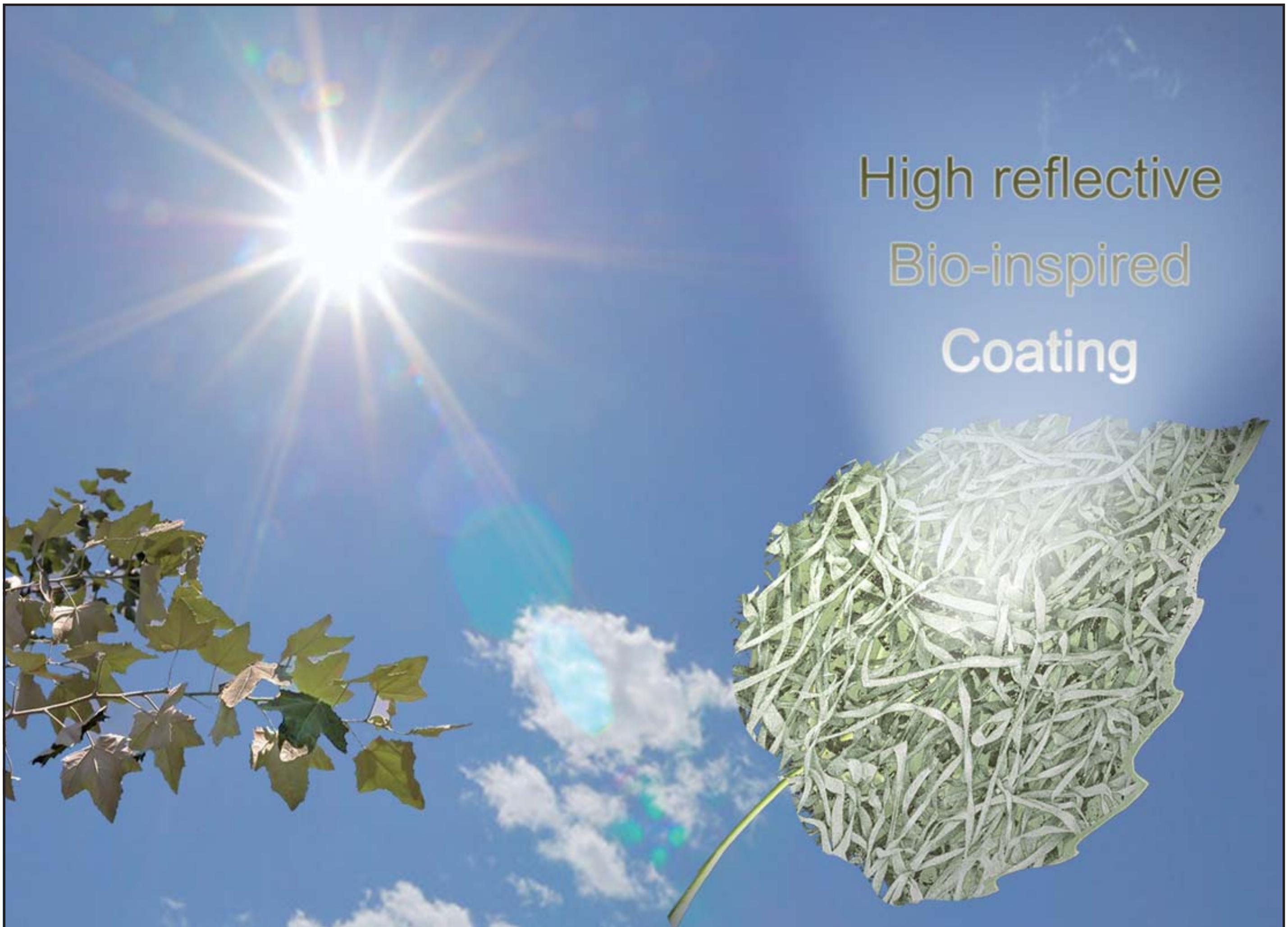

Showcasing research from Professor Yanlin Song's group at Institute of Chemistry, Chinese Academy of Sciences, Beijing, China.

Title: Highly reflective superhydrophobic white coating inspired by poplar leaf hairs toward an effective "cool roof"

Poplar leaf hairs, serving as the white coating on the leaf's lower surface, provide the leaf with an efficient "cool roof". By learning and mimicking this natural phenomenon, a highly reflective superhydrophobic white-coating is made. The artificial fibrous film has high reflectance over a broad wavelength and has great potential for effective and light-weight coating.

