Electrospinning to Surpass White Natural Silk in Sunlight Rejection for Radiative Cooling

Bo Kyung Park, In Chul Um, Sang M. Han, and Sang Eon Han*

1. Introduction

Nature exploits intriguing nanostructures to realize a vast range of optical effects such as iridescence, camouflage, solar rejection, metallic reflection, and extreme scattering. Cocoon silk fibers are an example that exhibits strong broadband light scattering with a metallic sheen, which effectively protects pupae from being overheated by direct sunlight. The strong light scattering of a silk fiber is due to its densely packed long fibrillar voids that are aligned along the fiber axis. With a size of hundreds of nanometers in diameter, these fibrillar voids guide light into the fiber axis direction through 2D Anderson localization with a low refractive index contrast of 1.55–1.58. Moreover, silk fibers have a high emissivity over the atmospheric transparency window in mid-infrared (IR), so that they tend to be cooled by radiating heat into the outer space. The combined effects of optical and mid-IR properties of silk nanostructures keep pupae in silk cocoons in a low temperature environment under sunlight.

Inspiration from the remarkable optical properties of silk fibers has directed research efforts to fabricating biomimetic nanoporous fibers with synthetic materials. Although natural biomaterials are often inspirational for the discovery of new synthetic materials, this does not necessarily mean that these biomaterials exhibit optimal properties. The view that biomaterials have been optimized by evolution has been popular, perhaps because of the observation that organisms are apparently very well adapted to their environment. However, this popular view has long been criticized within evolutionary thought, due to its many unsupported beliefs including a naïve supposition that current properties are the reasons for evolution. Even if the controversial view were to be accepted, optimization would not be for a single property but rather for a balance between various properties. These considerations suggest that, in many cases, biomaterials are far from optimum for a specific desired property and can be improved further for that property by artificial processing.

In this article, we address a question as to whether sunlight rejection power of white natural silk can be surpassed by restructuring the silk fibers into a very different, yet fiber-based, nanoporous morphology. To achieve this goal, we electrospin raw silk to create fibrous films with controlled fiber diameters, optically characterize the films, and measure the temperature variation of a substrate covered by the films under a clear sky over a day. For accurate optical characterization of the highly anisotropic fibrous films, we perform detailed analysis using optical anisotropic diffusion theory. We find that the restructured silk fibrous films can exhibit even stronger optical scattering than natural silk. Furthermore, we show that the stronger sunlight scattering of the synthetic films significantly enhances cooling...
Recently, anisotropic fibrous media that are similar to ours have been studied for radiative cooling applications.\cite{25-27} Li et al.\cite{25} used electrospun polyethylene oxide to have a mid-IR emissivity spectrum desired for radiative cooling. For maximum solar rejection, they determined that a fiber diameter should be in the range of 0.5–1.2 μm, comparable to solar wavelengths, based on scattering efficiency calculations (the optimum diameter would have been 0.746 μm, see Section 10, Supporting Information). Yalçin et al.\cite{26} performed comprehensive numerical study on anisotropic silica fibrous media, using Monte Carlo method to solve the radiative transfer equation (RTE). Although the method gives accurate results, it requires significant computation time. The numerical study showed that a fiber diameter of 0.4–0.5 μm at a fiber fraction of 0.04 yielded the maximum radiative cooling under sunlight when the film thickness was below 1 mm. Kim et al.\cite{27} used electrospun polyacrylonitrile to render low solar transmissivity and high mid-IR transmissivity. Ellipsoidal beadings on the fibers of a 0.067 μm in diameter increased solar reflectivity. Thus, previous studies report different fiber diameters for the maximum radiative cooling under sunlight. A reason for this discrepancy between the studies may be that scattering efficiency, calculated for light incidence direction normal to the fiber axis, was used to determine the diameter\cite{27} instead of a more rigorous approach\cite{26} of solving the RTE. However, direct solution to the RTE poses numerical problems such as ill-conditioning\cite{28} and the Monte Carlo approach is rather time consuming. In comparison, diffusion approximation offers a great practical solution by simplifying the problem substantially. Our study demonstrates success of the anisotropic diffusion theory in characterizing electrospun fibrous media. We analyze experimental results within the framework of our highly accurate anisotropic diffusion theory\cite{24} and determine that the maximum reflection over a wavelength range of 0.4–0.9 μm is achieved with a mean fiber diameter of 0.25 μm among a range of 0.25–1.76 μm. This diameter is similar to the mean fibril diameter in Cyphochilus white beetle scales (0.23 μm) which is close to optimum for maximal optical scattering.\cite{10}

