

Electronic Supplementary Information (ESI)

**Structure and properties of various hybrids fabricated by silk
nanofibrils and nanohydroxyapatite**

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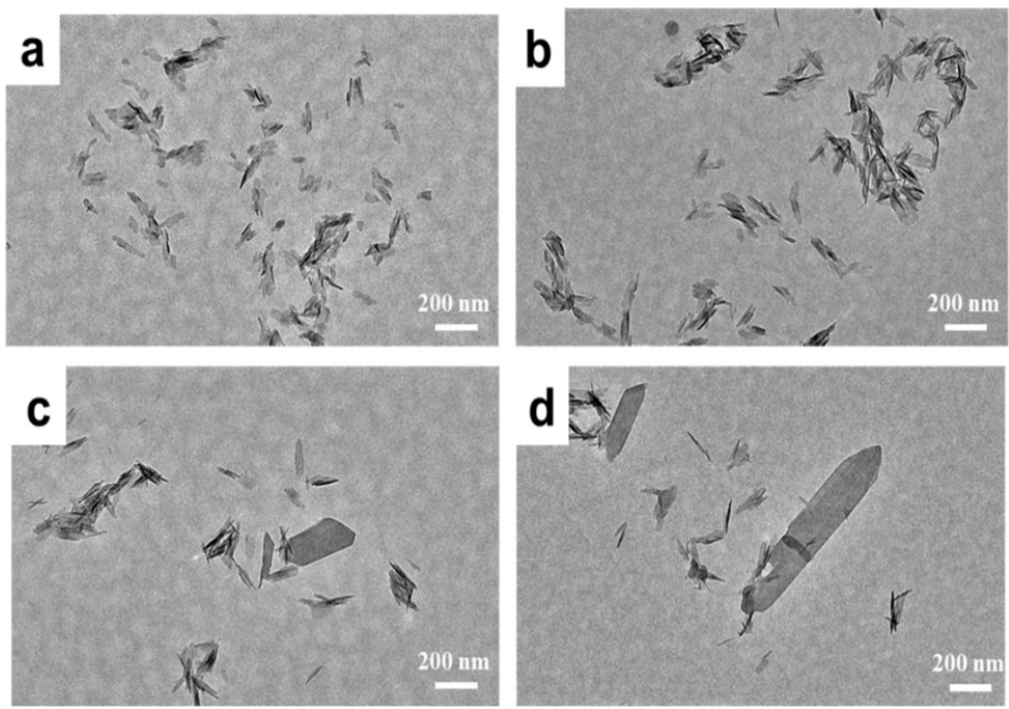


Fig. S1. TEM images of nanoHAP crystals prepared in the 0.15 wt% SF solution instead of SF nanofibrils. Mass ratio of HAP and SF: a 0.05; b 0.2; c 0.25; d 0.4.

