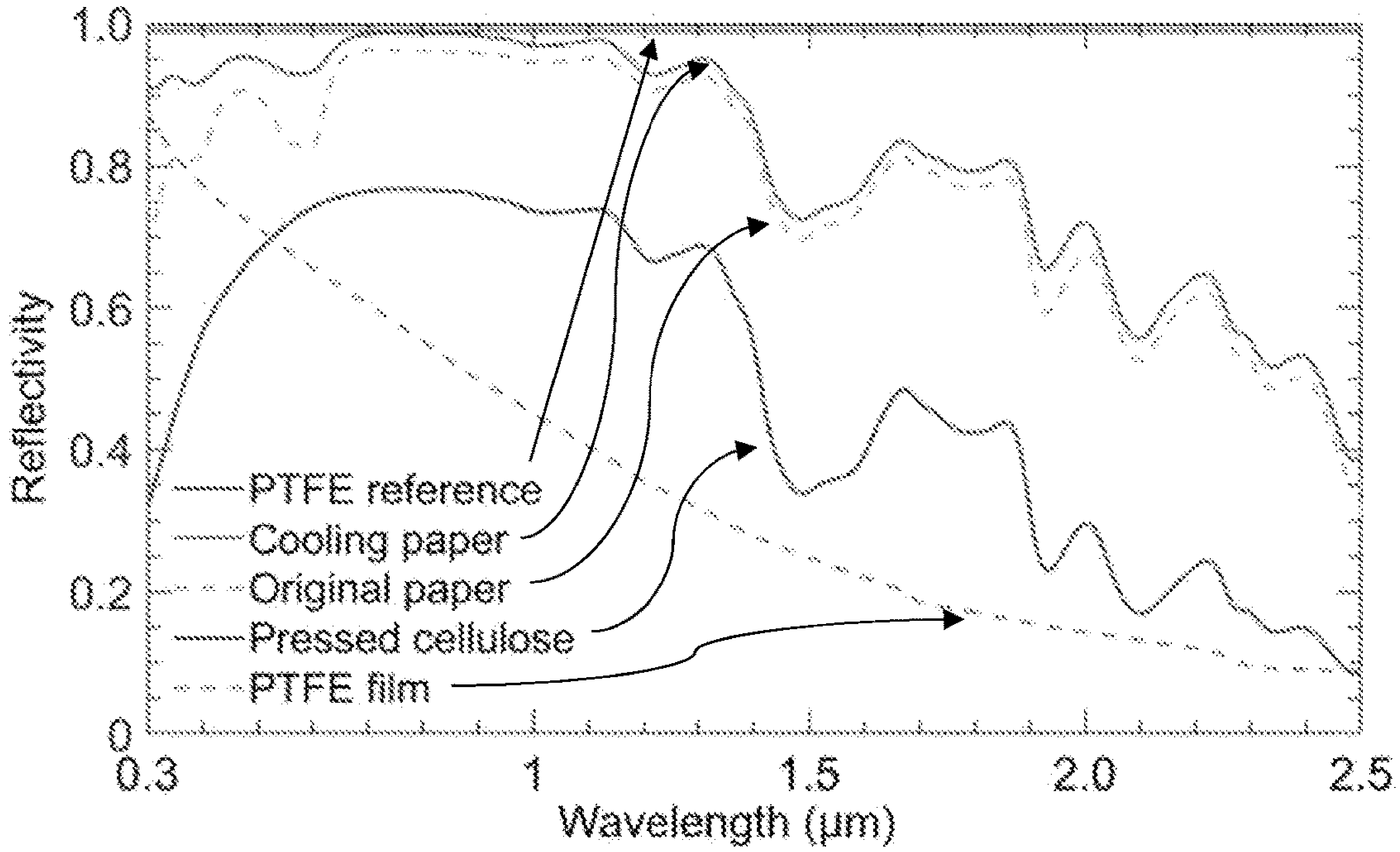

Reflectivity
1.0
0.8
0.6
0.4
0.2
0
PTFE reference
Cooling paper
Original paper
Pressed cellulose
PTFE film
0.3
1
1.5
2.0
2.5
Wavelength (μm)

FIG. 7

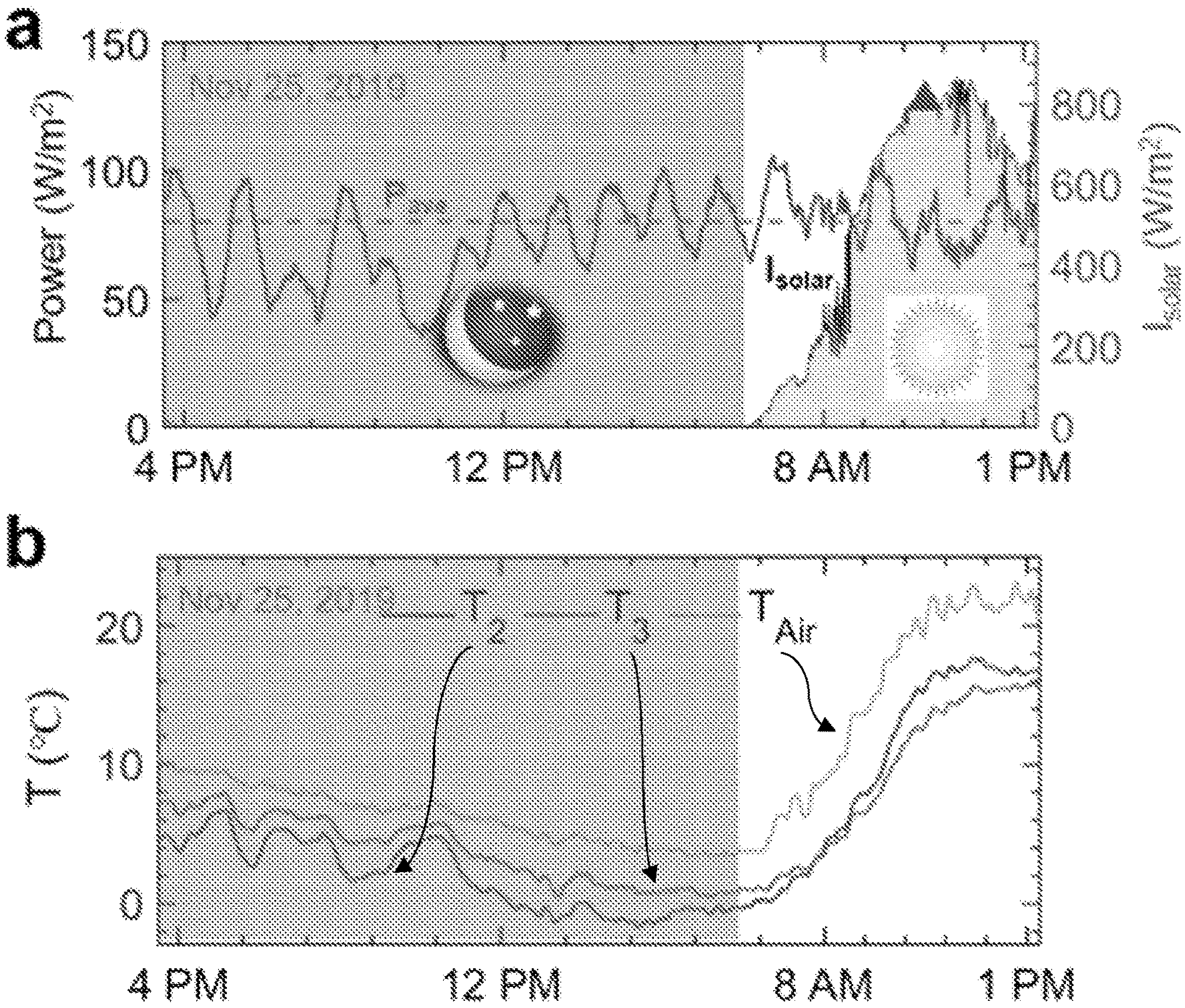

a
Nov 25, 2019
Power (W/m^2)
150
100
50
0
P_{rad}
I_{solar}
800
600
400
200
0
I_{solar} (W/m^2)
4 PM
12 PM
8 AM
1 PM
b
Nov 25, 2019
T_2
T_3
T_{Air}
T (°C)
20
10
0
4 PM
12 PM
8 AM
1 PM