2. Results and Discussion

2.1. Structure Characterization

Electrospinning of regenerated silk resulted in a fibrous film of anisotropic random media with various fiber mean diameters (d) as shown in Figure 1A(a)–(e). We controlled the d of the electrospun silk fibers by adjusting the concentration of the fibroin solutions. The fiber diameter near the needle tip during electrospinning is approximately proportional to \( \sqrt{\mu \rho Q} \), where \( \mu \), \( \rho \), and \( Q \) are the viscosity, density, and volumetric feed rate of the fibroin solution, respectively.\cite{24,31} The fiber diameter is reduced as the fiber travels from the needle tip to the collector. The solution concentration determines \( \mu \) and \( \rho \). Our method of varying the solution concentration was effective in controlling d.

Figure 1B shows that, as the concentration increases from 8 to 15 wt%, the d of the electrospun silk fibers increases from 0.25 to 1.76 μm, with a relative standard deviation of \( \sigma = 30–45\% \). In comparison, the raw silk fibers have \( d = 23.1 \mu m \) [Figure 1A(f)], with \( \sigma = -10\% \). Because the cross section of raw silk fibers deviates from circular shape, \( d \) is taken from diameters of the circles that have the same area as the noncircular cross sections of the fibers. For the purpose of later discussion, we call Figure 1A(a) and (e) structures as electrospun nanosilk and electrospun microsilk, respectively.

2.2. Determination of Mean Free Paths

Light propagation in electrospun silk fibrous films can be described by the diffusion model.\cite{24,31} For such highly anisotropic media, the conventional isotropic diffusion equation\cite{31} cannot be used, as has been done in previous studies,\cite{8,9,13} to describe light diffusion fully and accurately. For example, for Cyphochilus white beetle scales, the application of isotropic diffusion theory results in a large error in scattering strength.\cite{32} Thus, we analyze light propagation in the electrospun films by our rigorous anisotropic diffusion theory\cite{24} even though the analysis is rather complex. The anisotropic diffusion theory described in this section yields transmissivity and reflectivity that are almost indistinguishable from those by direct solution of the RTE and Monte Carlo simulation, so that the theory yields very high accuracy for the electrospun films (Figure S4, Supporting Information). Moreover, the solution to the anisotropic diffusion equation has an explicit form, enabling experimental data to be analyzed efficiently.

When light is normally incident on a film of anisotropic media with inversion symmetry, the diffusion equation becomes\cite{24}

\[
\frac{d^2 U_d}{dz^2} - \frac{3}{L_{d,zz}} \frac{U_d}{L_{d,zz}} = -\frac{3F_0}{4\pi} \left( \frac{\mu}{L_{zz}} + \frac{1}{L_{zz}^2} \right) \exp\left( -\frac{z}{L_{zz}} \right)
\]

(1)
where $U_3$ is the angle-averaged diffuse intensity, $z$ is the coordinate in the film thickness direction, $F_0$ is the incident light flux density, $\pi$ is the average cosine of scattering angles with respect to the $z$ direction, $1/L_{da}$ is the angle average of inverse diffusive absorption mean free paths, and $L_{zz}$, $L_{zz'}$, $L_{zz''}$ are the $zz$ component of scattering, transport, and extinction mean free path tensors, respectively. For anisotropic media, we define the effective transport mean free path $L_{zz''} = K_z L_{zz''}$, where $K_z = \| \pi \|$ is the $zz$ component of anisotropy tensor.\(^{[24,32]}\)

In this article, $L_{zz''}$ and $L_{da}$ are of particular interest among the mean free paths. $L_{zz''}$ is the $z$-direction length over which light propagation direction is randomized, and $L_{da}$ represents an angle-average length that diffusive light travels before being significantly absorbed. Thus, to achieve strong rejection of sunlight, $L_{zz''}$ should be reduced for enhanced optical scattering, and $L_{da}$ should be long enough for minimal absorption.