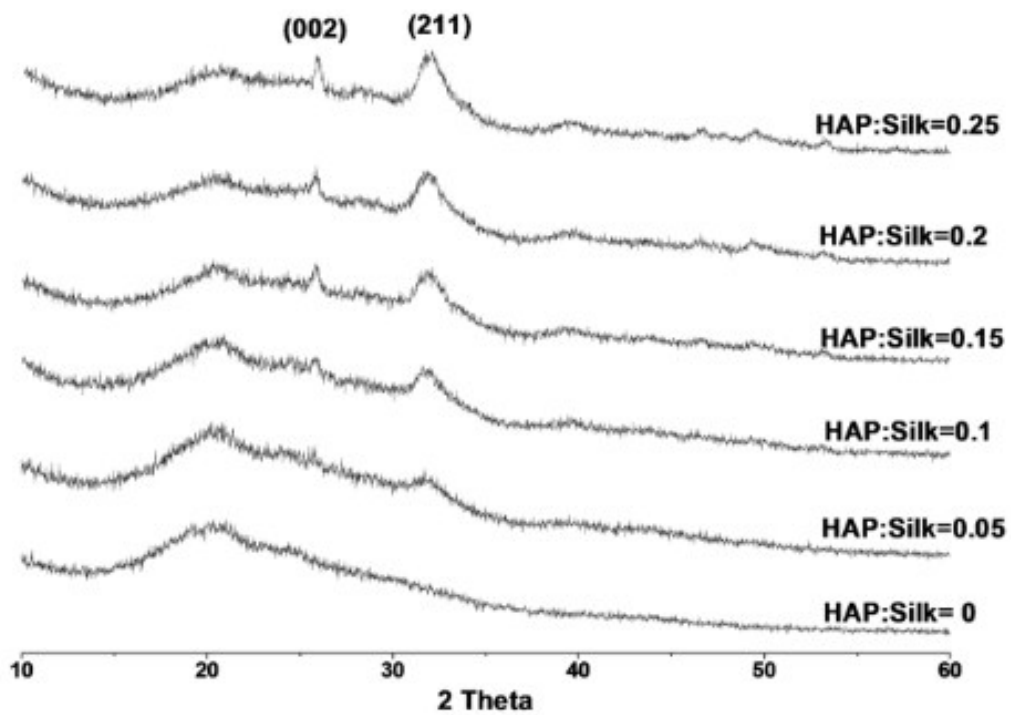


Fig. S2. XRD patterns of SF nanofibril/nanoHAP hybrid films. It should be noticed that the broad peak centered at about 20° was assigned to silk fibroin.

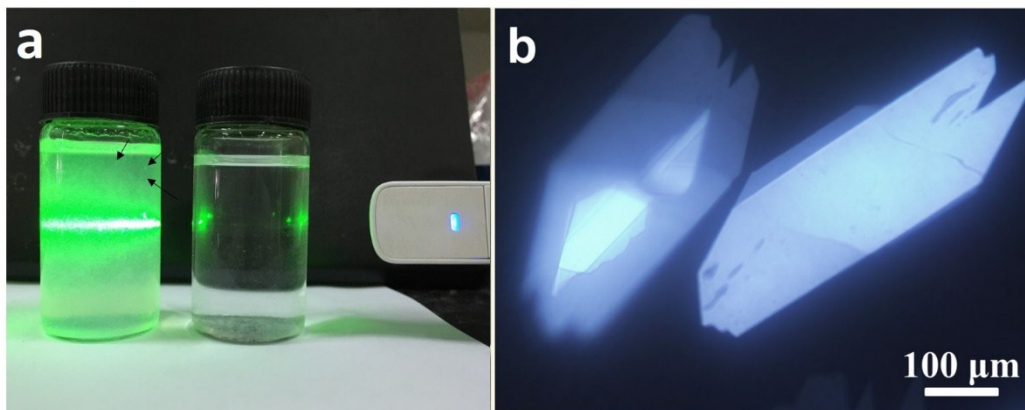


Fig. S3. (a) Images of the SF/HAP suspension after mineralization with SF nanofibril (left) and the SF/HAP solution after mineralization with the as-prepared Regenerated SF (right). Both samples were kept for more than 3 months. Light scattering could be observed in left bottle due to good dispersability of HAP in the suspension, and the HAP was eventually precipitated in the bottom of right bottle. (b) Polarized optical images of the typical produced hydroxyapatite.