FIG. 8

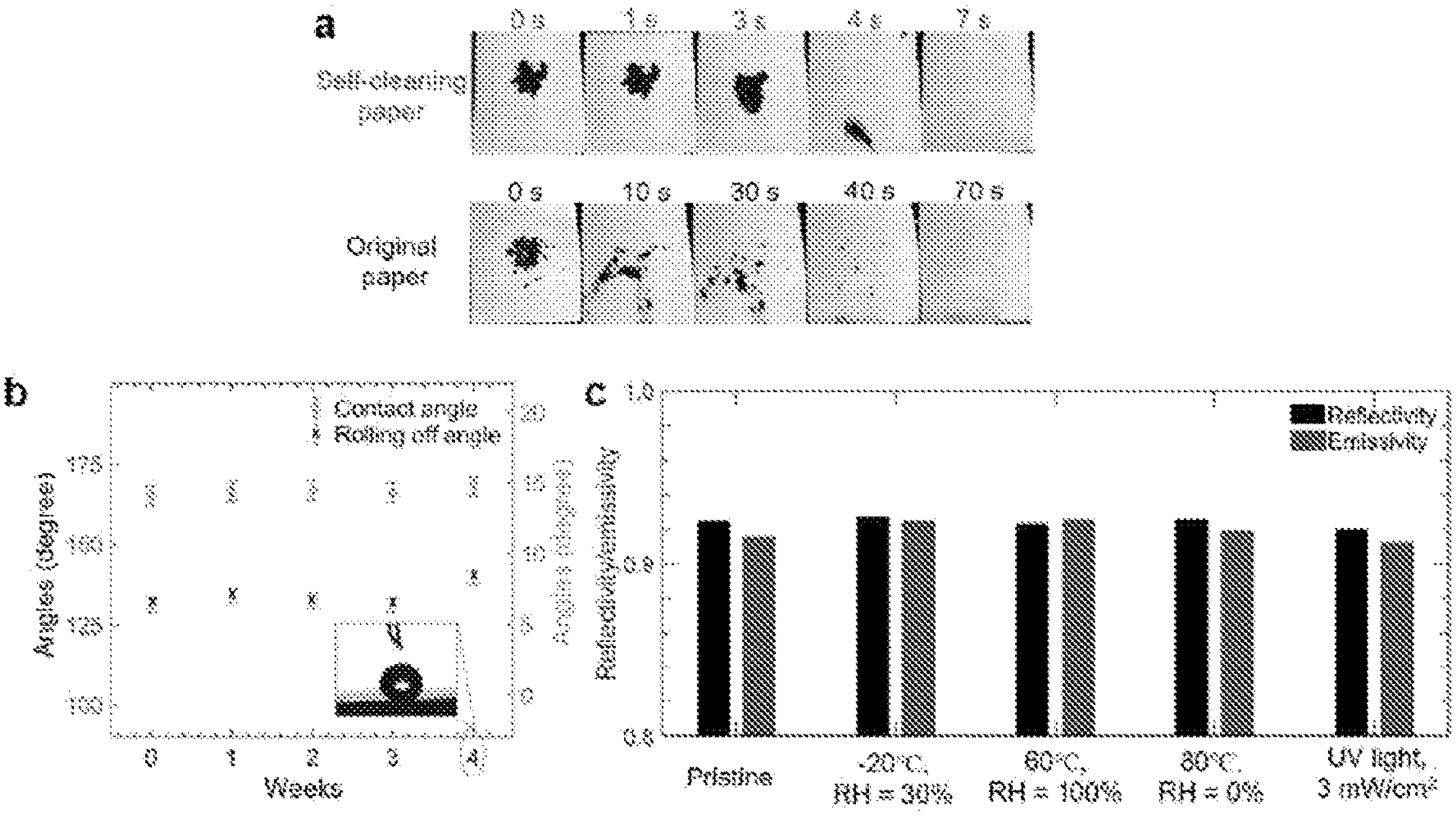

a
0 s
1 s
3 s
4 s
7 s
Self-cleaning paper
0 s
10 s
30 s
40 s
70 s
Original paper
b
Contact angle
Rolling off angle
Angles (degrees)
175
150
125
100
20
15
10
5
0
Angles (degrees)
0
1
2
3
4
Weeks
c
1.0
0.9
0.8
Reflectivity/emissivity
Reflectivity
Emissivity
Pristine
-20°C, RH = 30%
60°C, RH = 100%
80°C, RH = 0%
UV light, 3 mW/cm²

FIG. 9

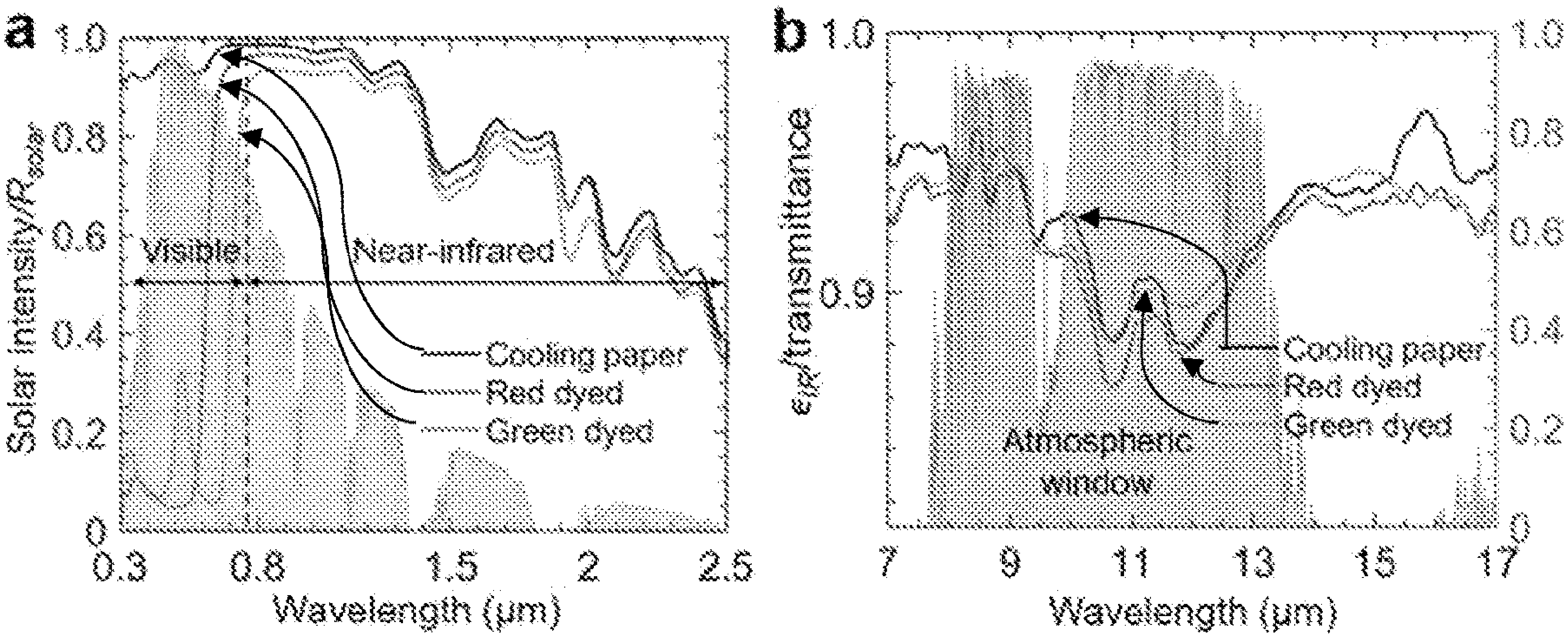
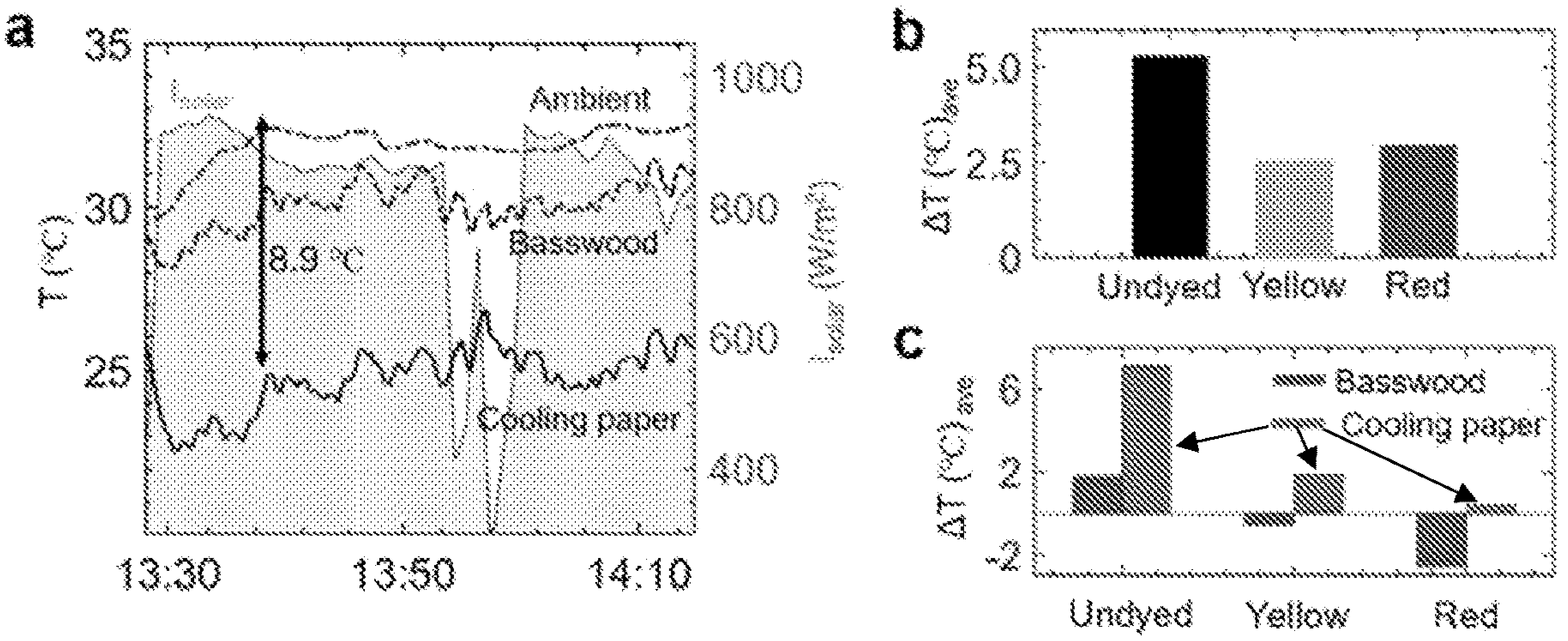