When the film thickness ($L$) is much greater than $L_{zz}$, transmissivity ($T$) and absorptivity ($A$) of the films are derived from Equation (1) as

$$T = 2kL_{zz''} \frac{(1 + \beta)D - \pi\beta}{(1 + \alpha)e^{\pi} - (1 - \alpha)e^{-\pi}} \tag{2}$$

$$A = 1 - (D - \beta) L_{zz''} \frac{1 + (1 + \alpha)e^{\pi} + (1 - \alpha)e^{-\pi} - 1}{2} \tag{3}$$

where $\pi^2 = 3/(L_{da} L_{zz})$, $D = ([\pi/L_{zz}^2 + 1/(L_{zz} L_{zz''})]/[1/L_{zz''}^2 - \pi^2])$, $\alpha = z\varepsilon L_{zz''} \kappa$, $\beta = z^2 L_{zz''} L_{zz''}/L_{zz}$, and $z\varepsilon$ is the extrapolation length ratio. For weakly absorbing films where $\varepsilon L \ll 1$ and $\alpha \ll 1$, Equation (2) is approximated by\(^{[24,32]}\)

$$T = \frac{1 + z\varepsilon/K_z}{L_{zz''} + 2z\varepsilon/K_z} \tag{4}$$

For our electrospin silk fibrous films, absorption was relatively weak, so that we used Equation (4) to obtain $L_{zz''}$. Specifically, we made a plot of $1/T$ versus $L$ from our experiments with $L$ ranging from 37 to 161 m, and obtained $L_{zz''}$ from the slope calculated by fitting the data to the inverse of Equation (4). In obtaining $L_{zz''}$ from the fitting, knowledge of $z\varepsilon$ and $K_z$ was required. $z\varepsilon$ was obtained by assuming that internal reflection of light at the film surfaces followed Fresnel's law. Accuracy in $z\varepsilon$ can be improved by directly calculating internal reflectance in model structures such as infinitely long cylinders.\(^{[33]}\) $K_z$ was calculated using our optical model that implemented the mean field theory (Section 1, Supporting Information).

To calculate $L_{da}$ for our electrospin silk fibrous films, we approximated $1/L_{zz} \approx 1/L_{zz} + 1/L_{da}$ in Equation (3), and fit the experimentally obtained $A$ for various $L$ to Equation (3) with $L_{zz}$ and $L_{da}$ as fitting parameters. To vary $L$, we stacked multiple electrospun fibrous films with air gaps in between\(^{[34]}\) so that 80 µm ≤ $L$ ≤ 650 µm ($L$ was determined without taking the gap thicknesses into account). This procedure would introduce an error by neglecting internal reflection at the film surfaces when $f$ is large enough. We assume that this error in $L_{da}$ is acceptable because of the low fill fractions ($f = 0.06–0.11$) of our electrospun silk fibrous films.

For our nonwoven raw silk fabrics, a slightly different method was used to obtain $L_{zz''}$, $L_{zz}$, and $L_{da}$, because $\varepsilon L$ was significantly greater than 1 at short wavelengths so that Equation (4) could not be used. Specifically, we obtained the mean free paths by directly fitting experimentally measured $T$ and $A$ for varying $L$ (75 µm ≤ $L$ ≤ 570 µm) to Equation (2) and (3). In the fitting, we assumed that $K_z = 1$ and $z\varepsilon$ was obtained from Fresnel’s law. Because of the relatively large fill fraction ($f = 0.35$) of the nonwoven raw silk fabric sheets, stacking the fabric sheets with air gaps in-between would introduce significant errors due to strong internal reflection. Thus, we used only solid films of nonwoven raw silk fabric of different thicknesses.

### 2.3. Optical Characterization

Figure 2 shows the fitting results of $L_{zz''}$ and $L_{da}$ spectra for Figure 1A(a)–(f) structures. Overall, $L_{zz''}$ shows only a weak spectral dependence over visible wavelengths, whereas $L_{da}$ increases significantly as the wavelength increases. At long wavelengths near $\lambda = 0.9$ µm, $L_{da}$ is more than two orders of magnitude greater than $L_{zz''}$ for all the structures, indicating that absorption is negligible. Because of the large difference between $L$ and $L_{da}$ at long wavelengths, the large values of $L_{da}$ may not be highly accurate and we do not discuss detailed features of $L_{da}$ near $\lambda = 0.9$ µm. Absorption is more pronounced at short wavelengths near $\lambda = 0.4$ µm. Overall, the raw silk has relatively small $L_{da}$ among our samples, and only Figure 1A(a) structure has smaller $L_{da}$ than the raw silk over most of the visible spectrum. Presumably, the reason is that Anderson localization in the raw silk enhances absorption\(^{[6,7,14]}\) and absorption in sericin in the raw silk may also affect $L_{da}$ at short wavelengths (Sections 2 and 3, Supporting Information).\(^{[15–37]}\)