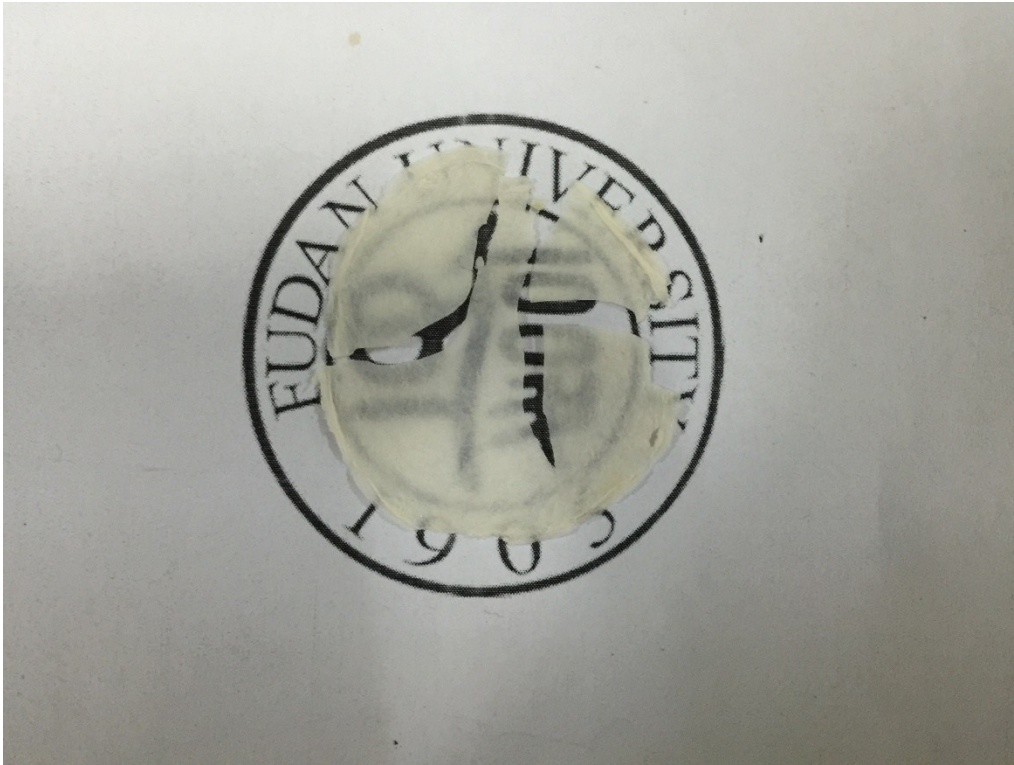


Fig. S4 Image of SF nanofibril/nanoHAP hybrid films (mass ratio of HAP and SF: 0.5) .