a
1.0
0.8
0.6
0.4
0.2
0
Solar intensity/R_{solar}
Visible
Near-infrared
Cooling paper
Red dyed
Green dyed
0.3
0.8
1.5
2
2.5
Wavelength (μm)
b
1.0
0.9
ϵ_{IR}/transmittance
1.0
0.8
0.6
0.4
0.2
0
Atmospheric window
Cooling paper
Red dyed
Green dyed
7
9
11
13
15
17
Wavelength (μm)

FIG. 10


a
35
30
25
T (°C)
1000
800
600
400
I_{solar} (W/m²)
I_{solar}
Ambient
Basswood
8.9 °C
Cooling paper
13:30
13:50
14:10
b
5.0
2.5
0
ΔT (°C)$_{ave}$
Undyed
Yellow
Red
c
6
2
-2
ΔT (°C)$_{ave}$
Basswood
Cooling paper
Undyed
Yellow
Red

RECYCLABLE, SELF-CLEANING CELLULOSE-FIBER COMPOSITES

RELATED APPLICATION

[0001] This application claims the benefit of priority to U.S. Provisional Patent Application No. 63/128,941, filed Dec. 22, 2020, which is incorporated herein by reference in its entirety.

GOVERNMENT SUPPORT

[0002] This invention was made with government support under Grant Number 1941743 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND

[0003] Compressor-based cooling systems, providing comfortable interior environments for infrastructures (e.g., buildings), accounted for about 20% of total electricity consumption around the world in 2020. The resultant heating effects and greenhouse gas emissions accelerate global warming and climate change.

[0004] The passive radiative cooling (PRC) technique can achieve sub-ambient cooling effects under direct sunlight without any energy consumption by reflecting sunlight (0.3-2.5 μm) and radiating excessive heat as infrared thermal radiation through the Earth's atmospheric window (8-13 μm). However, state-of-the-art PRC materials face challenges such as complicated and expensive fabrication approaches and performance degradation arising from surface contamination. Additionally, prior PRC materials are susceptible to contamination by floating dust, dirt, and soot when exposed to the outdoor environment, which deteriorates their solar reflectivity and thermal emissivity.

SUMMARY OF INVENTION

[0005] In certain aspects, the present disclosure relates to low-cost, recyclable, self-cleaning, and self-cooling cellulose-fiber-based composite materials. Exemplary uses of the composites include but are not limited to residential buildings, cars, warehouses, or other infrastructures. The composites may achieve efficient and cost-effective passive radiative cooling. In addition, composite materials of the present disclosure may be manufactured on a large scale at reduced costs and may require little or no maintenance. The composite materials may be manufactured from recycled materials to further decrease costs. Moreover, the passive cooling materials of the present invention may outperform the cooling performance cooling plastic films or paints known in the art.

[0006] In certain aspects, the present invention provides a paper comprising cellulose fibers; and a hydrophobic fluorocarbon; wherein the amount of the hydrophobic fluorocarbon is about 0.1 wt % to about 5 wt % of the paper.

[0007] In certain aspects, the hydrophobic fluorocarbon is polytetrafluoroethylene.

[0008] In certain aspects, the paper further comprises a dye.

[0009] In further aspects, the present invention provides a passive cooling material comprising a paper, comprising cellulose fibers; and a hydrophobic fluorocarbon;

[0010] wherein the amount of the hydrophobic fluorocarbon is about 0.1 wt % to about 5 wt % of the paper.

[0011] In certain aspects, the present invention provides a method for making a paper, comprising mixing cellulose fibers, a hydrophobic fluorocarbon, and water, thereby forming a pulp; pressing the pulp, thereby forming a pressed pulp; and drying the pressed pulp, thereby forming a paper.

[0012] In further aspects, the present invention provides a method for making a paper, comprising mixing cellulose fibers and water, thereby forming a pulp; pressing the pulp, thereby forming a pressed pulp; drying the pressed pulp, thereby forming a paper; and spraying the paper with a hydrophobic fluorocarbon.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] FIG. **1**A shows surface-wetting states and microstructures of paper without a hydrophobic fluorocarbon (the "original paper").

[0014] FIG. **1**B shows surface-wetting states and microstructures of PTFE-coated paper composites.

[0015] FIG. **1**C shows hemispherical spectral reflectivity ($R=1-\epsilon$) of the original paper and composites displayed with the normalized ASTM G-173 (AM 1.5) solar spectrum, the mid-infrared (MIR) atmospheric transparent window (MODTRAN 4), and the spectral irradiation of a 303 K blackbody.

[0016] FIG. **2**A shows solar reflectivity of PTFE-coated paper composites across various angles of incidence.

[0017] FIG. **2**B shows infrared thermal emissivity of PTFE-coated paper composites across various angles of incidence.

[0018] FIG. **3**A shows size distributions of the cellulose-fiber-based paper fibers and PTFE particles.

[0019] FIG. **3**B shows finite-difference time-domain (FDTD)-simulated scattering cross-section spectra of the cellulose fibers and PTFE particles.

[0020] FIG. **4**A shows transmission haze spectra of the paper fibers and PTFE particles with an incident angle of 0°.

[0021] FIG. **4**B is laser images showing the scattering effects of a red laser shining at cellulose fibers and PTFE particles sticking on a bi-axially oriented polypropylene tape film.

[0022] FIG. **5**A shows solar reflectivity (R_{solar}) of the PTFE-coated paper composites at different incident angles from 0 to 75° compared with the solid cellulose and PTFE films having the same thickness (700 μm).

[0023] FIG. **5**B shows infrared emissivity (ϵ_{IR}) of the original paper and cellulose film from 7 to 14 μm.

[0024] FIG. **6** shows reflectivity spectra of the original paper, PTFE-coated paper composites (cooling paper), pressed cellulose, and PTFE film.

[0025] FIG. **7**A shows the cooling power of the PTFE-coated paper composites over approximately one day.

[0026] FIG. **7**B shows temperature variations of the paper composites in chambers a-2, a-3, and the ambient over approximately one day.

[0027] FIG. **8**A shows photographs of the PTFE-coated paper composites and the original paper when stained with the garden soil at various times.

[0028] FIG. **8**B shows contact angle and rolling-off angle of the PTFE-coated paper composites after various times of outdoor exposure. The inset shows the water contact angle of paper composites after a four-week outdoor test.

[0029] FIG. **8**C shows overall solar reflectivity and thermal emissivity of the PTFE-coated paper composites after being subjected to various environmental factors for 30 days.

[0030] FIG. **9**A shows solar reflectivity spectra of red- and green-dyed papers composites compared to an undyed paper composite.

[0031] FIG. **9**B shows thermal emissivity spectra of red- and green-dyed papers composites compared to an undyed paper composite.

[0032] FIG. **10**A shows temperature variations (left axis) and solar intensity (right axis) in an outdoor test of basswood and paper composites.

[0033] FIG. **10**B shows average temperature difference between the ambient and the PTFE-coated paper composites.

[0034] FIG. **10**C shows average temperature difference between the ambient and the PTFE-coated paper composites and basswood (undyed, yellow-dyed, and red-dyed) in an outdoor test. Positive values show that the chamber temperature is lower than the ambient air, and vice versa.

DETAILED DESCRIPTION

[0035] Disclosed is a composite material (also referred to herein as a "paper," "cooling paper," or "paper composite") that includes one or more hydrophobic materials. In certain embodiments, the hydrophobic materials comprise tetrafluoroethylene (PTFE), such as PTFE microparticles. The PTFE microparticles coat cellulose fibers of the composite material. The composite materials preferably exhibit excellent self-cooling and self-cleaning capabilities. In some embodiments, the composite materials form paper-based passive radiative cooling (PRC) materials. The PRC materials may reduce or eliminate the need for the coolant, electricity, and compressor required by traditional mechanical cooling systems. In some embodiments, the present disclosure relates to the design, fabrication, and use of the composite materials.