Dependence of $L_{zz''}$ and $L_{da}$ at $\lambda = 0.6$ µm on $d$ is shown in Figure 2B and D, respectively. This wavelength is chosen to represent response to visible light approximately. $L_{zz''}$ monotonically increases as $d$ increases for the Figure 1A(a)–(e) structures, and $L_{da}$ is maximized when $d = 0.8–1.0$ µm in the structures. Such clear trend is not apparent when $L_{zz''}$ and $L_{da}$ are plotted as a function of fill fraction (Figure S6, Supporting Information). Figure 1A(a) structure (electrospun nanosilk) exhibits the smallest $L_{zz''}$ indicating the strongest scattering strength among the samples. Interestingly, electrospun nanosilk has $d = 0.25$ µm which is similar to the mean fibril diameter in Cyphochilus white beetle scales (0.23 µm) which is close to optimum for maximal optical scattering.\(^{[10]}\) When $d$ increases from 0.25 µm (Figure 1A(a), electrospun nanosilk) to 1.76 µm (Figure 1A(e), electrospun microsilk), $L_{zz''}$ increases by greater than eight times. Even for the electrospun microsilk, $L_{zz''}$ is still smaller than that of the nonwoven raw silk fabric but similar to that of a silk cocoon (Figure S2A, Supporting Information). The enhancement in the scattering strength ($1/L_{zz''}$) for the electrospun silk samples over both the nonwoven raw silk fabric and the natural silk cocoon is striking, when we consider the following two facts. First, Anderson localization in the natural silk cocoon may not happen in the electrospun silk samples. Second, our electrospinning resulted in a low fill fraction ($f = 0.06–0.11$) whereas $f = 0.35$ and 0.31 in our nonwoven raw silk fabric and the raw silk cocoon, respectively. Optimizing $f$ in the electrospun nanosilk may further enhance optical scattering (Figure S7, Supporting Information).
To evaluate the optical properties of the electrospun and raw silk fibrous films to be useful for outdoor applications, we measured visible and mid-IR absorptivity/emissivity of the electrospun nanosilk, electrospun microsilk, and nonwoven raw silk fabric samples coated on 2.5 cm × 2.5 cm black substrates. Our measured absorptivity/emissivity spectra are shown in Figure 3. A natural silk cocoon could not be flattened to cover the black substrate area and was not included in this experiment.

Thickness of the three silk fibrous films was \( L \approx 420 \text{ μm} \). At this thickness, \( κL \) is greater than or close to 1 in the visible wavelengths for the three fibrous films. These fibrous films are weakly absorptive in the long wavelengths of visible spectrum, such that \( κL' ≪ 1 \) (Figure S1, Supporting Information). When \( κL' ≫ 1 \) and \( κL'' ≪ 1 \), Equation (2) and (3) give

\[
T = \left[ 2(K_{zz} + z_e)(κL_{zz}'') - 4z_e(K_{zz} + z_e)(κL_{zz}''')^2 \right] \exp(-κL)
\]

and

\[
T + A = (K_{zz} + z_e)(κL_{zz}')
\]

\[
- \left[ (K_{zz} - \frac{1}{3}) \frac{L_{zz}}{L_{zz}''} + z_e(K_{zz} + z_e) \right] (κL_{zz}')^2 + O[(κL_{zz}')^3]
\]

where \( O[⋯] \) stands for truncation error order. The \( T + A \) in Equation (6) is absorptivity for a sample that consists of an absorptive scattering film on a completely black substrate.

![Figure 2](image-url)  
Figure 2. A,B) Effective transport mean free path and C,D) diffusive absorption length as a function of (A,C) wavelength \( λ \) and (B,D) mean fiber diameter at \( λ = 0.6 \text{ μm} \) for the Figure 1A(a)–(f) structures.