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Highly reflective superhydrophobic white coating inspired by poplar leaf hairs toward an effective "cool roof"†

Changqing Ye,[ab] Mingzhu Li,*[a] Junping Hu,[a] Qunfeng Cheng,[a] Lei Jiang[a] and Yanlin Song*[a]

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The hair layer consisting of hollow fibers provides the poplar leaf with an energy efficient "cool roof" to protect it from being burned by strong light. Inspired by the hair structure, we use coaxial electrospinning technology to achieve a highly reflective and superhydrophobic white coating towards making an eco-friendly and effective "cool roof".

Global warming and emissions of greenhouse gases are the most serious challenges today.[1,2] Immense efforts have been focused on reducing the emissions of heat-trapping gases, such as carbon dioxide.[3,4] Recently, Akbari and coworkers have demonstrated that using "cool roofs" with light colors and increasing the albedo of urban areas can potentially counteract the heating effect of carbon dioxide emissions.[5–10] More and more attention has been paid to the "cool roof" which is considered to be one of the lowest cost and most effective ways to reduce global carbon emissions and mitigate global warming. In fact, nature has already shown such energy-efficient "roofs" such as the hairs on edelweiss bracts and the scales of Cyphochilus spp. beetles.[11–14] Here, we demonstrate that poplar leaf hairs, serving as the white coating on the lower surface of the leaf, provide the leaf with an efficient "cool roof", and further advance a highly reflective superhydrophobic white coating using a similar structure to the leaf hairs. The artificial leaf hairs for white coating are fabricated using the coaxial electro-spinning technique which is eco-friendly and low-cost. The film has high reflectance in visible and infrared wavelengths. Moreover, the artificial leaf hairs are superhydrophobic and hollow, which can serve as an insulation layer to help prevent water damage and erosion.

Fig. 1 shows the morphology of the lower and upper surfaces of the poplar leaf. From the digital picture, the lower surface is white and covered with a thick cottony layer (Fig. 1a), while the upper surface is green and almost glabrous (inset of Fig. 1c). The cottony lower surface is a superhydrohobic surface with a contact angle (CA) of 146.0 ± 2.1° (the inset of Fig. 1a). The top-view scanning electron microscope (SEM) image clearly shows that the lower surface is covered by dense hairs with the hollow fibrous structure (Fig. 1b and the inset), while the upper surface bears few hairs (Fig. 1c). The width of the hairs is *ca.* 14 μm and the thickness of the hair layer is *ca.* 200 μm (see Fig. S1 of the ESI†).

The reflectance spectra of both surfaces are measured (Fig. 1d). For the upper surface, most of the reflectance is below 10% in the visible light range, except for a peak of 15% around 550 nm (Fig. 1d, dashed line), which is assigned to the absorption of chlorophylls. The chlorophylls absorb blue light (400–510 nm) and red (610–700 nm)

[a]Beijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Organic Solids, Laboratory of New Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, P. R. China. E-mail: ylsong@iccas.ac.cn; mingzhu@iccas.ac.cn; Fax: (+86) 10- 6252 9284
[b]Graduate University of Chinese Academy of Science, Beijing, 100049, P. R. China

† Electronic supplementary information (ESI) available: Cross-sectional SEM characterization of the leaf, the fibrous film and the control film; the reflectance comparisons of the two surfaces of the leaf; different extent of radiation damage under the strong light radiation; fresh leaves in response to adverse physical situations; UV-vis spectra of the extracts of the hairs; the reflectance spectra of fibrous films fabricated by two other polymers; the mechanical properties of the fibrous film; the shield application of the fibrous film. See DOI: 10.1039/c0ee00686f

Broader context

The phenomenon of urban heat islands is becoming increasingly urgent. Increasing the urban albedo could result in reflecting more of the incoming global solar radiation, reducing cooling costs and electricity consumption of buildings. Highly reflective urban surfaces, or "cool roofs", could contribute to significant energy savings and hence a reduction in greenhouse gas emissions. Therefore the global warming effects could be slowed down to some extent. Studies have demonstrated that when the reflectivity of the roof rises to about 60%, the energy consumed for cooling the building cooling is reduced by more than 20%. In this paper, we investigated the role of the hairs on the poplar leaves' lower surface in scattering sunlight, and found that the hollow hairs provide the poplar leaves with an effective coating against the strong light. By learning and mimicking the natural phenomenon, we made a highly reflective and superhydrophobic white coating after the hair structure. The achieved bio-inspired fibrous films have high reflectance over a broad range of wavelengths, and will be of great potential for an effective "cool roof".