Definitions

[0036] As used in this application, the singular form "a", "an" and "the" include plural references unless the context clearly dictates otherwise. Thus, for example, reference to "a compound" includes a plurality of compounds and reference to "a paper" includes a plurality of papers and the like. The use of "or" is inclusive and means "and/or" unless stated otherwise.

[0037] Unless specifically noted in the above specification, embodiments in the specification that recite "comprising" various components are also contemplated as "consisting of" or "consisting essentially of" the recited components; embodiments in the specification that recite "consisting of" various components are also contemplated as "comprising" or "consisting essentially of" the recited components; embodiments in the specification that recite "about" various components are also contemplated as "at" the recited components; and embodiments in the specification that recite "consisting essentially of" various components are also contemplated as "consisting of" or "comprising" the recited components (this interchangeability does not apply to the use of these terms in the claims).

[0038] Numeric ranges are inclusive of the numbers defining the range. Measured and measureable values are understood to be approximate, taking into account significant digits and the error associated with the measurement. As used in this application, the terms "about" and "approximately" have their art-understood meanings; use of one vs the other does not necessarily imply different scope. Unless otherwise indicated, numerals used in this application, with or without a modifying term such as "about" or "approximately", should be understood to encompass normal divergence and/or fluctuations as would be appreciated by one of ordinary skill in the relevant art. In certain embodiments, the term "approximately" or "about" refers to a range of values that fall within 25%, 20%, 19%, 18%, 17%, 16%, 15%, 14%, 13%, 12%, 11%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3%, 2%, 1%, or less in either direction (greater than or less than) of a stated reference value unless otherwise stated or otherwise evident from the context (except where such number would exceed 100% of a possible value).

[0039] The term "solar reflectivity" (R_{solar}) as used herein refers to the ability of a material to reflect solar energy. When described quantitatively, solar reflectivity is measured according to the methods described herein, unless indicated otherwise. "Solar reflectivity" may also be referred to as "solar reflectance."

[0040] The term "infrared thermal emissivity" (ξ_{IR}) as used herein refers to the ability of a material to radiate infrared energy. When described quantitatively, infrared thermal emissivity is measured according to the methods described herein, unless indicated otherwise. "Infrared thermal emissivity" may also be referred to as "infrared emissivity."

[0041] The term "paper" as used herein refers to any composite material according to the present disclosure.

[0042] The term "hydrophobic" as used herein refers to a material that has low or no affinity for water and/or repels water. Hydrophobic materials are not substantially wettable by water. Hydrophobicity can be determined by methods known in the art, such as, for example, static water contact angle measurement. In some embodiments, hydrophobic materials of the present disclosure have a static water contact angle of greater than about 90°, greater than about 100°, greater than about 110°, greater than about 120°, greater than about 130°, greater than about 140°, greater than about 150°, greater than about 160°, or greater than about 170°.

Embodiments of the Invention

[0043] In certain embodiments, the present invention provides a paper, comprising cellulose fibers; and a hydrophobic fluorocarbon; wherein the amount of the hydrophobic fluorocarbon is about 0.01 wt % to about 15 wt %, about 0.01 wt % to about 10 wt %, about 0.01 wt % to about 5 wt %, about 0.1 wt % to about 15 wt %, about 0.1 wt % to about 10 wt %, about 0.1 wt % to about 5 wt %, about 1 wt % to about 15 wt %, about 1 wt % to about 10 wt %, about 1 wt % to about 5 wt %, or about 5 wt % to about 10 wt % of the paper.

[0044] In some embodiments, the amount of cellulose is at least about 60%, at least about 70%, at least about 80%, at least about 90%, about 60% to about 99%, about 70% to about 99%, about 80% to about 99%, about 90% to about 99%, about 60% to about 95%, about 70% to about 95%, about 80% to about 9%, or about 90% to about 95% of the paper.

[0045] In certain embodiments, the hydrophobic fluorocarbon is polytetrafluoroethylene. In certain embodiments, the hydrophobic fluorocarbon is 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane.

[0046] In certain embodiments, the paper further comprises a dye. In certain embodiments, the dye is a food dye. For example, in some embodiments, the food dye is brilliant blue (E133), indigo carmine (E132), tartrazine (E102), sunset yellow FCF (E110), or Allura Red AC (E129). The dye adds color to the paper, which may be used, for example, to add colored surfaces to a building for esthetic purposes.

[0047] In certain embodiments, at least some of the cellulose fibers are derived from recycled paper. In certain embodiment, the paper further comprises hemicellulose and lignin. In certain embodiments, at least some of the hemicellulose and lignin fibers are derived from recycled paper. It is contemplated that the paper may be formed from, among other things, recycled paper products. It is further contemplated that the paper may be recycled to form another paper product of the present disclosure.

[0048] In certain embodiments, the cellulose fibers have an average fiber diameter of about 5 μm to about 50 μm, about 15 μm to about 40 μm, or about 20 μm to about 50 μm. In certain embodiments, the cellulose fibers have an average fiber diameter of about 28 μm.

[0049] In certain embodiments, the cellulose fibers have an average fiber length of about 1 mm to about 10 mm or about 1 mm to about 5 mm.

[0050] In certain embodiments, the hydrophobic fluorocarbon is in the form of a plurality of particles. The plurality of particles may have an average particle diameter of about 0.1 μm to about 5 μm, about 0.3 μm to about 2.5 μm, about 0.5 μm to about 2.5 μm, or about 0.7 μm to about 2.3 μm. In some embodiments, the plurality of particles has an average particle diameter of about 1.4 μm or about 1.5 μm. In certain embodiments, the cellulose and other materials of the paper form microsized pores, inside of which the particles reside. In certain embodiments, the cellulose fibers form a porous material having an average pore size of about 10 μm to about 30 μm. In certain embodiments, the average pore size is about 20 μm. In some embodiments, the pores have an average pore diameter of about 0.1 μm to about 5 μm, about 0.3 μm to about 2.5 μm, about 0.5 μm to about 2.5 μm, or about 0.7 μm to about 2.3 μm. In some embodiments, the pores have an average pore diameter of about 1.4 μm or about 1.5 μm.

[0051] In certain embodiments, the paper has a thickness of about 0.1 mm to about 15 mm, about 0.1 mm to about 10 mm, about 0.1 mm to about 5 mm, about 0.1 mm to about 3 mm, about 1 mm to about 15 mm, about 1 mm to about 10 mm, about 1 mm to about 5 mm, or about 1 mm to about 3 mm. In certain embodiments, the paper has a thickness of about 0.3 mm to about 1.2 mm.

[0052] In certain embodiments, at least one surface of the paper is impervious to water. For example, in some embodiments, the hydrophobic fluorocarbon forms a hydrophobic coating on the cellulose-fiber-based paper. Such a coating protects the cellulose-fiber-based paper from water wetting and/or dust contamination, while also reinforcing its solar reflectivity by sunlight backscattering. In some embodiments, the hydrophobic coating has a static water contact angle of greater than about 160°, such as about 165°.

[0053] In certain embodiments, the paper is planar. In certain embodiments, the cellulose fibers form a planar layer, comprising a first planar surface and a second planar surface; and the hydrophobic fluorocarbon coats the first planar surface of the planar layer. In some embodiments, the thickness of the coating is about 5 μm to about 50 μm, about 25 μm to about 35 μm, or about 30 μm. In certain embodiments, the hydrophobic fluorocarbon coats the second planar surface of the planar layer.

[0054] In certain embodiments, the cellulose fibers and the hydrophobic fluorocarbon are uniformly distributed.

[0055] In certain embodiments, the present invention provides a passive cooling material, comprising a paper. In certain embodiments, the paper comprises cellulose fibers; and a hydrophobic fluorocarbon; wherein the amount of the hydrophobic fluorocarbon is about 0.01 wt % to about 15 wt %, about 0.01 wt % to about 10 wt %, about 0.01 wt % to about 5 wt %, about 0.1 wt % to about 15 wt %, about 0.1 wt % to about 10 wt %, about 0.1 wt % to about 5 wt %, about 1 wt % to about 15 wt %, about 1 wt % to about 10 wt %, about 1 wt % to about 5 wt %, or about 5 wt % to about 10 wt % of the paper. The paper of the passive cooling material may be one of the papers described herein and may be referred to as a "cooling paper."

[0056] In certain embodiments, the cellulose-fiber-based composites of the present disclosure are super white in the solar wavelengths, resulting from the backscatter of sunlight by the randomized structure of the cellulose microfibers and hydrophobic fluorocarbon microparticles (e.g., PTFE microparticles), and are infrared black in the atmospheric window because of the molecular vibrations of chemical bonds in cellulose and hydrophobic fluorocarbon (e.g., PTFE). In certain embodiments, the super white and black features at different wavelengths results in passive cooling materials that achieve net radiative heat loss even under sunlight.

[0057] In certain embodiments, the passive cooling material has a solar reflectivity of at least about 0.8. In certain embodiments, the passive cooling material has a solar reflectivity of at least about 0.9. In certain embodiments, the passive cooling material has a solar reflectivity of at least about 0.92. In certain embodiments, the passive cooling material has a solar reflectivity of about 0.93. In certain embodiments, the passive cooling material has a solar reflectivity of about 0.96.

