Supporting Information

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UV-Cross-Linking Silk Fibroin Using Stilbene

Stilbene chromophore and its derivatives have been used as photoreactive building blocks or dopants for imaging and resist techniques (24, 26, 44). Polymers with stilbene can be cross-linked upon exposure to deep-UV light. The dominant photoreactions in stilbene-doped silk solutions under the deep-UV exposure are intrachain \( [2\pi + 2\pi] \) cycloadditions (involving \( cis \)-\( trans \)-isomerization) and radical reactions (26). Fig. S1A shows the attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of amorphous and cross-linked silk films. Along with the absorbance band at 1,641 cm\(^{-1}\), indicative of a typical random coil organization of amorphous proteins (16), the cross-linked silk film exhibits an absorbance band at 1,607 cm\(^{-1}\) that originates from the \( C = C \) stretching of \( trans \)-exo-cyclic bonds (26). This result is a strong indicator for the formation of intrachain \( [2\pi + 2\pi] \) cycloadditions. In addition, fluorescence analyses were performed to investigate the structure of the silk films (Fig. S1B) because it is acknowledged that the isomerization of the \( cis \)-configuration causes loss of the loss the fluorescence of stilbene (26). As expected, increasing UV irradiation intensity dramatically decreases the intensity of the stilbene emission.

Interestingly, when energy-rich UV light is used, radical reactions can occur. Tyrosine residues in silk fibroin form tyrosyl radicals by UV light (25). Two tyrosyl radicals can then form a dityrosine bond that chemically cross-links the silk backbones. Note that byproducts generated during the dityrosine cross-linking are known to be biocompatible (45). The presence of dityrosine can be confirmed by fluorescence spectroscopy. Fig. S1B shows that, along with decreases in fluorescence intensity, dityrosine fluorescence at 415 nm is observed.

Refractive Index of the Swollen Silk Hydrogen Film

To analyze the optical response of hydrogel inverse opals, it is important to determine the RIs of the swollen matrix because absorbed water reduces the mean RI of the matrix. Experimentally, the RI of a material can be determined by measuring the deflection of a beam as it enters and leaves the interface between materials at an angle (46). The quantitative statement of refraction is described by Snell’s law, \( n_1 \sin(\theta_1) = n_2 \sin(\theta_2) \), where \( \theta_1 \) \( (\theta_2) \) is the angle of incidence (refraction). As shown in Fig. S4, a rectangular silk film was prepared and a red laser beam was directed at the silk-air interface. For \( \theta_2 \) of 62°, we obtained \( \theta_1 \) of 38°, providing an RI for the swollen silk of 1.43. Using the average model \( n_{\text{silk,hydrogel}}^2 = n_{\text{silk}}^2(1 - f) + n_{\text{water}}^2 f \), where \( f \) is the filling factor of water (volume) (47), we can determine that water in the silk hydrogel accounts for about 50% of its total volume.

FDTD Simulations for Effects of Lattice Constant on Reflectance Spectra

We performed numerical simulations using the FDTD method to calculate reflectance spectra for the inverse opal structures in the L-point direction. As shown in Fig. S5A and B (Right), the lattice constants varied in the \( x \)- (or \( y \)-) direction (parallel to the incident surface) and \( z \) direction (vertical to the incident surface). The reflectance spectra were investigated in the \(-10\% \) (compressed) to \(+10\% \) (stretched) range of strains. Fig. S5A reveals that the shape of the reflectance spectra, and the peak wavelength of reflection \((\lambda = 618 \text{ nm})\), remains unaffected by strain in the lateral direction. On the contrary, as shown in Fig. S5B, the reflection peak wavelength was very sensitive to strain in the vertical \( z \) direction. It is reasonable to expect that the incident photons were affected by changes in effective refractive indices of the media, through the path of propagation. We can experimentally estimate the strain in the \( z \) direction from the measured reflection peak, as well as also the Poisson ratio of the SHIO.

Optical Loss Caused by Curvature of the Waveguide

Because the angle of total internal reflection is not consistent through the curved waveguide, propagating light leaks to the outside of the curved surface. We tried to reduce the optical loss by placement of the SHIO structure on the curved surface as a reflector. As shown in Fig. S7A, red light was illuminated onto an edge of a commercial contact lens by a diode laser. The path of the red light through the curved waveguide can be seen (yellow dotted line) and the propagated light was collected at the opposite side of the incident edge. To investigate the performance of the reflecting SHIO structure, the SHIO structure was placed at the center of the contact lens (Fig. S7B, Inset). Fig. S7B shows that the intensity of propagated light increased by over 50% when the SHIO structure was present (red line) compared with when the SHIO was absent (blue line). This result indicates that the leaked light was effectively reflected by the SHIO and recoupled back into the curved waveguide.

