

Supporting Information

Silk Fibroin-Mediated Biomineralization of Calcium Carbonate at the Air/Water Interface

Wei Hao,^a David Porter,^b Xianting Wang^a and Zhengzhong Shao^{*a}

^a State Key Laboratory of Molecular Engineering of Polymers, Advanced Materials Laboratory, Department of Macromolecular Science, Fudan University, Shanghai, 200433, People's Republic of China. E-mail: zzshao@fudan.edu.cn

^b Department of Zoology, University of Oxford, South Parks Road, Oxford OX1 3PS, UK.

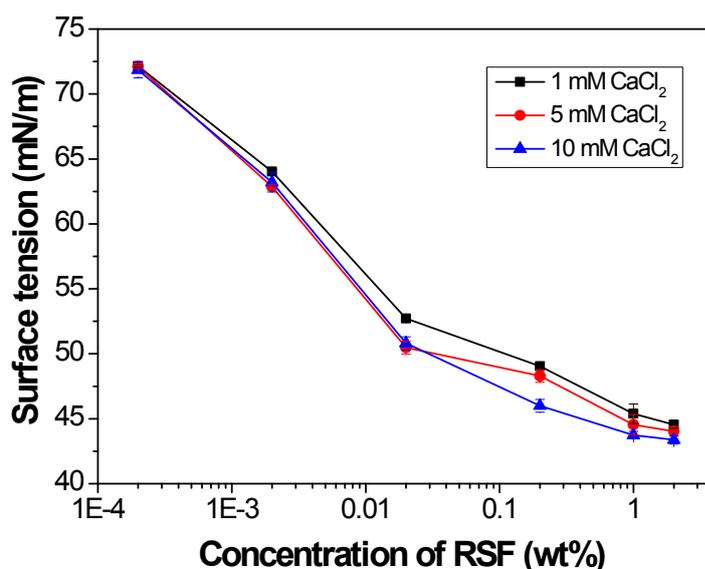


Figure S1 Surface tension of the RSF-83 in the mineralization solution measured by Wilhelmy Plate method (Dataphysics DCAT 21). The platinum plate is pre-cleaned by flame treatment. The RSF solution is placed in a clean glass vessel. The presented data are average of 3 measurements.

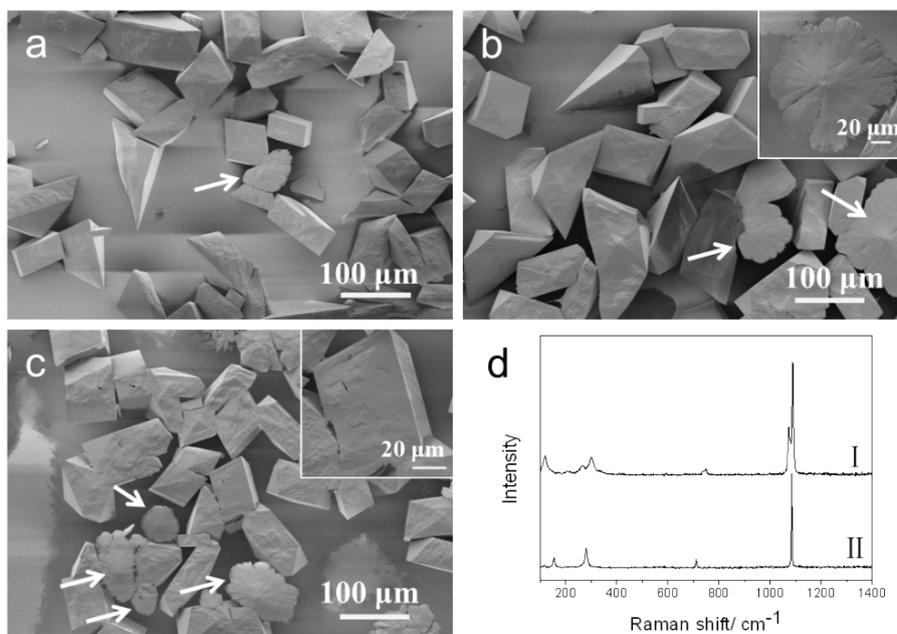


Figure S2 FE-SEM images of CaCO_3 particles obtained at the air/water interface without any additive (control experiment). (a) $[\text{Ca}^{2+}] = 1 \text{ mmol/L}$. (b) $[\text{Ca}^{2+}] = 5 \text{ mmol/L}$. (c) $[\text{Ca}^{2+}] = 10 \text{ mmol/L}$. Mineralization time: 72 h. The white arrows indicate vaterite particles. Insets in (b) and (c) show the vaterite particle and calcite particle, respectively. (d) Raman spectra of (I) vaterite and (II) calcite particles.