[0058] In certain embodiments, the passive cooling material has an infrared thermal emissivity of at least about 0.9. In certain embodiments, the passive cooling material has an infrared thermal emissivity of at least about 0.95. In certain embodiments, the passive cooling material has an infrared thermal emissivity of at least about 0.99. In certain embodiments, the passive cooling material has an infrared thermal emissivity of at about 0.92.

[0059] In preferred embodiments, the passive cooling material has both high solar reflectivity and high infrared thermal emissivity. For example, in certain embodiments, the passive cooling material has a solar reflectivity of at least about 0.9 and an infrared thermal emissivity of at least about 0.95. In some embodiments, the passive cooling material has a solar reflectivity of at least about 0.9 and an infrared thermal emissivity of at least about 0.95 after 30 days under environmental conditions selected from (a) −20° C., relative humidity (RH) 30%, (b) 60° C., RH=100%, (c) 80° C., RH=0%, and (d) under UV light exposure (3 mW/cm^2). In some embodiments, the solar reflectivity and infrared thermal emissivity are angle independent.

[0060] In certain embodiments, the passive cooling material has a sub-ambient cooling performance of about 1° C. to about 10° C., about 5° C. to about 10° C., about 6° C. to about 10° C., about 5° C., or about 6° C., under a solar irradiance of about 600 W/m^2 to about 850 W/m^2. In certain embodiments, the passive cooling material has a radiative cooling power of about 100 W/m^2 to about 110 W/m^2, or about 104 W/m^2, under a solar intensity of about 671 W/m^2.

[0061] In certain embodiments, the passive cooling material further comprises an adhesive. In certain embodiments, the adhesive attaches the passive cooling material to brick, metal, wood, or concrete.

[0062] In certain embodiments, the present invention provides a method for making a paper, comprising mixing cellulose fibers, a hydrophobic fluorocarbon, and water, thereby forming a pulp; pressing the pulp, thereby forming a pressed pulp; and drying the pressed pulp, thereby forming a paper.

[0063] In certain embodiments, the method further comprises spraying the paper with a second hydrophobic fluorocarbon. In certain embodiments, spraying the paper with the second hydrophobic fluorocarbon comprises mixing PTFE with ethanol in a homogenizer and applying the mixture to the paper with an air spray gun.

[0064] In certain embodiments, pressing the pulp further comprises simultaneously applying heat. In certain embodiments, after the pressing step, the paper is allowed to passively cool.

[0065] In certain embodiments, the hydrophobic fluorocarbon is polytetrafluoroethylene. In certain embodiments, the hydrophobic fluorocarbon is 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane.

[0066] In certain embodiments, the method further comprises mixing the cellulose fibers, a dye, and water, thereby forming the pulp. In certain embodiments, the dye is a food dye. For example, in some embodiments, the food dye is brilliant blue (E133), indigo carmine (E132), tartrazine (E102), sunset yellow FCF (E110), or Allura Red AC (E129).

[0067] In certain embodiments, at least some of the cellulose fibers are derived from recycled paper. In certain embodiments, the method further comprises mixing the cellulose fibers, hemicellulose, lignin, and water, thereby forming the pulp. It is contemplated that the paper may be formed from, among other things, recycled paper products. It is further contemplated that the paper may be recycled to form another paper product of the present disclosure.

[0068] In certain embodiments, the cellulose fibers have an average fiber diameter of about 5 μm to about 50 μm, about 15 μm to about 40 μm, or about 20 μm to about 50 μm. In certain embodiments, the cellulose fibers have an average fiber diameter of about 28 μm.

[0069] In certain embodiments, the cellulose fibers have an average fiber length of about 1 mm to about 10 mm or about 1 mm to about 5 mm.

[0070] In certain embodiments, the hydrophobic fluorocarbon is in the form of a plurality of particles. The plurality of particles may have an average particle diameter of about 0.1 lam to about 5 μm, about 0.3 lam to about 2.5 lam, about 0.5 lam to about 2.5 lam, or about 0.7 lam to about 2.3 lam. In some embodiments, the plurality of particles has an average particle diameter of about 1.4 lam or about 1.5 lam. In certain embodiments, the cellulose and other materials of the paper form microsized pores, inside of which the particles reside. In certain embodiments, the cellulose fibers form a porous material having an average pore size of about 10 μm to about 30 μm. In certain embodiments, the average pore size is about 20 μm. In some embodiments, the pores have an average pore diameter of about 0.1 μm to about 5 μm, about 0.3 μm to about 2.5 μm, about 0.5 μm to about 2.5 μm, or about 0.7 μm to about 2.3 μm. In some embodiments, the pores have an average pore diameter of about 1.4 lam or about 1.5 μm.

[0071] In certain embodiments, the pressed pulp has a thickness of about 0.1 mm to about 15 mm, about 0.1 mm to about 10 mm, about 0.1 mm to about 5 mm, about 0.1 mm to about 3 mm, about 1 mm to about 15 mm, about 1 mm to about 10 mm, about 1 mm to about 5 mm, or about 1 mm to about 3 mm. In certain embodiments, the pressed pulp has a thickness of about 0.3 mm to about 1.2 mm. In certain embodiments, the pressed pulp is planar.

[0072] In certain embodiments, the method is for making one of the papers described herein. In certain embodiments, the method is for making a passive cooling material, such as one of the passive cooling materials described in the present disclosure.

[0073] In certain embodiments, the present invention provides a method for making a paper, comprising mixing cellulose fibers and water, thereby forming a pulp; pressing the pulp, thereby forming a pressed pulp; drying the pressed pulp, thereby forming a paper; and spraying the paper with a hydrophobic fluorocarbon. In certain embodiments, spraying the paper with the hydrophobic fluorocarbon comprises mixing PTFE with ethanol in a homogenizer and applying the mixture to the paper with an air spray gun.

[0074] In certain embodiments, the method further comprises mixing the cellulose fibers, a second hydrophobic fluorocarbon, and water, thereby forming the pulp.

[0075] In certain embodiments, pressing the pulp further comprises simultaneously applying heat. In certain embodiments, after the pressing step, the paper is allowed to passively cool.

[0076] In certain embodiments, the hydrophobic fluorocarbon is polytetrafluoroethylene. In certain embodiments, the hydrophobic fluorocarbon is 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane.

[0077] In certain embodiments, the method further comprises mixing the cellulose fibers, a dye, and water, thereby forming the pulp. In certain embodiments, the dye is a food dye. For example, in some embodiments, the food dye is brilliant blue (E133), indigo carmine (E132), tartrazine (E102), sunset yellow FCF (E110), or Allura Red AC (E129).

[0078] In certain embodiments, at least some of the cellulose fibers are derived from recycled paper. In certain embodiments, the method further comprises mixing the cellulose fibers, hemicellulose, lignin, and water, thereby forming the pulp. It is contemplated that the paper may be formed from, among other things, recycled paper products. It is further contemplated that the paper may be recycled to form another paper product of the present disclosure.

[0079] In certain embodiments, the cellulose fibers have an average fiber diameter of about 5 μm to about 50 μm, about 15 μm to about 40 μm, or about 20 μm to about 50 μm. In certain embodiments, the cellulose fibers have an average fiber diameter of about 28 μm.

[0080] In certain embodiments, the cellulose fibers have an average fiber length of about 1 mm to about 10 mm or about 1 mm to about 5 mm.

[0081] In certain embodiments, the hydrophobic fluorocarbon is in the form of a plurality of particles. The plurality of particles may have an average particle diameter of about 0.1 μm to about 5 μm, about 0.3 μm to about 2.5 μm, about 0.5 μm to about 2.5 μm, or about 0.7 μm to about 2.3 μm. In some embodiments, the plurality of particles has an average particle diameter of about 1.4 μm or about 1.5 μm. In certain embodiments, the cellulose and other materials of the paper form microsized pores, inside of which the particles reside. In certain embodiments, the cellulose fibers form a porous material having an average pore size of about 10 μm to about 30 μm. In certain embodiments, the average pore size is about 20 μm. In some embodiments, the pores have an average pore diameter of about 0.1 μm to about 5 μm, about 0.3 μm to about 2.5 μm, about 0.5 μm to about 2.5 μm, or about 0.7 μm to about 2.3 μm. In some embodiments, the pores have an average pore diameter of about 1.4 μm or about 1.5 μm.

[0082] In certain embodiments, the pressed pulp has a thickness of about 0.1 mm to about 15 mm, about 0.1 mm to about 10 mm, about 0.1 mm to about 5 mm, about 0.1 mm to about 3 mm, about 1 mm to about 15 mm, about 1 mm to about 10 mm, about 1 mm to about 5 mm, or about 1 mm to about 3 mm. In certain embodiments, the pressed pulp has a thickness of about 0.3 mm to about 1.2 mm. In certain embodiments, the pressed pulp is planar.