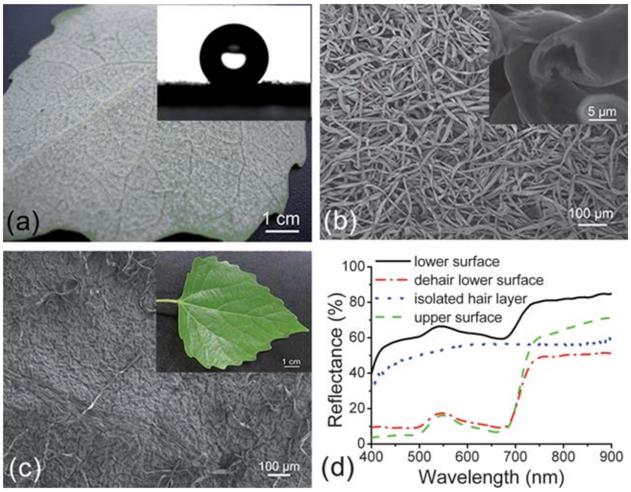

Fig. 1 (a) Digital photo of the lower surface of poplar leaf. Inset: The CA of the cottony lower surface is 146.0 ± 2.1°. (b) SEM image of the ribbon-like hairs on the leaf lower surface. Inset: The cross section of a single hair shows a hollow fiber structure. (c) SEM image of glabrous upper surface bearing few hairs. Inset: Digital photo of the upper surface. (d) Reflectance spectra of the two surfaces of the leaf, the lower surface with hairs removed, and the isolated hair layer removed from the leaf. Most of the reflectance of the upper surface is below 10%, except for a peak of 15% around 550 nm. All the reflectance of the lower surface is higher than 55%. When the hair layer is removed, the reflectance decreases to *ca.* 10%, similar to the upper surface reflectance. Most of the reflectance of the isolated hair layer is higher than 50%.

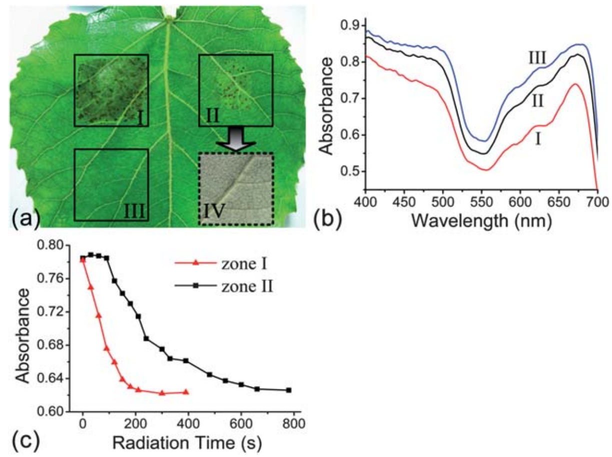

Fig. 2 (a) Digital photo of different radiation damage under strong light radiation: *Zone I*, the upper surface exposed; *Zone II*, the lower surface exposed; *Zone III*, normal surface. Inset: *Zone IV*, the lower surface after being exposed. (b) Absorbance of the three zones on the leaf (*I*, *II*, *III*). (c) The absorbance of *zone I* and *zone II* at the wavelength of 625 nm as a function of radiation time.

light, and reflect green light (510–600 nm).[15] Thus the upper surface appears in green color (inset of Fig. 1c). For the lower surface, its reflectance is higher than 55% for the wavelength range of 420–900 nm (Fig. 1d, solid line). Owing to its broad high reflectance in the whole visible wavelength range, the lower surface appears in white color (Fig. 1a). The reflectance of the lower surface is more than ten times higher than that of the upper surface particularly in the wavelength range from 393 nm to 502 nm, which corresponds to the absorption of the chlorophyll (Fig. 1d, Fig. S2 of the ESI†). When the hairs are removed from the lower surface using an adhesive tape, the lower surface reflectance decreases to *ca.* 10% (Fig. 1d, dash-dotted line), close to the upper surface reflectance. It indicates that the high reflectance of the lower surface mainly originates from the hair layer of the lower surface. The reflectance spectrum of the isolated hair layer is measured in Fig. 1d (dotted line). Most of the reflectance of the isolated hair layer is above 50%.