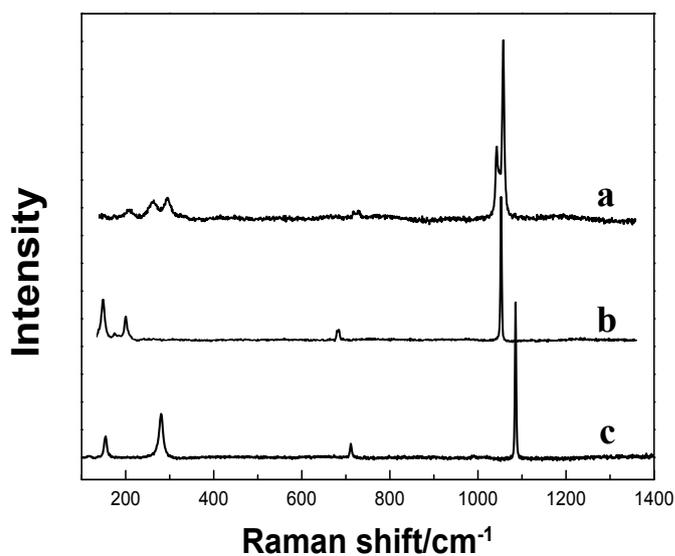


Figure S3 Raman spectra of (a) vaterite, (b) aragonite and (c) calcite collected at the air/water interface with different concentration of RSF-83 and Ca^{2+} .

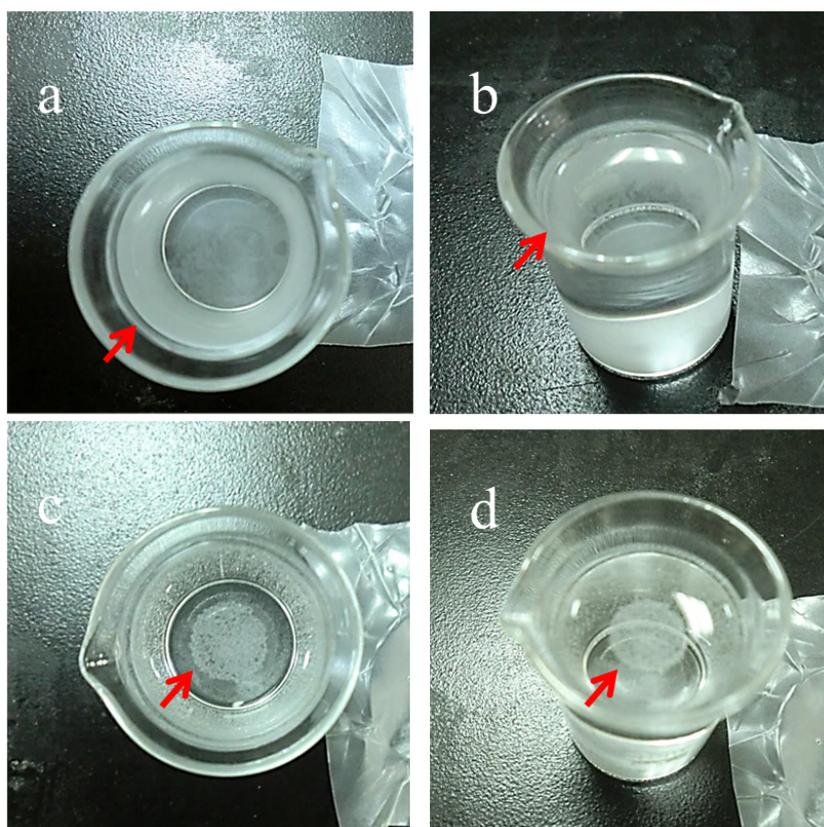


Figure S4 Film-like CaCO_3 layers (red arrow) formed at the air/solution interface with (a) and (b) $[\text{RSF-83}]=0.02$ wt%, (c) and (d) $[\text{RSF}]=0$ wt%. $[\text{Ca}^{2+}]= 10$ mmol/L. Mineralization time: 72 h.