![Figure 3](image-url)  
Figure 3. Absorptivity/emissivity spectra of electrospun nanosilk, electrospun microsilk, and raw silk at a thickness of \( \approx 420 \text{ μm} \) placed on a black substrate over the A) visible and B) mid-IR wavelengths. \( κL'' \) values at \( λ = 0.6 \text{ μm} \) for the three samples are displayed in (A). Atmospheric transparency window is highlighted in yellow in (B).
Equation (6) reproduces Figure 3A well for the electrospun nanosilk and deviates from Figure 3A by as much as 0.13 for the raw silk. According to Equation (6), \( \kappa L^2 = \sqrt{3L^2 + L_0^2} \) determines \( T + A \) and needs to be minimized to decrease absorptivity in our samples. At \( \lambda = 0.6 \mu m \), \( \kappa L^2 \) values for the electrospun nanosilk, electrospun microsilk, and raw silk samples are 0.05, 0.11, and 0.18, respectively, as shown in Figure 3A and Figure S1, Supporting Information.

As with solar absorptivity, the mid-IR emissivity of the silk samples is significantly affected by the structures as shown in Figure 3B. For example, over the atmospheric transparency window (\( \lambda = 8-13 \mu m \)) highlighted in yellow in Figure 3B, the electrospun nanosilk exhibits an average emissivity of 0.97, which is higher than that of 0.89 for the electrospun microsilk. In comparison, over the spectral window, the raw silk sample has an average emissivity of 0.93, which is between the emissivities of the electrospun nanosilk and microsilk samples. Thus, the mid-IR emissivity of electrospun silks can increase or decrease relative to raw silk, depending on fiber diameter. Based on both solar and mid-IR emissivity spectra, the electrospun nanosilk would be most effective among the three samples for radiative cooling under sunlight.

Although Figure 3 shows that electrospun nanosilk mats would be useful as an outdoor cooling wrapper that desirably contacts an object to be cooled, they would also have a strong potential as sunshades for noncontact applications because their high emissivities of the samples resulted in almost same temperatures during the time of intense sunlight. For example, during 11 a.m.–4 p.m., the average temperatures of the electrospun nanosilk, electrospun microsilk, and raw silk are 34.7, 38.2, and 42.2 °C, respectively. Thus, using electrospun nanosilk instead of nonwoven raw silk fabric, we can lower the temperature of an underlying black substrate by 7.5 °C during daytime. The daytime temperatures of the three samples are in agreement with our heat transfer modeling results that are based on the absorptivity/emissivity spectra in Figure 3 (Section 6, Supporting Information). At night, the temperatures of the three samples are \( \approx 3 °C \) below the ambient temperature due to the high emissivities of the samples over the atmospheric transparency window (Figure 3B). The differences between the mid-IR emissivities of the samples resulted in almost same temperatures within an experimental error at night, in agreement with our heat transfer modeling results in Figure S5, Supporting Information.

2.4. Radiative Cooling Test

To evaluate the cooling performance of the three silk samples on black substrates in Figure 3, we used the setup shown in Figure 4A,B. A photograph of the three samples is shown in Figure 4C inset, and details of the setup are described in the Experimental Section. The samples were located \( \approx 1 \) m above the ground (Figure 4A) to minimize influence of ground heat. We measured the sample temperatures at the University of New Mexico in Albuquerque, New Mexico on June 28th, 2019. The sky was mostly clear for the day. The sample temperatures are compared to the ambient temperature measured from an official weather station (BestForecast, KNMALBUQ11) located on the University of New Mexico campus.

Figure 4C shows the measured temperature variation. Both electrospun samples exhibit temperatures lower than the raw silk over the entire day, with the electrospun nanosilk maintaining a lower temperature than the electrospun microsilk within an experimental error of \( \pm 0.5 °C \). Compared to the ambient temperature, the electrospun nanosilk temperature is lower by \( \approx 3 °C \) at night and almost the same during the day (higher only by \( \approx 0.3 °C \) on average between 11 a.m. and 4 p.m.). The temperature differences between the samples are most pronounced during the time of intense sunlight. For example, during 11 a.m.–4 p.m., the average temperatures of the electrospun nanosilk, electrospun microsilk, and raw silk are 34.7, 38.2, and 42.2 °C, respectively. Thus, using electrospun nanosilk instead of nonwoven raw silk fabric, we can lower the temperature of an underlying black substrate by 7.5 °C during daytime. The daytime temperatures of the three samples are in agreement with our heat transfer modeling results that are based on the absorptivity/emissivity spectra in Figure 3 (Section 6, Supporting Information). At night, the temperatures of the three samples are \( \approx 3 °C \) below the ambient temperature due to the high emissivities of the samples over the atmospheric transparency window (Figure 3B). The differences between the mid-IR emissivities of the samples resulted in almost same temperatures within an experimental error at night, in agreement with our heat transfer modeling results in Figure S5, Supporting Information.