[0083] In certain embodiments, the method is for making one of the papers described herein. In certain embodiments, the method is for making as passive cooling material, such as one of the passive cooling materials described in the present disclosure.

[0084] In certain embodiments, the passive cooling materials described in the present disclosure are used for coating residential buildings, warehouses, cooler boxes, cars, and other infrastructures. In certain embodiments, the passive cooling materials are integrated directly into various infrastructure materials such as brick, basswood, and concrete to enhance their cooling performance.

Exemplary Advantages of the Invention

[0085] The advantages of the materials disclosed herein include but are not limited to: use of natural and abundance materials; use of low-cost materials that can be manufactured at a large scale; strong mechanical properties including strength and anti-scratch properties; self-cleaning properties that limit maintenance and extend lifespan; thermal stability; recyclability without significant loss of cooling properties; possibility of esthetic variety due to inclusion of dyes; ease of installation and removal; improved cooling performance compared to commonly used building materials such as brick, basswood, and concrete; and ability to withstand harsh environmental conditions such as humidity, UV exposure, and temperature.

Examples

[0086] Materials

[0087] 100 lb paper was provided by International Paper. The spray adhesive was obtained from Gorilla. The PTFE film was purchased from CS Hyde Company. The black dye was obtained from AmeriColor Corporation. Red and yellow dyes were obtained from Rite LLC. All reagents were used as received without further purification. Black 3.0 paint was purchased from the Culture Hustle. A Coleman cooler box was purchased on Amazon.

[0088] Methods

[0089] Fabrication of White Paper Composites. Poly-(tetrafluoroethylene) (PTFE) microparticles (3 g, 1.4 μm average size in diameter, Sigma-Aldrich) were added into 30 g of ethanol (95% denatured, Innovating Science) and homogenized by a high-speed emulsifier (MXBAOHENG, FSH-2A) at 22 000 rpm for 3 min. The resultant suspension was sprayed on a 12 cm×13 cm paper using an airbrush equipment (nozzle diameter 0.8 mm) at an air pressure of around 70 psi with a distance of about 10 cm. The mass density of the PTFE coating on the paper was around 2 mg/cm^2. The sprayed paper was dried at 100° C. for 30 min.

[0090] Fabrication of Colored Paper Composites. The dye (5 g, Rite LLC) was dissolved into 10 g of DI water and was subsequently sprayed onto a 12 cm×13 cm paper with the same airbrush using the same parameters with the fabrication of the white paper composites. The paper can also be dyed by dipping it into the dye suspension. The sprayed or dip-coated paper was then dried at 60° C. for 30 min.

[0091] Fabrication of the Solid Cellulose Film. Dried cellulose powders (2 g) were placed into a dry pellet pressing die with an inner diameter of 13 mm, and it was pressed at a pressure of 60 MPa for 45 s to form a uniform solid film.

[0092] Fabrication of the Black 3.0 Painted Paper. Black 3.0 paint was diluted with DI water under mechanical stirring for 5 min to get a homogeneous mixture. The mass ratio of DI water to Black 3.0 paint was ~0.4 in the dilution process. Subsequently, the diluted Black 3.0 paint was sprayed onto the paper sheet with a thickness of 0.35 μm using a spray gun (Paasche Airbrush) with a 0.8 mm spray head at a pressure of 70 psi. The distance between the spray head and the paper sheet was about 25 cm. The sprayed paper was dried using a hot blower (Yihua Electronic Equipment Co., Ltd., Guangzhou, China) after each spray at a temperature of 190° C. for 5 min.

[0093] Fabrication of the Colored Wood. The red and yellow dyes were thinned with DI water and the mass ratio of dye to water was 1:2. Then, the thinned dye was sprayed on a 2 mm thick basswood sheet using a spray gun with a 0.8 mm spray head at a pressure of 70 psi. The distance between the spray head and the wood sheet was about 10 cm. The sprayed wood sheet was left in the air for 6 h to dry before the dyed wood fabrication.

[0094] Recycling Process of Paper Composites. The paper composites were cut into small pieces, and immersed in water for 1 h. After that, the swelled paper was smashed into paper pulp using a high-speed blender for 3 min (Vitamix E310). The paper pulp was thermally pressed into a paper sheet by a hydraulic press machine (DABPRESS, 10 Ton) under 20 MPa and 200° C. until the paper was dry. The regenerated paper can be reused for fabricating self-cooling and self-cleaning paper composites by recoating the PTFE particles.

[0095] Material Characterization

[0096] Morphology Characterization. The surface morphologies of samples were examined using a scanning electron microscope (SEM, S5200, Hitachi Company) under an acceleration voltage of 10 kV. The morphology of the pencil-scratched samples was observed using a trinocular metallurgical microscope (ME300TZA-3M) with a 50× lens.

[0097] Surface-Wetting Characterization. The water contact angle (CA) of the sample was measured using a contact angle goniometer (DSA-25, Kriiss, Germany) with a 7 μL DI water droplet at room temperature according to the sessile droplet method. The reported static contact angles were calculated by averaging the measured values from both the left and right sides of the droplet. Six data points were collected at six different positions on the sample surface and were used for calculating the final average values.

[0098] Paper Composition Characterization. The paper composite sample (1 g, ±0.0001 g) was dried at 100° C. for 30 min and was weighed to calculate the moisture content. The PTFE content was identified by measuring the mass change of the paper before and after spraying PTFE. Ethanol (400 mL; 95%) was mixed with 100 mL of HNO3 for etching other components of the paper to obtain the cellulose. The paper composite sample (1 g, ±0.0001 g) was mixed with 25 g of ethanol—HNO3 solution in a 250 mL conical flask with a condenser and was subsequently refluxed for 1 h at 100° C. These procedures were repeated 2-3 times until the paper fibers were white. The above fibers were washed using ethanol until the pH of the filtrate was near 7. Finally, these fibers were dried at 105° C. (±2° C.) and were weighted for calculating the cellulose content.

[0099] Optical Characterization. The reflectivity spectra (0.3-2.5 μm) were measured using a Jasco V770 spectrophotometer at an incident angle of 6° with the ISN-923 60 mm $BaSO_4$-based integrating sphere equipped with PMT and PbS detectors. The reflectivity spectra were normalized by a PTFE-based reflectance standard. The reflectivity spectra (2.5-20 μm) were measured using a Jasco FTIR 6600 at an incident angle of 12° with the PIKE upward gold integrating sphere equipped with a wide-band MCT detector. Angular-dependent reflectivity spectra were measured using wedges with different angles at the sample port of these two integrating spheres. The single-valued R_{solar} and ξ_{IR} were calculated by integrating the reflectivity spectra or emissivity spectra based on the AM 1.5 or 303 K blackbody spectra, respectively.

[0100] Refractive Index Characterization. The complex refractive index of the sample was measured using an ellipsometer (J. A. Woollam, M-2000DI) with an incident angle of 60-70° and a spectral range of 0.38-0.9 μm.

[0101] Size Distribution Characterization. The size distribution of the cellulose fibers and PTFE particles was determined by ImageJ software according to the SEM images, in which 200 points were randomly selected for each image.

[0102] Finite-Difference Time-Domain (FDTD) Simulation. FDTD simulation was executed using Lumerical FDTD Solution 2018a. Two-dimensional models were employed, and a total-field scattered field source coupled with two scattering cross sections of cellulose fibers and PTFE particles was used to calculate the scattering efficiency. The cross section of the paper fibers was 28 μm×28 μm, and the cross section of the PTFE particles was a circle with a diameter of 1.4 μm Different shapes of cross sections were also simulated to check the effects of various shapes on the scattering efficiency.

[0103] Scattering Effects Measurement. One layer of paper fibers was peeled off from the original paper using the Tape King packaging tape. PTFE particles (0.2 g) were uniformly smeared on the adhesive side of the packing tape (CS Hyde company). These cellulose fibers and PTFE particles were placed at the aperture position, which is between the laser pens (red, green, and purple) and the blackboard. The area of scattered laser spots was used to indicate the scattering effect of paper fibers and PTFE particles.

[0104] Infrared Image Measurement. Infrared images were taken using an FUR A655C thermal camera with a 25° lens at a resolution of 640×480.

[0105] Cooling Power and Temperature Tracking. All of the materials were placed inside a 100-Quart modified cooler box (excellent thermal insulation) with the removal of the top lid. For the cooling power measurement chamber, the top surface of the paper composites (12 cm×13 cm×2 mm) faces the clear sky through a 20 μm thick HDPE film. The air gap between the paper composites and the HDPE film was around 5 mm. The paper composites were glued to the supporting copper sheet below (12 cm×13 cm×0.9 mm, thermal conductivity, TC, 380 W/(m·K)) using a silver thermal compound paste (TC, 8.5 W/(m·K)). The Kapton thin-film heater (11 cm×11 cm×0.4 mm) was glued to the supporting copper sheet with the same silver thermal paste, and the temperature of the paper composites sample was measured using the K-type thermocouples connected to the National Instruments (NI) PXI-6289 multifunction I/O module. The "ON" and "OFF" of the heater were controlled by the NI PXI-2586 relay module driven by a home-built LabVIEW program using the PID control algorithm to maintain the temperature of the paper composites by tracking the ambient air. The K-type thermocouples were welded to the copper sheet using epoxy resin. The 6 mm thick aerogel blankets used here have a thermal conductivity of –23 mW/(m K) to reduce the heat transfer between the PVC insulation foam and samples. The PVC insulation wall has a thickness of 25 mm with thermal conductivity of –31 mW/(mK).

