Supplementary materials

Influence of Film Thickness on the Surface Structure and Mineralization-Templating of Silk Fibroin

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Experimental Section

Aqueous solutions of silk fibroin were obtained through dissolving degummed *Bombyx mori* silk fibers (SF) with 9.5 M LiBr solution, followed by dialysis against deionized water for 8 days. The concentration of the obtained SF solution was about 4 wt%. 28 wt% SF solution was prepared by vacuum concentration, according to the established method (China Patent No. ZL 20111000201.8).

150 nm SC films and 1 μm SC films were prepared by spin-coating 4 wt% and 28 wt% concentration SF solution on hydrophilic silicon wafer respectively, which were further immersed in methanol for 15 min to induce the β-sheet crystal formation. The spin coating was maintained at 500 rpm for 18s and then 3000 rpm for 60s. Thickness of the films was tested by Veeco Dektak, peaking 10 points on different areas of the film. The thickness of 4 wt% SF spin-coated film was 150 nm-180 nm, while 28 wt% SF spin-coated film was 900 nm-1000 nm, which was the maximum thickness obtainable using spin-coating.

For films thicker than 1 μm, CC films were cast on a PS dish with different concentration SF. After evaporation of solvent, 1 μm CC film was rinsed in methanol for 15 min, while 10 μm and 250 μm films were rinsed in methanol for 1 day to induce a conformation transition thoroughly.

250 μm CC was treated with 5 M aqueous LiBr solution at room temperature for 10 min and then thoroughly washed with DIW to remove the salt. On the other side, 250 μm CC were treated with 10 U/ mL aqueous chymotrypsin solution at 37 °C for 12 h and then thoroughly washed with DIW.

SF film with oriented molecular chains was produced on an electric heating plate at 60 °C. 1 wt% SF solution was dipped on a silicon wafer. Then we dragged the solution with a blade to form a film. The thickness of this film was about 80 nm. The film was then immersed in methanol for 15 min.

Mineralization was conducted in a 10 mL beaker containing a mixture solution of an appropriate amount of silk fibroin solution (1 wt%) and $[Ca^{2+}]$ (20 mmol/L) via the CO_2 vapor diffusion method (modified from a classical procedure) at room temperature (around 25 °C). Different films were inverted and placed into the above beaker, which were covered by parafilm with six pinholes and then transferred into a large closed desiccator (about 6.5 L). 3 g of crushed ammonium carbonate in another small beaker covered with parafilm with 6 pinholes was placed