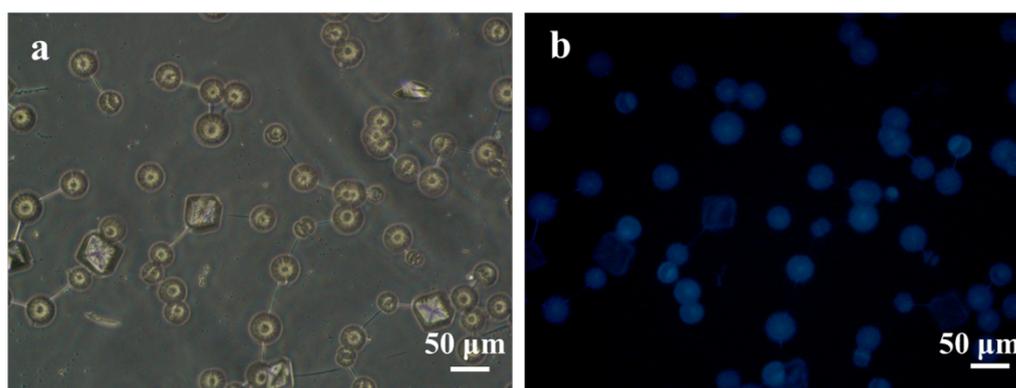


Figure S5 Confocal fluorescence microscope images of calcite particles obtained at the air/water interface without washing by DIW. $[\text{RSF-83}] = 0.1$ wt%, $[\text{Ca}^{2+}] = 5$ mM. (a) is bright field images, (b) is dark field images. Mineralization time: 72 h. The excitation wavelength: 405 nm. Blue: RSF.

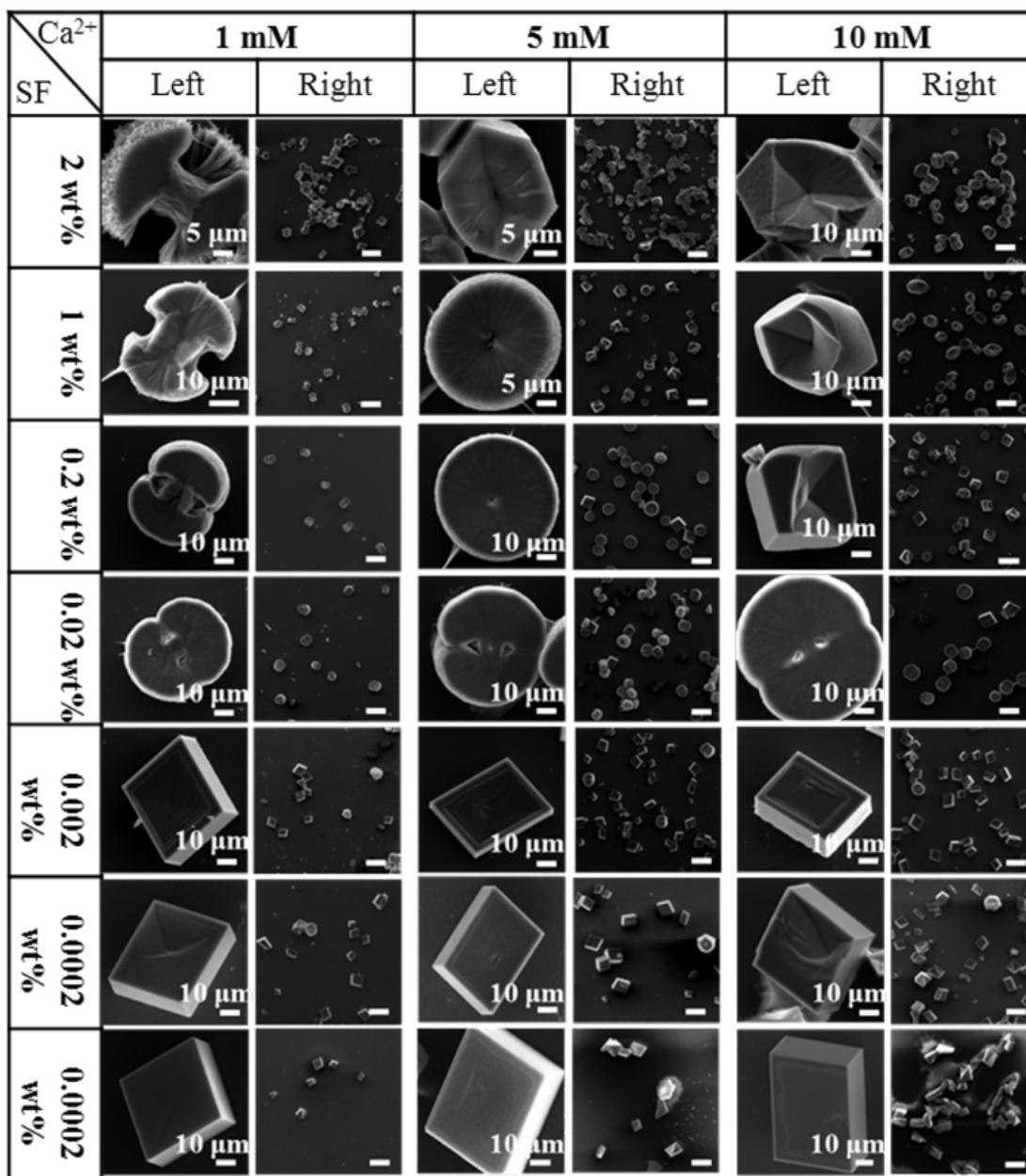


Figure S6 SEM images of calcium carbonate crystals collected at the air/water interface with different concentration of RSF-185 and Ca²⁺ (as noted in the figure). The microscope images are upper surface views. Left images are the enlarge images of the dominant crystal in the right images. Mineralization time: 72 h. Bars in right are 100 μm.