Comparison Between a Human Eye and a Cat (or Other Nocturnal) Eye

Fig. S8 shows diagrams for a human eye and a cat eye. The human eye gathers light through a crystalline lens and passes it to the retina to secure vision. In comparison, cats and other nocturnal animals have a tapetum lucidum, a layer of periodically arranged collagen fibers, behind the retina (22, 48). The tapetum lucidum reflects light directly back to the retina, thereby increasing the quantity of light passing through the retina. This process maintains the sharpness and contrast of the image on the retina. Because of this, cats have superior night vision. The existence of the tapetum lucidum can be confirmed by the shine observed in nocturnal photographs of these eyes. We applied the SHIO to mimic these eyeballs and confirmed the possibility of its application as an ocular prosthesis. In our experiment, the SHIO acts as a reflector and increases absorption of light by the blue dye solution. Therefore, if the SHIO is applied to the back of the retina, it is expected to complement the night vision of a human.
Fig. S1. Effect of UV light on silk polymorphism. (A) ATR-FTIR microscopy spectra of amorphous and UV-cross-linked silk films. All silk films showed a dominant absorbance at 1,641 cm\(^{-1}\), indicating the presence of the amorphous protein. The spectrum of the UV-exposed silk film had an additional absorbance peak at 1,607 cm\(^{-1}\), consistent with the \([2\pi + 2\pi]\) cycloaddition of stilbene. (B) Photoluminescence spectra of amorphous and UV-cross-linked silk films. As exposure time is increased, the intensity of fluorescence decreases, consistent with the trans-cis isomerization of stilbene. (C) Normalized photoluminescence spectra. Whereas the spectra showed an overall decrease in intensity, the peak at 415 nm (dityrosine) increased relatively.

Fig. S2. Stress versus strain curves for the SHIO and the silk hydrogel bulk films. Weights were hanged on one side of the samples and strained lengths were observed. The SHIO and the silk hydrogel bulk films exposed to UV radiation for 2 and 4 h were named SHIO_2h, Bulk_2h, and Bulk_4h, respectively.

Fig. S3. Optical responses of the SHIO to strain. (A) Reflection spectra showing the blue shift. The optical response of the SHIO significantly weakened at the higher strain than the elastic deformation range (>10%). (B) Positions of the reflection peak wavelength.
**Fig. S4.** Photograph showing a deflection of a laser beam at the silk–air interface. By measuring the angles of incidence and refraction, the RI of the silk hydrogel film (represented by the shaded rectangular region) can be obtained.

**Fig. S5.** FDTD simulations of reflectance spectra of SHIO. The lattice constants of the SHIO structure were altered (A) in the lateral x direction, and (B) in the vertical z direction. (Inset) Calculated peak wavelength in function of the strain. A and B (Right) are schematic displays of the SHIO models for strain investigation.
Fig. S6. Absorption spectrum of the aqueous solution of the blue gardenia dye.

Fig. S7. (A) Photograph showing light propagation through the contact lens. The yellow dotted arrow indicates the beam path in the curved waveguide. (B) Measured spectra of the propagated light through the contact lens with (red line) and without (blue line) the SHIO. (Inset) Photograph of the SHIO structure placed on the contact lens.
Fig. S8. Diagram of a human eye and a cat eye. Incoming light is reflected by the tapetum lucidum of the cat and then reabsorbed by the retina, enhancing visibility.

Fig. S9. Enzymatic degradation of water-insoluble silk hydrogel films prepared by UV cross-linking. The silk hydrogel films were exposed to protease XIV solution. \( n = 5 \).

Fig. S10. Images of silk hydrogel films exposed to protease XIV solution for (A) 0, (B) 8, and (C) 29 h. The transparency of the silk hydrogel was maintained during degradation.
Table S1. Tensile stress, yield stress, elastic modulus, and elastic range of the SHIO and the silk hydrogel bulk films

<table>
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<th>Sample type</th>
<th>Tensile stress, N/mm²</th>
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<th>Elastic modulus, N/mm²</th>
<th>Elastic range, %</th>
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