into the desiccator for releasing CO_2. After mineralization for 3 days, the films with deposits were rinsed by DIW and dried in vacuum overnight for further characterization.
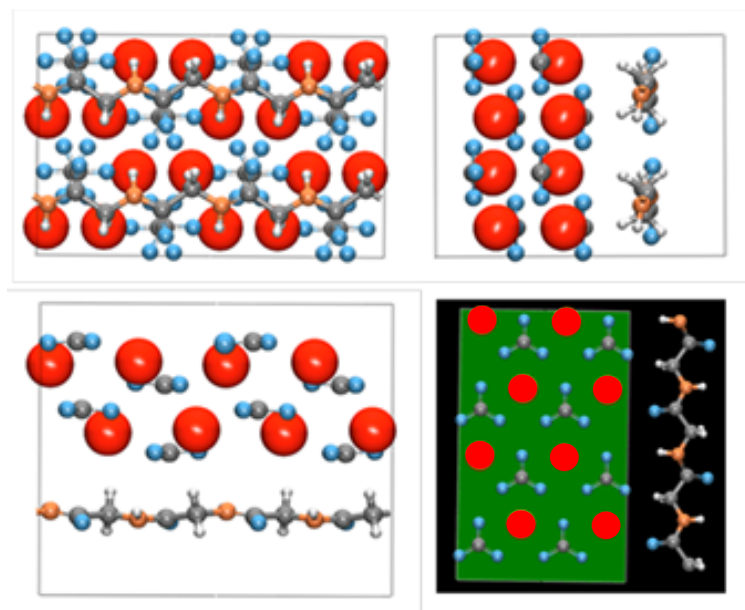
Supplementary Figure S1 Modeling of the matching of silk β-strand and the aragonite (010) face (white background). The three views are from different directions relative to the (010) face, top left. Red=calcium; blue=oxygen; yellow= nitrogen; grey= carbon; white= hydrogen. The simplified structures (black background) show the good match between periodic interatomic distances between complementary charged pairs: -NH- pairs with carbonate and -CO- pairs with Ca. Note that the silk configuration is for simple extended chain β-strand, rather than the slightly less linear β-sheet form. Cited from (T. Wang, D. Porter and Z. Z. Shao, Adv. Funct. Mater., 2012, 22, 435-441.).
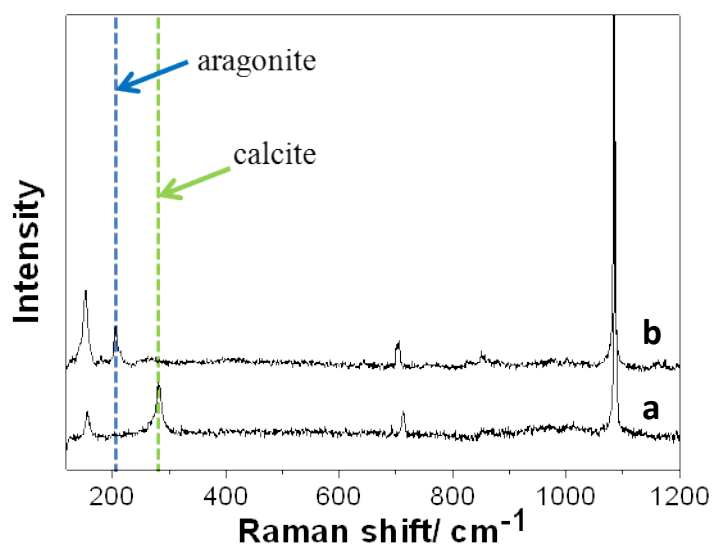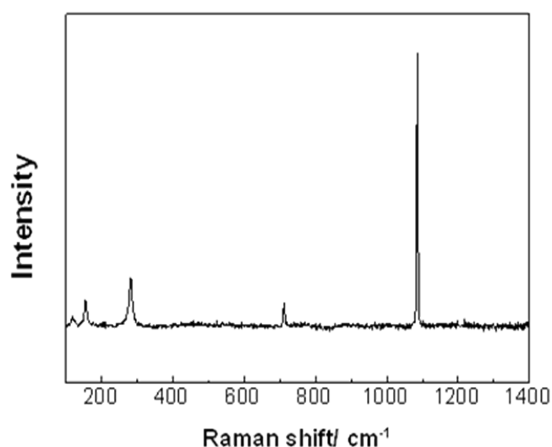
Supplementary Figure S2 Raman spectra of (a) calcite particles and (b) aragonite planets grew on the spin-coated and cast-coated silk films. Green dashed line represents the characteristic peak of calcite, while blue dashed line represents the characteristic peak of aragonite.
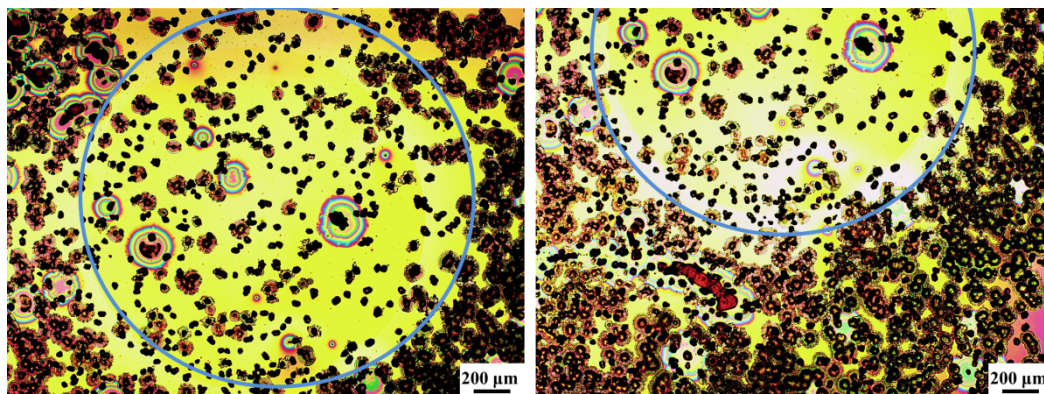

Supplementary Figure S3 The light microscope images of 150 nm SC locally treated by a drop of water. The blue arcs represent the edge of the water treated area.