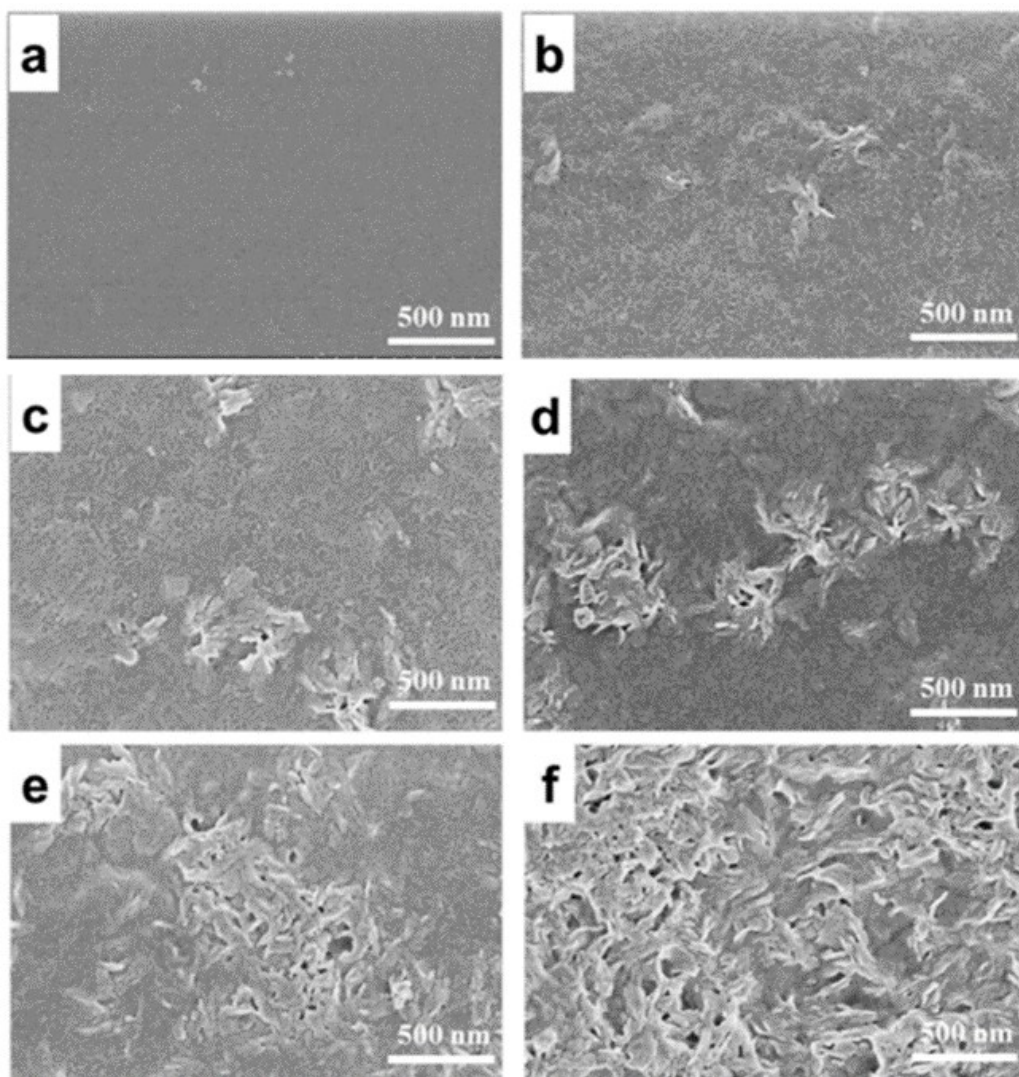


Fig. S5. Surface morphology of nanofibril/nanoHAP films with different theoretical contents of hydroxyapatite. Mass ratio of HAP and SF: a, 0; b, 0.05; c, 0.1; d, 0.15; e, 0.2; f, 0.25.