Exposing leaves to strong light could result in the photodamage of photosynthetic pigments.[16] The photodamage rate is proportional to the intensity of the incident light. To test the resistance to photodamage of the upper and lower surfaces, the photodamage experiments are carried out under the same strong light. First, *zone I* of the upper surface (Fig. 2a, *zone I*) was directly irradiated by the visible strong light from the solar simulator (80 mW cm^{-2}) for 180 s. Then, the same experiment was carried out on the *zone II* by exposing the lower surface to the strong light (Fig. 2a, *zone II*). From the digital photo, most leaf tissues in *zone I* of the upper surface are burned and turn brown after irradiation, while there are only a few brown dots in the irradiated *zone II*. This color change of the leaf from normal green to dark brown is assigned to the damage of the leaf tissues. Fig. 2b shows the absorbance spectra of the two zones after 180 s irradiation and that of the normal leaf (*zone III*). For the zones exposed to the strong light, the absorbance of the leaf decreases. After 180 s irradiation, the absorbance decrement of *zone I* is over twice as much as that of *zone II*, even more than three times in the wavelength range of 400–494 nm and 586–690 nm (see Fig. S3 of the ESI†). This wavelength range agrees well with the characteristic absorbance of the chlorophylls, the most essential compounds for leaf photosynthesis.

The leaf absorbance at 625 nm as a function of the amount of time for which the leaf is exposed to visible strong light (radiation time) is plotted in Fig. 2c. For *zone II*, the hair layer on the lower surface is exposed to the strong light, and there is little decrease of the absorbance in the first 90 s radiation. For *zone I*, the upper surface is exposed to the strong light, and the absorbance decreases quickly from 0.78 to 0.68 after 90 s irradiation. It takes 210 s for the leaf absorbance to decrease to 0.62 when the upper surface is exposed to the strong light (*zone I*). It takes 800 s when the lower surface is exposed to the strong light (*zone II*). These results demonstrate that the thick hair layer on the lower surface of the poplar leaf can protect the leaf tissue from photodamage more effectively.[17,18] Moreover, under the strong light radiation, the poplar leaves turn their lower surfaces outwards when the cooling effect of water evaporation in the transpiration cannot counteract the heat generated by radiation (see Fig. S4, 5 of the ESI†).

Normally, the natural hairs are biopolymer composite composed mainly of cellulose, hemicelluloses, lignin and *et al.*[19] Some chemical nature of the hairs has also been explored (see Fig. S6 of the ESI†). They have little characteristic absorption in the visible wavelengths. Thus, the structure of the hairs plays a key role in scattering the light.

Inspired by the structure of the leaf hairs on the lower surface, we fabricated a series of hollow fibrous polymer films with high reflectance using coaxial electro-spinning technology. Among lots of synthetic and fabrication methods, coaxial electro-spinning is an effective, fast and controlled technique to construct channels into fibers. It provides a simple approach to fabricate hollow fibers that are exceptionally long in length, uniform in shape, and diversified in composition.[20–25]

The experimental setup was characterized by the spinneret system, which was fabricated by inserting a metallic capillary into a blunt metal needle to form a compound nozzle.[25] The polymer solution flowed through the space between the outer needle and the inner capillary, and the paraffin liquid was pumped out separately from the inner metallic capillary. The diameter of the fiber was controlled by a series of independent experimental parameters including the electric field strength, the concentration of outer solution and the flow rate of the inner and outer fluids.[26] By increasing the flow rate of the inner fluids from 3.0 mL h^{-1} to 31.0 mL h^{-1}, the fiber diameter increased from 3 μm to 33 μm. A plate covered with a piece of aluminium foil was connected to the anode as a collecting substrate. The homogenous fibrous polymer films were collected on the surface of aluminium foil. The thickness of the fibrous film was controlled by the length of time for which voltage power was supplied.

Firstly, the fiber is fabricated from polystyrene (PSt). Fig. 3a shows the fibrous film fabricated by the coaxial electro-spinning. The as-prepared PSt fiber shows a flat hollow tube cross-section[27] and is about 15.6 μm in width, which is similar to the hair of the leaf (the inset in Fig. 3a). The CA of the as-prepared fibrous films is 147.0 ± 1.1° (Fig. 3c). The fibrous film has a high broad reflectance above 60% (Fig. 4a, solid line). The control film is fabricated by treating the as-prepared fibrous film with THF solvent to remove the fiber structure and then drying naturally. Thus the PSt fibres are merged into a block of membrane (Fig. 3b, Fig. S7b†). The reflectance of the treated control film with similar thickness (see Fig. S7 in the ESI†) decreases to 20% (Fig. 4a, dashed line). It further confirms that the high reflectance arises from the fibrous structure.