Supplementary Table S1 Chemical composition of different SF film surfaces calculated from XPS scan spectra

| Surface	Atomic concentration (%)			Atomic ratios	
	C 1 s	O 1 s	N 1 s	N/C	O/C
150 nm SC	63.42	20.51	16.07	0.253	0.323
150 nm SCw	58.17	23.72	9.47	0.162	0.408
250 μm CC	76.78	17.87	1.02	0.013	0.233

Supplementary Figure S4 Raman spectra of calcite particles deposited on the SF film treated by LiBr. Green dashed lines represent the characteristic peaks of calcite.
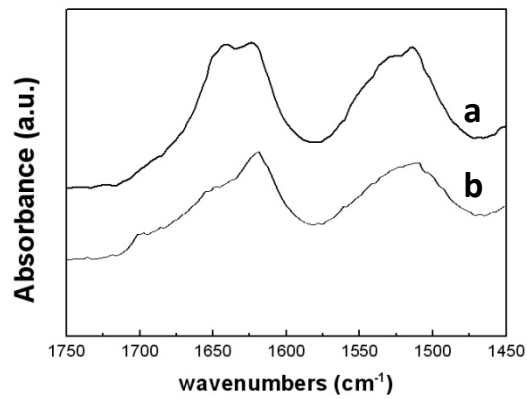
Supplementary Figure S5 ATR spectra of 250 μm CC (a) before and (b) after treated by 10 U/ mL chymotrypsin for 12 h.
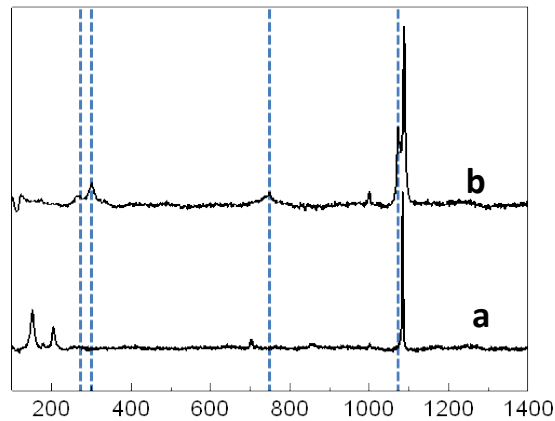

Supplementary Figure S6 Raman spectra of (a) calcite particles and (b) vaterite on the SF film treated by chymotrypsin. Blue dashed lines represent the characteristic peaks of vaterite.
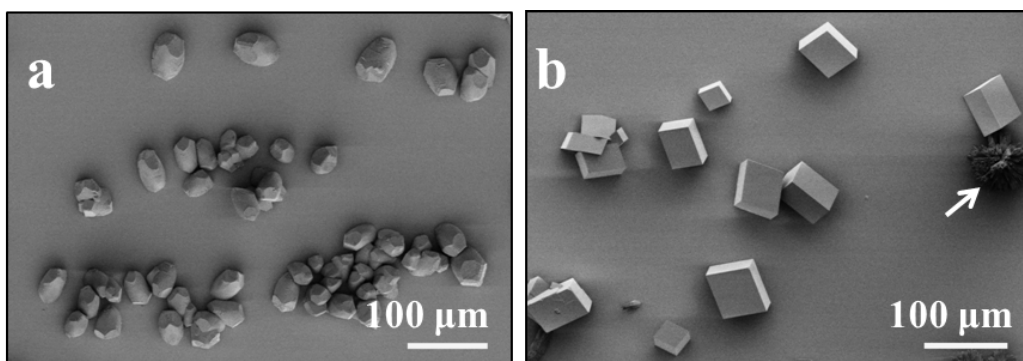

