Supporting Information

Rapid fabrication of silk films with controlled architectures via electrogelation

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Experimental procedures

Preparation of silk fibroin solution

Regenerated silk fibroin (RSF) solution was produced through slight modifications to the standard process [1, 15, 32]. Degumming time within a 0.02 M sodium carbonate solution was limited to a 10 minute boil, shorter than in preceding papers discussing the e-gel process, to minimize fibroin protein degradation [1, 2]. Correspondingly, fibroin was solubilized in 9.3M lithium bromide for 16 hours in a 60˚C oven to allow for more complete unfolding of the comparatively longer fibroin chains. The chaotropic salt was subsequently removed through dialysis (3.5 kDa MWCO) against Milli-Q water for a

total of 72 hours, yielding an 8% (w/v) silk solution. The resulting liquid was then purified by centrifugation at 8,800 rpm over two 25-minute long periods, with the temperature held constant at 4˚C.

Analysis of e-gel formation

To examine the temporospatial evolution of pH gradients within silk solution exposed to DC current, 5 μL of methyl red indicator dye (Riedel-de-Haën) was added to 2 mL of silk solution. Methyl red is an azo dye that appears red below pH 4.4 and yellow above pH 6.2. The initial RSF pH, measured by short-range pH paper (Micro Essential Lab, Hydrion) was 6.5. Gold-plated rods, 0.6 mm in diameter, were used as electrodes at a separation distance of 5 mm. Video was recorded for 10 minutes at 10V, constant voltage (Mastech, HY3005D-3 DC).

Formation of silk films via electrogelation

Ring-shaped electrodes were produced from a selection of gold (0.2 mm diameter) and gold-plated (0.6, 0.8 and 1.0 mm diameter) wires (Alfa Aesar and Paramount Wire Company). To assure reproducibility, each anode was created by hand by twisting the wire around rigid plastic cylinders of known diameter, ranging from 7 to 20 mm. Meanwhile, the cathode remained a straight segment of gold wire. For film fabrication, 2 mL of silk solution were deposited into polystyrene tubes prior to introduction of the ring anode and straight cathode. Current was delivered to the solution through a power supply at 5, 10 or 25V, constant voltage, for durations between 0.5-10 minutes. The positive electrode, circumscribing a silk film, was subsequently removed and allowed to air dry. Changes in silk concentration between the e-gel film and the surrounding solution were

measured by comparing the wet and dry masses of samples collected following electrical stimulation. Gels were dried at 22°C and RH= 40%.

Silk fibroin films characterization

Films were studied using a host of analytical tools. SEM (Carl Zeiss, Ultra55) images were collected, after sputter coating (Cressington, 208HR**)** with a Pt/Pd target, using both InLens and secondary backscatter detectors. AFM (Veeco, Nanoscope III) images were recorded in air using Research Nanoscope software version 7.30 (Veeco). A 225 mm long silicon cantilever with a spring constant of 3 N/m was used in tapping mode. Optical transmission was measured in software (Ocean Optics, SpectraSuite) using a tungsten-halogen light source (Ocean Optics, LS1) and a visible-range spectrometer (Ocean Optics, USB2000) Refractive index was determined using a commercial refractometer (Metricon, 2010 M prism coupler). Raman spectra were collected using a JASCO NRS 3100 laser Raman spectrophotometer (JASCO, Tokyo, Japan). Samples were mounted on a glass microscope slide and excited at 784 nm with a laser focused using a 100x objective. Spectra were obtained by measuring from 1800 cm^{-1} to 200 cm^{-1} using a resolution of 0.5 cm^{-1}, and 5 accumulations per sample with an exposure time of 20 s. FTIR spectra (Jasco, Tokyo, Japan) were collected with a single reflection ATR module (MIRacle, Pike technologies, USA) using a diamond coated ZnSe crystal. A resolution of 4 cm^{-1} and 64 scans per sample were used in the 4000-650 cm^{-1} IR range.