Supplementary information

Tunable thermal diffusivity of silk protein assemblies based on their control of structures and photo-induced chemical cross-linking

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Materials. All other reagents were purchased from Nacalai Tesque. Ultrapure water with a resistivity of more than 18.2 MΩ·cm was supplied by a Milli-Q system (Merck Millipore) and was used for all experiments.

Silk fibroin (SF) sample preparation Degummed B. mori silk fibers and films were prepared by a procedure described previously.[1] Silk cocoons were first cut into pieces, boiled in 0.02 M Na2CO3 for 30 min and washed with ultrapure water to remove sericin. Degummed fibers were obtained after drying. To prepare the silk film, the dried silk fibers were dissolved in a 9.3 M LiBr solution at 60 °C for 4 h. Then the silk solution was dialyzed against water, which was followed by casting on a plastic Petri dish. After drying, a silk film was obtained. The silk film was further immersed into a mixed solution of methanol and ultrapure water (1/1, vol). The immersed film was subsequent stretching with different elongation rations (10%, 20%, and 30%) using a manual uniaxial stretching machine, and dried in an ambient atmosphere, or subsequent irradiation of UV light (365 nm, HLK-3AAA-1w-365nm, HOLKIN) as necessary.

Polarized optical microscopy (POM) observation SF films were mounted onto the stage of a polarized optical microscope (Eclipse LV100ND, Nikon). Then, the samples were observed at ambient temperature. Images with a sample rotation of 45° were recorded to identify the oriented structures.

Attenuated total reflection/Fourier transform infrared (ATR/FT-IR) absorption spectroscopy To record the ATR/FT-IR spectra of the emulsions, the SF films were deposited on a gold substrate several times and dried under vacuum conditions. The IR absorption spectra of the samples were measured using a JASCO FT/IR-4100 spectrometer with a cumulative number of 100 and a resolution of 2.0 cm^{-1} under ambient conditions.

Thermal diffusivity measurements Thermal diffusivity of the SF films in the thickness direction was measured using an ai-Phase mobile 1u system (ai-Phase Co. Ltd. Tokyo, Japan) based on temperature wave analysis methods.[2] The thermal diffusivity (α) of a film with a thickness of *d* was calculated from the relationship of the square root of the angular frequency (√ω) and the phase delay (Δθ) of the temperature wave as shown in the following equation:

$$\Delta\theta = -\sqrt{\frac{\omega}{2\alpha}}d - \frac{\pi}{4}$$

Fluorescence spectroscopy measurements. The SF films were recolonized in 1,1,1,3,3,3-hexafluoro-2-propanol. The fluorescence spectra of the solution exited at 275 nm were recorded with a fluorescence spectrophotometer (FP-6500, Jasco).

Absorbance measurements. The spectra of SF films were recorded with an ultraviolet-visible spectrophotometer (V-760, Jasco). The spectra were normalized at 360 nm.

Scanning electron microscopy (SEM) observation M13 phage membranes were dry for 1 day in a dried chamber. The samples were mounted on substrates using carbon tape and then coated with osmium. The surface of the membrane was observed by field-emission scanning electron microscopy (JSM-500F, JEOL) at an accelerating voltage of 3 kV.

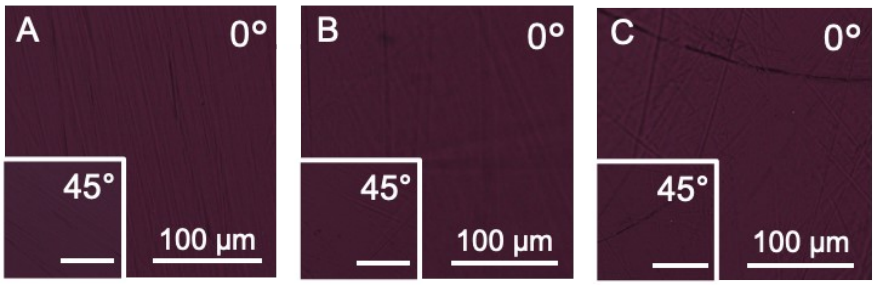

Fig. S1 Polarized optical microscopy (POM) image of the SF films at the (A) periphery, (B) midpoint, and (C) center.

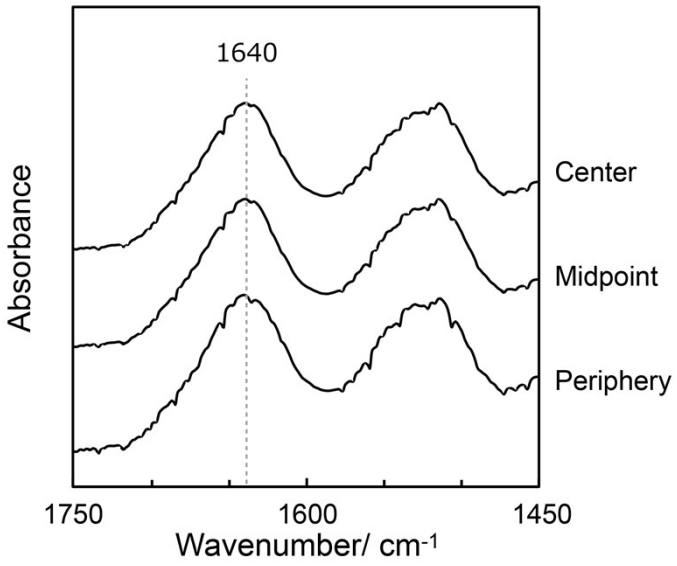

Fig. S2 Attenuated total reflection Fourier transform infrared (ATR/FT-IR) spectroscopy of the SF films at the various position.