Supplementary Figure S7 SEM images of (a) decorated calcite particles deposited directly on the Si substrate. The mineralization is with the presence of silk fibroin solution. (b) a lot rhombus calcite and less aragonite (pointed by the white arrow) deposited on the 150 nm SC without the presence of silk fibroin solution.
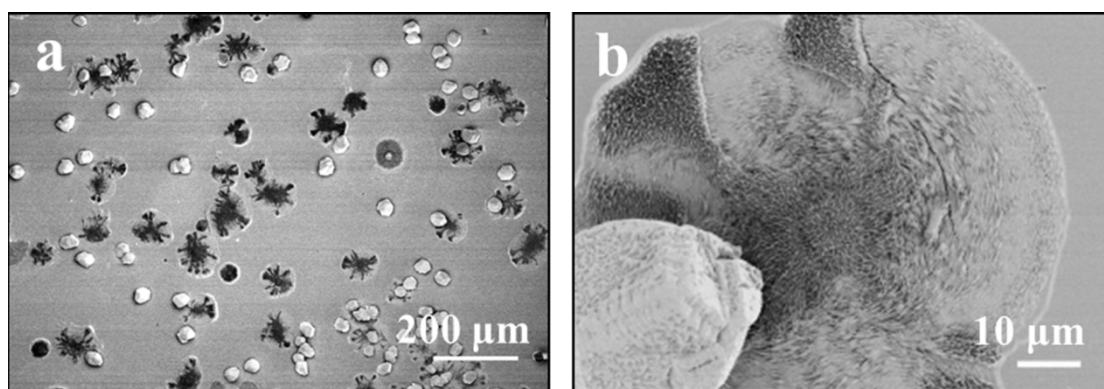
Supplementary Figure S8 SEM images of aragonite and calcite growing on the 200 nm cast coating SF on silicon with some calcite deposited on the film surface.
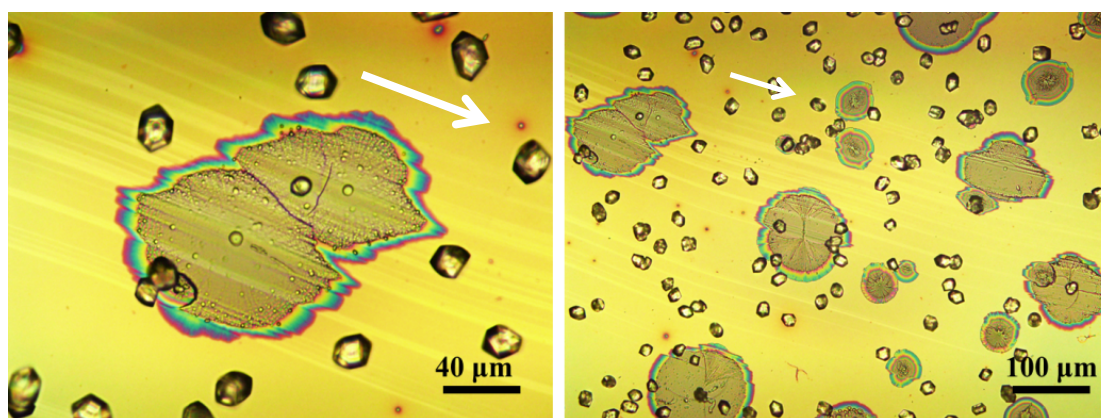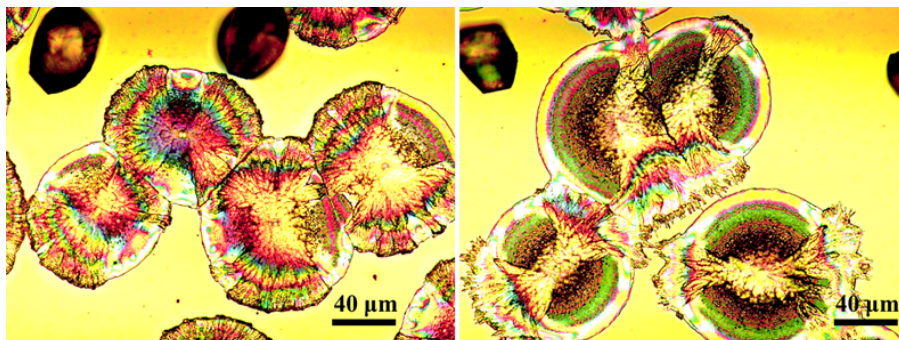

Supplementary Figure S9 Light Microscope images of aragonite and calcite grew on the silk fibroin film with oriented molecular chains in the presence of silk fibroin solution. Arrows present the longitudinal axis of the film in the direction of the blade movement.
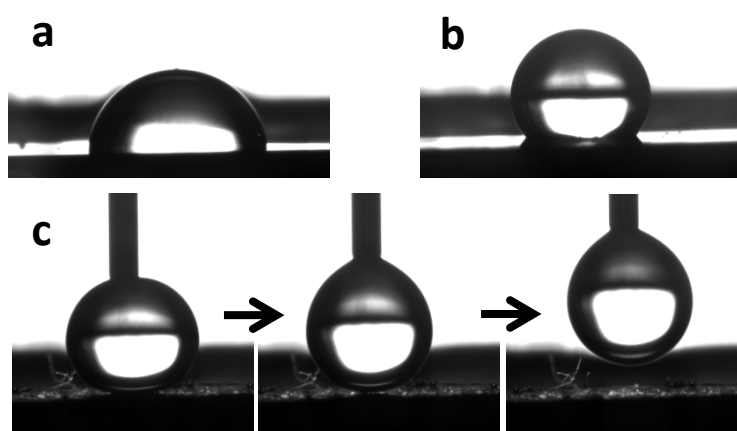
Supplementary Figure S10 The profile of oil droplets (5 μL, 1,2-dichloroethane) underwater on (a) Si substrate, (b) silk fibroin film and (c) aragonite layer. The contact angle of (a) and (b) is

80±2°and 125±5°respectively. Oil does not adhere on the surface of aragonite in (c), indicating that the aragonite surface is superoleophobic underwater.

Supplementary Figure S11 Light Microscope images of aragonite and calcite grew on the silk fibroin film in the presence of silk fibroin solution.