A series of hollow fibrous films with different fiber width from 3 μm to 33 μm are fabricated by controlling the flow rate of inner fluids. Fig. 4b shows the reflectance of the single fiber at the wavelength of 625 nm as a function of the fiber width. Each reflectance is averaged from five different fibers measurements. The fiber reflectance increases over four times (from 2.3% to 9.3%) as the fiber width increases from 3 μm to 11 μm. Once the fiber width exceeds 16 μm, the fiber width change has little effect on its reflectance. The optimal fiber width is *ca.* 14 μm, agreeing well with the structure of the leaf hair.

The film thickness is another crucial factor for its reflectance. Fig. 4c shows the film reflectance at the wavelength of 625 nm as

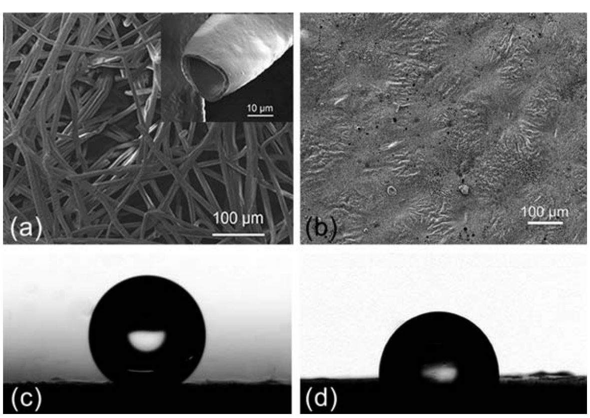

Fig. 3 (a) SEM image of fibrous film. Inset shows that the fiber is hollow. (b) The control film, achieved by treating the as-prepared fibrous film with solvent. (c) The CA of the fibrous film is 147.0 ± 1.1°. (d) The CA of the control sample is 97.6 ± 1.3°.

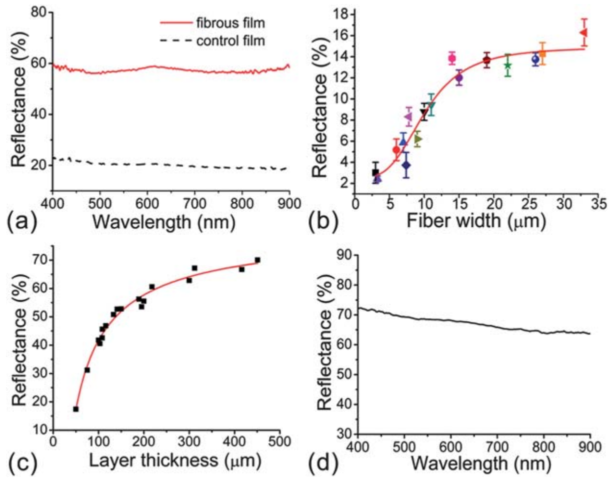

Fig. 4 (a) Reflectance spectra of the fibrous film (solid line) and the control film without fibrous structures (dashed line). (b) The relationship between the reflectance of the single fiber and the fiber width at the fixed wavelength of 625 nm. (c) Reflectance of the fibrous films increases with increasing film thickness at a fixed wavelength of 625 nm. (d) Reflectance spectrum of the fibrous films with a thickness of approximately 450 μm.

a function of the film thickness. The fiber width is controlled around 14 μm. As the random fibers network gets thicker from 50μm to 150 μm, the reflectance increases from 17.0% to 52.8%. However, the reflectance could not increase unlimitedly with the increase of the fibrous film thickness. As the thickness of the film increases to around 200 μm, its reflectance gets to around 60%. This is good enough to serve as an effective reflectance shield against strong light and reduce the solar absorption. After that, the growth rate of the reflectance becomes slow with the film thickness growth. As shown in Fig. 4d, when the thickness is approximately 450 μm, the reflectance has a broad reflectance of around 60–70% in the visible light wavelengths.

To prove that common materials are also suitable for this mimic white coating fabrication, poly(vinylidene fluoride (PVDF) and poly vinylpyrrolidone (PVP) are chosen for such mimic fabrication. The size of the prepared fibrous films is around 16 μm in fiber width and 400–450 μm in film thickness. The bio-mimic fibrous films made of these polymers also have a high reflectance above 60% (Fig. S8†).