[0106] Thermal Conductivity Measurement. The thermal conductivity of the one-layer paper was characterized by the TPS 2500s thin-film module, while the thermal conductivities of the basswood and concrete were measured by the isotropic standard module of TPS 2500s.

[0107] Mechanical Strength Measurement. The mechanical strengths of the paper sheet (2 cm×6 cm×0.35 mm) and a basswood slab (2 cm×6 cm×1.5 mm) were measured using a Mark-10 ESM tensile tester at room temperature.

[0108] Validation of the Self-Cleaning for Paper Composites. The original paper and the self-cleaning paper composites with a dimension of 10 cm×8 cm×0.35 mm were placed on a wedge with an oblique angle of 10°. One drop of black dye (0.12 g) and 0.31 g of garden soil were stained on the original paper and the self-cleaning paper. Then, water from the squeeze bottles washed the black dye and the garden soil, and the wash process was recorded in a phone camera.

[0109] Abrasion Robustness Tests. A sandpaper abrasion test was carried out using a 400 grit SiC sandpaper as an abrasion surface. The sample was fixed to a glass slide with a loaded weight of 50 g and placed face down onto the sandpaper, and then moved 10 cm along the ruler. Subsequently, the sample was rotated by 90° and again moved 10 cm along the ruler. The two aforementioned steps are defined as one abrasion cycle. This process guarantees that the paper composite surface is abraded longitudinally and transversely in each cycle.

[0110] Antiscratch Tests. A set of pencils with different hardness (**10**B-**9**B-**8**B-**7**B-**6**B-**5**B-**4**B-**3**B-**2**B-B-F-HB-H-2H-3H-4H-5H-6H-7H-8H-9H) were selected to make a scratch on the paper composite surface. The pencil was held at 45° to the paper composites and pushed for a scratch length of 10.0 mm. The micrographs of the paper after scratch tests were used to analyze its antiscratch property.

[0111] Raindrop Tests. The simulated raindrop tests were conducted using a syringe pump at a flow rate of 3 mL/h from a 17 gauge syringe needle for 7 days. The needle head was about 35 cm over the paper composites. The oblique angle of the paper composites was fixed at 10°.

[0112] Peel-off tests. An XFasten tape (6 cm×2 cm) was pressed onto the paper composites and was peeled off at a speed of about 1 cm/s.

[0113] Harsh Environment Exposure. To test the long-term durability of the paper composites under different harsh environment exposures, the paper composites were placed in a freezer (−20° C.), an incubator (60° C., RH 100%), a convection oven (80° C., RH 0%), and a UV lamp (UV density, 3 mW/cm^2) for 30 days, respectively.

Results

Hydrophilic Contact Angle

[0114] The original paper consisted of random-stacked cellulose fibers with porous structures. The paper composites were fabricated by air-spraying the homogeneous PTFE microparticle suspension (3 g/30 g, PTFE/ethanol) onto the original paper followed by solvent evaporation to form a self-cleaning and self-cooling surface. The PTFE microparticles with an average size of 1.4 μm were embedded into the microsized pores (20 μm) of the cellulose-fiber-based paper formed by the stacked cellulose fibers and form a white coating. The PTFE particles formed a rough surface with micro/nanostructures, which transformed the paper from a hydrophilic (contact angle, θ=) 86° to a superhydrophobic state (θ=165°), as shown in FIGS. **1**A and **1**B. This feature enables the waterproof and self-cleaning surface of the composites for outdoor applications.

Solar Reflectivity and Thermal Emissivity

[0115] Interestingly, R_{solar} of the cellulose-fiber-based paper was enhanced from 0.89 to 0.93 after PTFE coating, compared with the original paper. This result could be attributed to the PTFE microparticle coating that reinforces the sunlight scattering of the paper, as shown in FIG. **1**C. Without intending to be bound by theory, the high hemispherical solar reflectivity (nearly "white") and infrared emissivity (nearly "black") of the composites ensure that it radiates a net heat flux to the cold outer space sink as infrared thermal radiation. The heat radiated by the composites exceeds the heat gained from the solar absorption and the atmosphere, thus leading to subambient cooling effects. Both solar reflectivity and thermal emissivity of the paper composites were angle-independent even at a large angle of incidence (AOI, θ=75°. The randomly arranged cellulose fibers and PTFE particles gave rise to a polarization-independent R_{solar} and ϵ_{IR} (FIGS. **2**A and **2**B). The cellulose-fiber-based composites showed the diffused white and black features from 6 to 75° in the solar wavelengths and atmospheric transmittance window, respectively, yielding high R_{solar} and ϵ_{IR} (greater than 0.9) when the paper composites face toward different angles of the sky in real-life applications.

Infrared Spectra

[0116] Fourier transform infrared (FTIR) transmission spectra were obtained, showing that cellulose, lignin, and PTFE in the paper composites exhibit strong emission bands at 800-1200 and 1040 cm^{-1}. The negligible extinction coefficient, measured for cellulose and PTFE from 0.38 to 0.9 μm (covering half wavelength range of the solar irradiance), makes the paper composites an ideal reflector of the solar irradiance. The innate structure of the paper composites with PTFE microparticles and cluttered cellulose fibers presented high R_{solar} and ϵ_{IR}. The diameter of cellulose fibers ranged from 6 to 50 μm centering at 28 μm, while the PTFE particles spanned within 1.4±0.9 μm (FIG. **3**A). The cellulose microfibers efficiently backscatter the sunlight, which is further enhanced by adding submicron PTFE particles, as shown by the scattering cross section efficiency spectra simulated using the finite-difference time-domain (FDTD) methods (FIG. **3**B). The transmission haze spectra of the paper and PTFE particles showed that the self-cooling paper has a high haze value of about 0.8 on average (FIG. **4**A). The scattering effects of the cellulose fibers and PTFE particles were visualized using a red laser beam with a wavelength of 650 nm traveling through the cellulose fibers and PTFE particles sticking on a clear tape film (FIG. **4**B). The illuminated area was much larger than that of the one of the clear tape films indicating strong scattering effects from the paper fibers and particles; similar phenomena are observed for the green and violet laser beams. Reflectivity spectra and infrared emissivity spectra were obtained for the paper composites ("cooling paper"), cellulose film, PTFE film, and an infrared-ultrablack paint.

[0117] The disordered cellulose fibers and PTFE particles result in a diffused white surface compared to the solid cellulose and PTFE films (FIGS. **5**A and **6**) with an AOI from 0 to 75°. The paper composites had a higher infrared emissivity than the cellulose film (FIG. **5**B). The high ϵ_{IR} of the paper composites is comparable to that of an infrared-ultrablack paint (black 3.0, $\epsilon_{IR} \approx 0.99$).

Outdoor Validation of the Paper Composites Cooling Performance

[0118] The subambient cooling performance of the paper composites during a one-day cycle was demonstrated on a rooftop at Northeastern University, Boston, MA. A six-layer paper was glued layer by layer as the test sample with the top layer sprayed with PTFE microparticles from an ethanolic PTFE suspension. Test samples were placed in one of three chambers (referred to as chambers "a-1," "a-2," and "a-3"). Each chamber was partially surrounded by 25 mm of PVC insulation foam, with the rest of the chamber either covered by HDPE film or open to air. In chamber a-1, the cooling paper was placed on a copper sheet, which was on a heater (in the "ON" position), which was on an aerogel blanket. Chamber a-1 was covered by HDPE film. A type K thermocouple was used to measure the temperature of the paper. Chamber a-2 was the same as chamber a-1, but without a PID temperature tracking system, and the heater was in the "OFF" position. Chamber a-3 was the same as chamber a-2, but without the HDPE film covering the chamber.

The properties of the paper composites were measured, as described in Table 1.