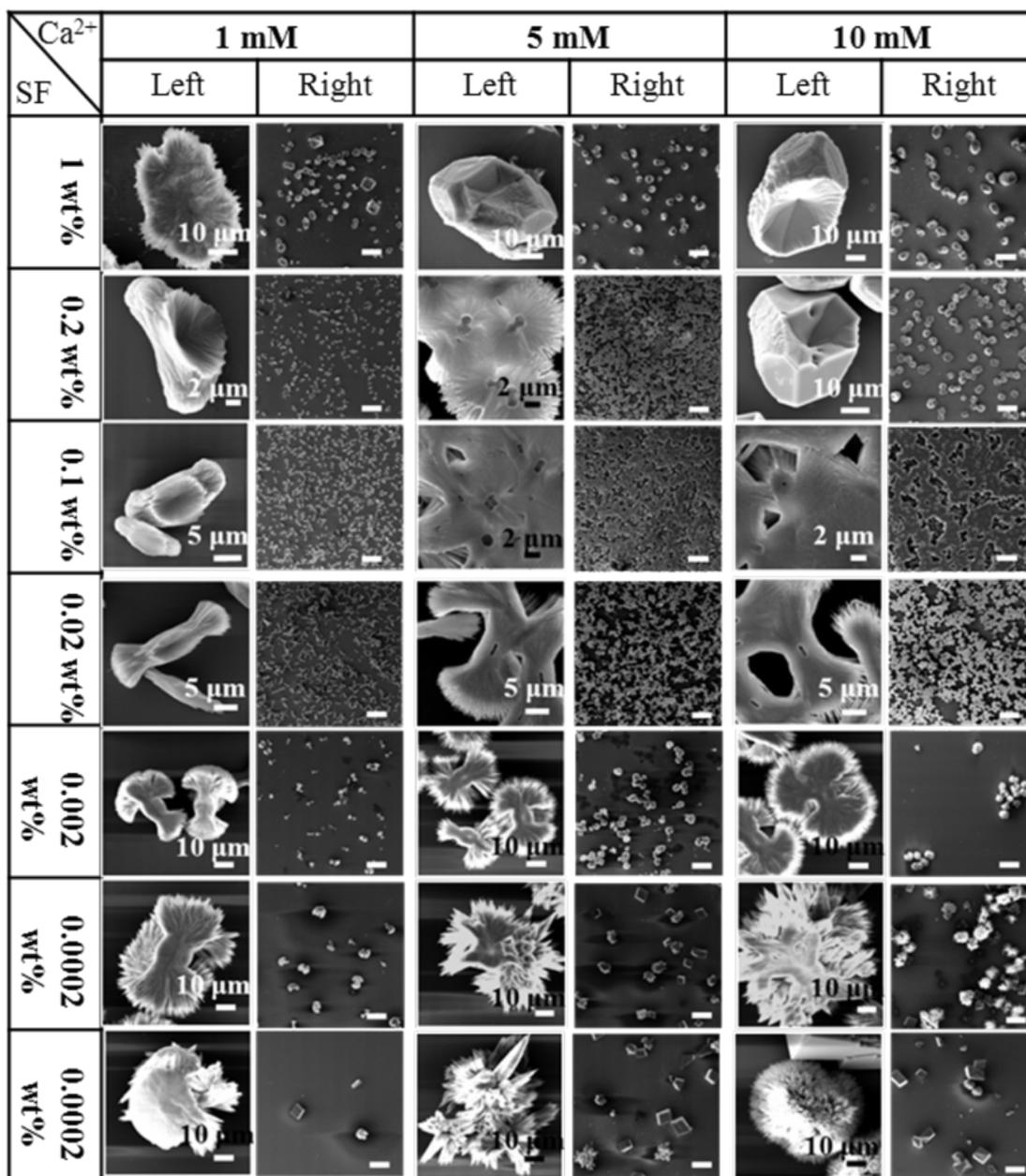


Figure S7 SEM images of calcium carbonate crystals collected at the air/water interface with different concentration of RSF-36 and Ca²⁺ (as noted in the figure). The microscope images are upper surface views. Left images are the enlarge images of the dominant crystal in the right images. Mineralization time: 72 h. Bars in right are 100 μm.