Moreover, the PSt fibrous film is superhydrohobic and free-standing with certain mechanical property. The CA of the fibrous film is 147.0 ± 1.1° (Fig. 3c), similar to the hair layer of the leaf. The mechanical property of the PSt fibrous film was characterized on a DMA Q800 machine (TA instrument Inc.). Its tensile strength is 0.54 ± 0.09 MPa and its Young's modulus is 14.45 ± 2.14 MPa. The typical stress-strain curves of PSt fibrous films are shown in Fig. S9.† These results provide a potential strategy for a highly effective and economic shield for strong light protection.

We further examined the photo-chromic change of a classical diarylethene compound (DTE) solution with the fibrous film shield to elucidate the reflective effect of polymeric materials. The DTE molecule can undergo a photo-cyclization from closed-ring isomer (in red color) to open-ring isomer (colorless) under the radiation of visible light.[28] Three cuvettes filled with DTE solution are covered with nothing (cuvette 1), the control film (cuvette 2) and the as-prepared fibrous film (cuvette 3). The control film and the fibrous film are the same as the ones presented in Fig. 3. The control film (Fig. 3b) was made from the fibrous film (Fig. 3a) by removing the fiber

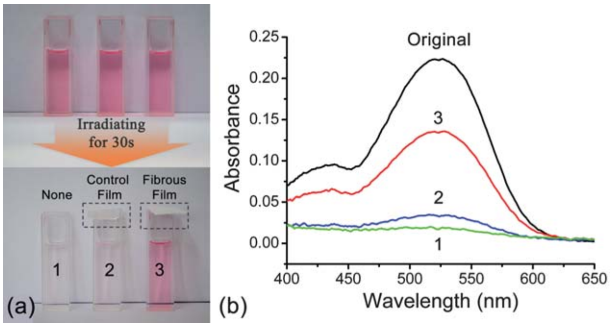

Fig. 5 (a) Photo-chromic change of a DTE solution in three cuvettes with different covers to elucidate the shield function of the fabricated fibrous film under strong light. (b) The absorbance of the DTE solution before the visible light radiation (Original) and after 30s radiation (cuvette 1, cuvette 2, cuvette 3). The photo-chromic change rate of the DTE solution is greatly reduced with the artificial fibrous film cover in the cuvette 3.

structure using THF solvent. With the thickness about 300 μm, the fibrous film has a reflectance about 58%, while the control film has a reflectance about 20% at the DTE's absorbance peak wavelength of 527 nm. Their reflectance spectra are shown in Fig. 4a. They are directly irradiated by the visible strong light using the solar simulator (80 mW cm^{-2}) from the cover (experiment details see in the ESI†).

As Fig. 5a shows, after 30 s irradiation, the DTE solution in cuvette 1 turns colorless while the solution in cuvette 3 remains red in color. The peak absorbance of solution in *cuvette 1* has a decrease of 0.204 from 0.223 to 0.019 at the wavelength of 520 nm (Fig. 5b). In *cuvette 2*, the peak absorbance has a decrease of 0.198. In *cuvette 3*, the peak absorbance of the solution reduces little (by 0.088). In the *cuvette 3* with the artificial fibrous film cover, the photo-chromic change rate of the DTE solution is greatly reduced due to the shielding function of the fibrous film. These results demonstrate that the artificial fibrous film can scatter off the light effectively and protect the sample from photodamage in strong light. Moreover, the fibrous films remain unchanged under the strong light radiation with the intensity of 80 mW cm^{-2} over hours, which is as strong as the full solar light in the case of the leaf.

In summary, we achieve a series of highly reflective white coatings, inspired by the function and structure of the poplar leaf hair. When the white coatings are *ca.* 14 μm in the fiber width and *ca.* 200 μm in the film thickness, their reflectance are around 60%. The films can be made from various common polymers such as PSt, PVDF and PVP. Furthermore, these highly reflective coatings are lightweight due to their hollow fibrous structure and they are superhydrophobic. They are promising for eco-friendly and effective "cool roofs" to offset CO_2 emission and mitigate global warming by reflecting more sunlight back into space. Additionally, these white coatings could be applied in developing low-cost and light-weight coatings to improve the efficiency of large areas of lighting by using them as a backing material.

Acknowledgements

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