TABLE 1

Physical parameters of the paper composites in outdoor validation test

Property	Value
Size (cm)	12 × 13
Thickness (mm, six layers)	2.0
Thermal conductivity (W/m2 · K)	0.096
Specific heat (kJ/kg · K)	1.34
Thermal emissivity	0.92
Solar reflectivity	0.93
Visible reflectivity (0.38 μm to 0.75 μm)	0.94
Near-infrared reflectivity (0.75 μm to 2.5 μm)	0.91

[0119] Temperature was tracked over about 21 hours, indicating that the top surface temperature of the composites followed the ambient temperature with a bias of ±0.2° C., indicating a reliable measurement accuracy of the radiative cooling performance of the composites. The paper composites had an averaged radiative cooling power of about 75 W/m^2 over a one-day cycle. The average cooling powers of the paper composites were 82.3 and 71.6 W/m^2 at the daytime and nighttime, respectively (FIG. **7**A). This difference was attributed to the nighttime relative humidity (70% RH, averaged, low atmospheric transmittance) being higher than that during the daytime (55.3%, averaged, high atmospheric transmittance) and the nighttime wind speed (1.9 km/h, averaged, low air convection) being much lower than that during the daytime (5.4 km/h, averaged, high air convection). The averaged $\Delta T2$ (4.4° C.) was higher than the averaged $\Delta T3$ (2.4° C.) during the night and vice versa during the day ($\Delta T2=5.1°$ C.$<\Delta T3=6.1°$ C.) (FIG. **7**B). During the nighttime, the solar heating effects disappeared, and the only heating effect came from the radiative heat transfer from the ambient air and the nonradiative heating from the heat conduction of the supporting structure for the sample and the wind convection heating. The HDPE cover served as a wind cover to block convection heating from air. Thus, chamber a-2 with the HDPE cover had a larger temperature drop during the nighttime. During the daytime, since the HDPE film is not fully transparent to the mid-infrared wavelengths (averaged transmittance is around 0.9 based on the 303 K blackbody radiation), it will block part of the radiative heat transfer between the self-cooling paper and the cold outer space. At the same time, the HDPE has an average transmissivity of around 0.89 over the solar radiation wavelengths, and it reflects parts of the solar irradiation to the surface of the self-cooling paper and the air in the small space between the self-cooling paper and the HDPE cover. The increasing temperature of the small space also heats the self-cleaning paper up. The wind temperature is lower than the ambient since the ambient temperature thermocouple was enclosed inside a wind cover similar to the weather station. This method to measure the ambient temperature is also used in meteorology. The wind brought heat from the self-cooling paper in a-3 immediately. Therefore, the temperature of a-2 was greater than that of a-3 because the HDPE windshield blocked the heating from the air at night resulting in lower temperatures from the radiative cooling effect. However, the cooling effect from the high-speed wind was partially blocked by the HDPE film in a-2 compared with the one in a-3. Consequently, the PTFE-coated cellulose-fiber-based composites exhibited a subambient cooling of −5° C. under a solar irradiance of 834 W/m^2 and a radiative cooling power of 104 W/m^2 under a solar intensity of 671 W/m^2 (as marked by a triangle in FIG. **7**A). The various external factors (solar intensity, nonradiative heat transfer, and atmospheric transmittance) were considered in measuring cooling power. Similar measurements were obtained for common building materials such as wood and concrete. The temperature of the composites was 8.1° C. lower than the one made of basswood, attributing to the self-cooling function and the lower thermal conductivity of the composites than that of the basswood and concrete. The composites in a-3 without a windshield were 2.8° C. cooler than the ambient and had an averaged 32 W/m^2 cooling power at noontime in the mid-summer.

Surface Stability of Paper Composites

[0120] The paper composites can be easily cemented to common materials like brick, metal, wood, and concrete for outdoor utilization. We examined the long-term stability of the composites under a simulated environment. Black dye and garden soil were employed to contaminate both the original paper and paper composites. The original paper was easily dyed by black dye and the soil on its surface was not easily washed away, resulting in reduced light reflectivity. In contrast, the paper composites remained clean without any dying or residual soil because of their excellent self-cleaning ability arising from the superhydrophobic PTFE coating (FIG. **8**A). The self-cleaning durability of the cellulose-fiber-based composites was demonstrated by a four-week outdoor exposure with little changes observed in the contact angle and the rolling-off angle (FIG. **8**B). A 15-min water immersion test showed good waterproof properties for outdoor utilization. Additionally, different harsh environmental tests, such as UV exposure, raindrop impact, low and high-temperature exposure, high humidity exposure, and mechanical abrasions, did not lead to any change in the optical performance and self-cleaning property (FIG. **8**C). This indicates good surface stability of the paper composites, which is a benefit to keeping its good cooling performance for outdoor applications. The PTFE layer of the composites also reduced the friction of the surface of the composite, avoiding scratches from hard objects in scratch tests. After cyclic tape peel-off tests, the reflectivity and emissivity of the paper composites showed no significant change (both were within 3%), demonstrating their robust cooling performance. It was also experimentally demonstrated that recycled composites still yielded self-cooling performance by spectroscopic analysis, elongating their life span. The recycled paper composite is optionally recoated with a layer of PTFE particles by following the same procedure of fabricating the self-cooling paper.

Colorful Paper with Efficient Cooling Performance and Esthetics

[0121] The composite materials may be died to reflect a certain wavelength band in the visible region to display colors, while maximizing R_{solar} in near-infrared (NIR) wavelengths (0.7-2.5 μm), where 51% of the solar energy lies to minimize the solar heating, and possessing a high ϵ_{IR} in the atmospheric window (8-13 μm) to radiate heat efficiently to the cold outer space. Red- and green-dyed papers were formed, which efficiently reflected the NIR sunlight with a high RNIR of 0.89 and 0.87, respectively, to prevent from being heated up by the NIR solar wavelengths (FIGS.

9A and **9**B). To further validate the efficient cooling performance of the white and colorful papers under hot midsummer weather, mini houses made of the white, yellow, and red-dyed paper composites were fabricated and their "room" temperatures were recorded during the noontime (13:30 to 14:15) on Jul. 9, 2020. The mini houses made of basswood with different colors were selected as control groups. We found that the white house made of the cellulose-fiber-based composites was 7.1° C. cooler on average than the ambient air and even 5.3° C. lower on average than that of the basswood-made house (FIG. **10**A). Similar trends of the cooling performance were observed in the yellow and red mini houses made of dyed paper composites and corresponding basswood (FIGS. **10**B and **10**C). The dyed paper composites provide a promising alternative for colored radiative cooling utilization, greatly expanding their scope of applications.

INCORPORATION BY REFERENCE

[0122] All of the U.S. patents and U.S. and PCT published patent applications cited herein are hereby incorporated by reference.

EQUIVALENTS

[0123] The foregoing written specification is considered to be sufficient to enable one skilled in the art to practice the invention. The present invention is not to be limited in scope by examples provided, since the examples are intended as a single illustration of one aspect of the invention and other functionally equivalent embodiments are within the scope of the invention. Various modifications of the invention in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description and fall within the scope of the appended claims. The advantages and objects of the invention are not necessarily encompassed by each embodiment of the invention.

1. A paper, comprising:
cellulose fibers; and a hydrophobic fluorocarbon;
wherein the amount of the hydrophobic fluorocarbon is about 0.1 wt % to about 5 wt % of the paper.

2. The paper of claim **1**, wherein the hydrophobic fluorocarbon is polytetrafluoroethylene.

3. The paper of claim **1**, wherein the hydrophobic fluorocarbon is 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane.

4. The paper of claim **1**, further comprising a dye.

5. The paper of claim **4**, wherein the dye is a food dye.

6. The paper of claim **5**, wherein the food dye is brilliant blue (E133), indigo carmine (E132), tartrazine (E102), sunset yellow FCF (E110), or Allura Red AC (E129).

7. The paper of claim **1**, further comprising hemicellulose and lignin.

8. (canceled)

9. The paper of claim **1**, wherein the cellulose fibers have an average fiber diameter of about 5 μm to about 50 μm.

10. (canceled)

11. (canceled)

12. The paper of claim **1**, wherein the cellulose fibers have an average fiber length of about 1 mm to about 5 mm.

13. The paper of claim **1**, wherein the cellulose fibers form a porous material having an average pore size of about 10 μm to about 30 μm.

14. The paper of claim **1**, wherein the hydrophobic fluorocarbon is in the form of a plurality of particles having an average particle diameter of about 0.5 μm to about 2.5 μm.

15. (canceled)

16. The paper of claim **1**, wherein the paper has a thickness of about 0.1 mm to about 15 mm.

17. The paper of claim **16**, wherein the paper has a thickness of about 1 mm to about 3 mm.

18. The paper of claim **1**, wherein at least one surface of the paper is impervious to water.

19. The paper of claim **1**, wherein the paper is planar.

20. The paper of claim **19**, wherein the cellulose fibers form a planar layer, comprising a first planar surface and a second planar surface; and the hydrophobic fluorocarbon coats the first planar surface of the planar layer.

21. The paper of claim **20**, wherein the hydrophobic fluorocarbon coats the second planar surface of the planar layer.

22. (canceled)

23. A passive cooling material, comprising the paper of claim **1**.

24-31. (canceled)

32. A method for making the paper of claim **1**, comprising:
mixing cellulose fibers, a hydrophobic fluorocarbon, and water, thereby forming a pulp;
pressing the pulp, thereby forming a pressed pulp; and
drying the pressed pulp, thereby forming the paper.

33-50. (canceled)

51. A method for making the paper of claim **1**, comprising:
mixing cellulose fibers and water, thereby forming a pulp;
pressing the pulp, thereby forming a pressed pulp;
drying the pressed pulp, thereby forming the paper; and
spraying the paper with a hydrophobic fluorocarbon.

52-69. (canceled)

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