3. Conclusion

In conclusion, we have demonstrated that raw silk can be restructured to enhance solar rejection performance. We restructure white raw silk by a conventional simple method of electrospinning. When a mean diameter of silk fibers is 0.25 μm, reflection over a wavelength range of 0.4–0.9 μm is maximized among a
diameter range of 0.25–1.76 μm. When the electrospun nanofibrous film and the nonwoven raw silk fabric placed on substrates are exposed to the direct sunlight, the electrospun nanosilk achieves an average substrate temperature lower by 7.5 °C than the raw silk over 11 a.m.–4 p.m. Moreover, the electrospun nanosilk maintains the temperature of its underlying substrate almost the same as or lower than the ambient temperature throughout the day. These results are remarkable when we consider that our restructured silk may no longer support Anderson localization, which happens in raw silk fibers, and have a low fill fraction of fibers \( f = 0.06–0.11 \) for optical scattering. Optimization of structural parameters in the electrospun silk, such as fill fraction and diameter distribution of fibers, may further enhance optical scattering. Our results suggest that one can enhance solar reflection even more by electrospinning synthetic polymers that are less absorptive than silk, especially at short wavelengths near ultraviolet. This potential is strong as many low-loss polymers can be electrospun at a mean diameter near 0.25 μm.\(^\text{27,28}\) A foreseeable problem of such nanofibrillar polymeric mats in utility applications would be their weak mechanical strength. To enhance durability, the nanoscale fiber mats can be sandwiched between mechanically strong fabrics. With the further improvements mentioned earlier, i.e., optical optimization and mechanical improvement, electrospun nanofiber mats would find diverse practical applications including traspertation cooling wrappers, car sunshades, outdoor canopies, roller blinds for windows, etc.

### 4. Experimental Section

**Preparation of Regenerated Silk Fibroin Powder:** Silk fibroin powder was derived from *Bombyx mori* (Geumokjam) white silk cocoons after removing sericin by a process called degumming. Whiteness of the cocoons was determined using CIE 1931 color coordinates as \( (x, y) = (0.3205, 0.3387) \) under the CIE Standard Illuminant D\(_65\), which were slightly different from the perfect white \( (x, y) = (0.3128, 0.3290) \) under the same illuminant (Figure S8, Supporting Information). For degumming, an aqueous solution of 0.2% w/v sodium carbonate and 0.3% w/v sodium oleate was heated at 105 °C. Silk cocoons were heated in the solution for 90 min to ensure almost complete removal of sericin from the cocoons. The weight ratio between the silk cocoons and the aqueous solution (liquor ratio) was 1:25. The degummed silk cocoons, which were comprised mostly of fibroin, were rinsed with distilled water at 100 °C for 150 s to remove degumming agents (i.e., sodium carbonate and sodium oleate) and residual sericin from the silk cocoons. After further rinsing with cold distilled water, the silk cocoons were dried at 80 °C for a day. To obtain regenerated silk fibroin in a powder form, the degummed silk was dissolved at a liquor ratio of 0.1:2.5 in a CaCl\(_2\)/H\(_2\)O/EtOH (1/8/2 molar ratio) mixture solvent at 85 °C for 30 min. To remove CaCl\(_2\) and ethanol from the dissolved silk fibroin, the solution was placed in a tube of a cellulose membrane and was dialyzed for 4 days by circulating distilled water around the tube. The membrane was impenetrable to fibroin of molecular weight over 12 000–14 000. The dialyzed silk fibroin solution was filtered through a polyelectrolyte porous membrane to remove any extraneous dirt. The filtered solution of regenerated silk fibroin was dried and ground into powder.

**Electrospinning of Regenerated Silk Fibroin:** Regenerated silk fibroin powder was dissolved in 98% formic acid for 3 h at a concentration varying from 8 to 15 wt% and filtered through a polyelectrolyte porous membrane. The fibroin solution was loaded into a syringe with a 21 gauge stainless steel needle (inner diameter of 0.495 mm) for electrospinning. We applied 22.5 kV to the needle and electrically grounded a 9 cm diameter drum-shaped collector. The distance between the needle tip and the collector surface was 15 cm. The drum collector was rotated about its axis at 34 rpm. The regenerated silk fibroin at the solution concentrations (8–15 wt%) was electrospun onto the collector for 8 h.