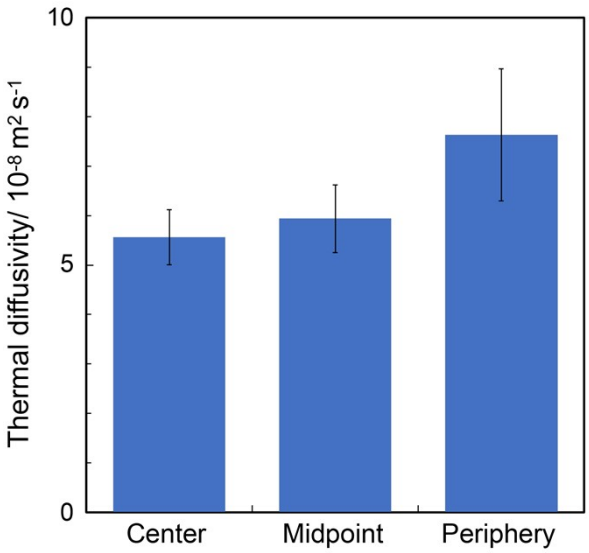

Fig. S3 Comparison of the thermal diffusivity values of the original SF film at the center, midpoint, and periphery.

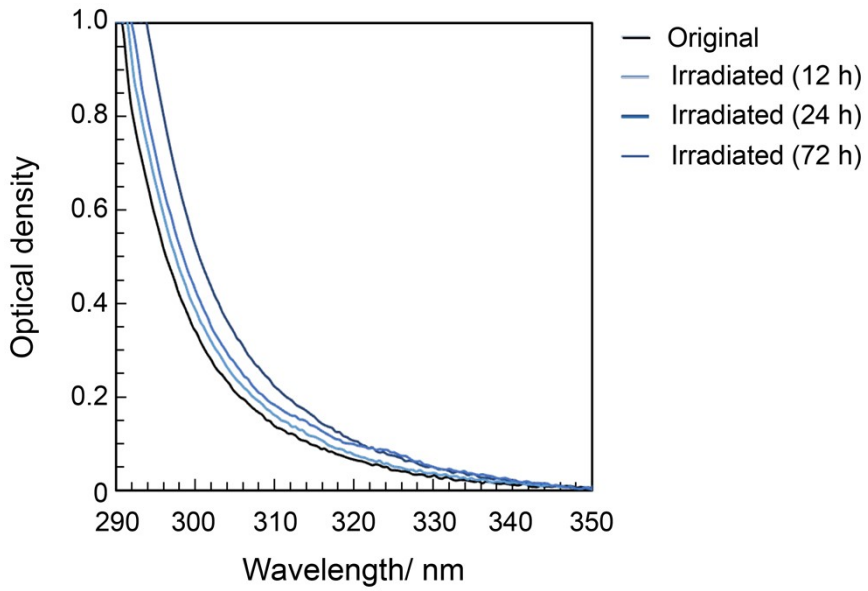

Fig. S4 Absorbance spectra of the original and irradiated SF films.

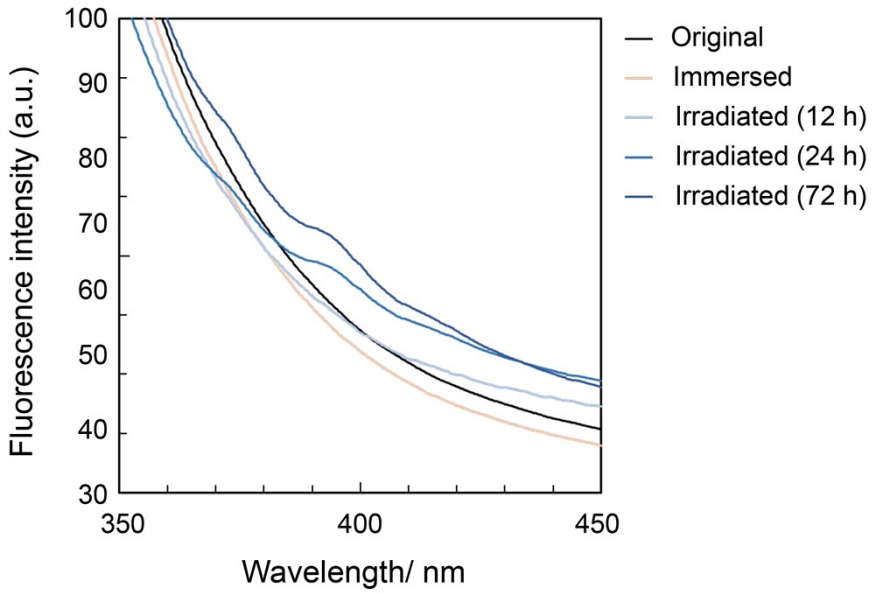

Fig. S5 Fluorescence spectra of the resolubilized original, immersed, and irradiated SF films in 1,1,1,3,3,3-hexafluoro-2-propanol.

References

1. D. N. Rockwood, R. C. Preda, T. Yucel, X. Q. Wang, M. L. Lovett and D. L. Kaplan, *Nat. Protoc.*, 2011, **6**, 1612-1631.
2. J. Morikawa and T. Hashimoto, *J. Appl. Phys.*, 2009, **105**, 113506.