**Preparation of Nonwoven Raw Silk Fabrics:** Sheets of nonwoven raw silk fabric were prepared at varying thicknesses from 75 to 570 μm from *Bombyx mori* white silk cocoons. To prepare the sheets, the silk cocoons were immersed in distilled water at 85 °C for an hour to render the fibers more flexible by swelling sericin in them. Then, the silk cocoons were transferred into a water bath at 50 °C. One end of a silk fiber in each cocoon was attached to a cylindrical bobbin after passing through a slit. For fiber winding (SNWFM-2, Dong-A machine, South Korea), the winding speed of the rotating bobbin was 152 cm s\(^{-1}\), and the slit oscillated parallel to the bobbin axis at 9.3 cm s\(^{-1}\). The bobbin and slit speeds resulted in an angle of 7° between two crossing silk filaments. The silk fiber was wound on the bobbin into a layer, which was then cut into eight pieces. These pieces were stacked by successively rotating each layer by 90° in the plane. The layer rotation in stacking approximated the random orientation of silk fibers in directions parallel to the surface of cocoon shells. After the stacking, distilled water was sprayed onto the top layer, and the water was allowed to penetrate into the underlying layers for 5 min. The stacked layers were subsequently pressed twice by a hot presser (HK 2008-1, Hankuk Industry Co., South Korea) at 200 °C for 10 s. To prevent the outer layers from adhering to the hot press plates, the plate surfaces were covered by a nonwoven polyester fabric.\(^\text{40}\) The nonwoven raw silk fabric sheets prepared by the above processing steps exhibited a reduced scattering power relative to natural silk cocoons, in addition to slight yellowing (compare Figure S8 and S9, Supporting Information), as shown in Figure S2, Supporting Information.

\( f = \frac{\rho_s}{\rho_{SF}} \) (7)

where \( \rho_s \) and \( \rho_{SF} \) are the density of the fibrous films and the silk fibroin, respectively. \( \rho_s \) was measured directly from the weight and volume of the fibrous films. To measure \( \rho_{SF} \), an end of a vertically standing aluminum wire was connected to the sensor of a scale and the other end was attached to a weighing pan that was immersed in an n-hexane bath. Samples cut into 1.5 cm \( \times \) 1.5 cm pieces were placed on the weighing pan in the n-hexane bath and the weight reading by the sensor was recorded as \( m \). \( \rho_{SF} \) was then obtained by

\( \rho_{SF} = \frac{m_S}{m_S - m_{PH}} \) (8)

where \( m_S \) is the mass of the fibrous films and \( m_{PH} \) is the n-hexane density. Fill fraction of nonwoven raw silk fabric was measured by the same method as earlier. In this case, \( \rho_{SF} \) is an average density of fibroin and sericin in the raw silk.

**Optical and Structural Characterization:** Transmissivity and reflectivity spectra of silk fibrous films were measured by spectrophotometers with integrating spheres. In the visible spectrum from 0.4 to 0.9 μm, the measurement setup was a detector (USB4000-VIS-NIR, Ocean Optics) coupled to an integrating sphere (ISP-50-8R, Ocean Optics). In the mid-IR spectrum from 1 to 25 μm, the measurement system (INVENIO R, Bruker) was purged with a nitrogen gas to eliminate absorption by air. The diameters of more than 100–135 fibers were measured per sample from scanning electron microscopy (SEM) images (JSM-IT 100, JEOL, USA). Mean values and relative standard deviations of the diameters were calculated from the measurements.

**Radiative Cooling Characterization:** The fibrous film samples were mounted on a black-painted glass substrates, and each substrate bottom was connected to a thermostate. The samples were enclosed in separate low-density polyethylene (LDPE) compartments in a box of dimensions 42 cm \( \times \) 40 cm \( \times \) 20 cm. The setup was similar to the one used in the study by Kou et al.\(^\text{41}\) All six sides of each compartment were LDPE films. Although the LDPE box was used to reduce convective heat transfer, the LDPE films vibrated by wind, which caused moderate convective heat...
transfer within the box. To prevent solar heating of the box, the thin box frames and the thermocouple wires were painted white. To prevent heating of the samples by sunlight reflected from the ground, their back side was also painted white.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
electrospinning, light scattering, silk, solar rejection, white beetle scales

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