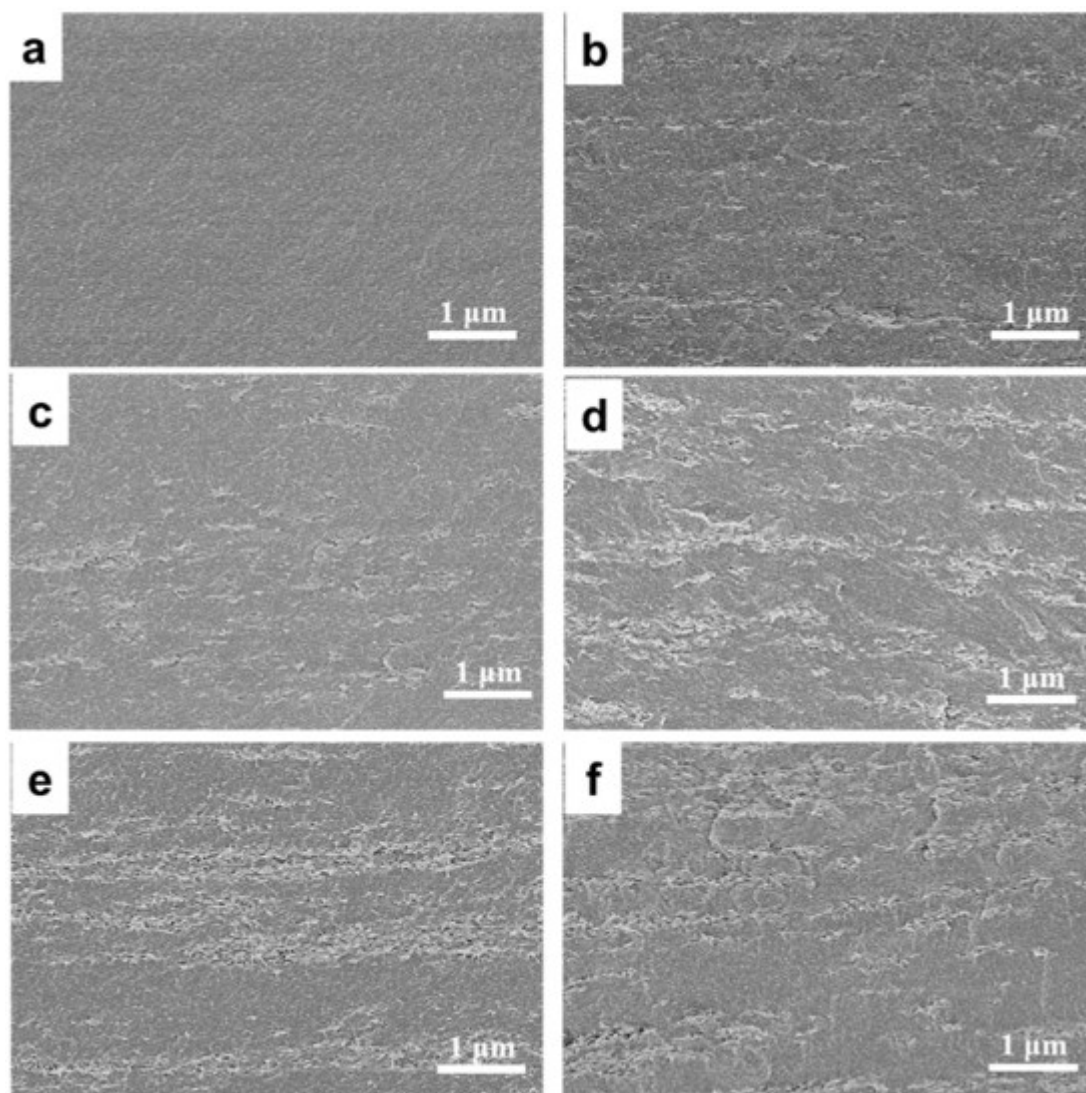


Fig. S6. Cross-section morphology of nanofibril/nanoHAP films with different theoretical contents of hydroxyapatite. Mass ratio HAP and SF: a, 0; b, 0.05; c, 0.1; d, 0.15; e, 0.2; f, 0.25.

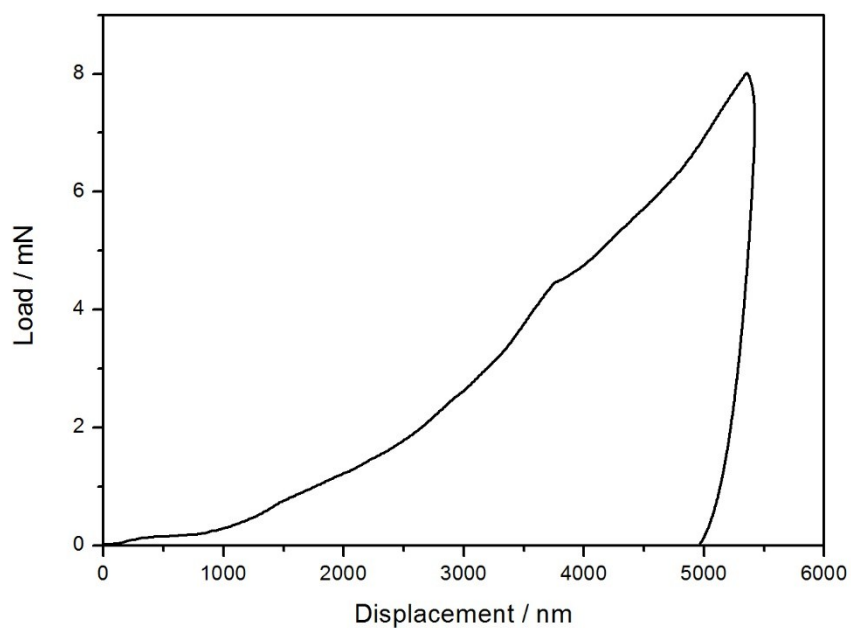


Fig. S7. Load–Displacement data from a nanoindentation test of nanofibril/nanoHAP films. Mass ratio of HAP and SF: 0.25. Elastic modulus = 8.9056 MPa

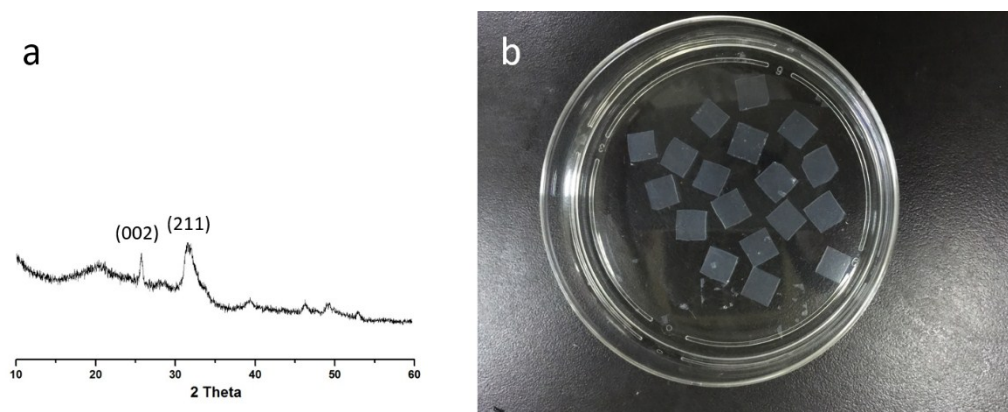


Fig. S8 (a) XRD patterns of the air-dried SF nanofibril/nanoHAP hybrid film after immersing in PBS for 14 days; (b) Images of the films after immersing in PBS for 14 days (pH=7.2, 37°C, mass ratio of HAP and SF:0.25) .

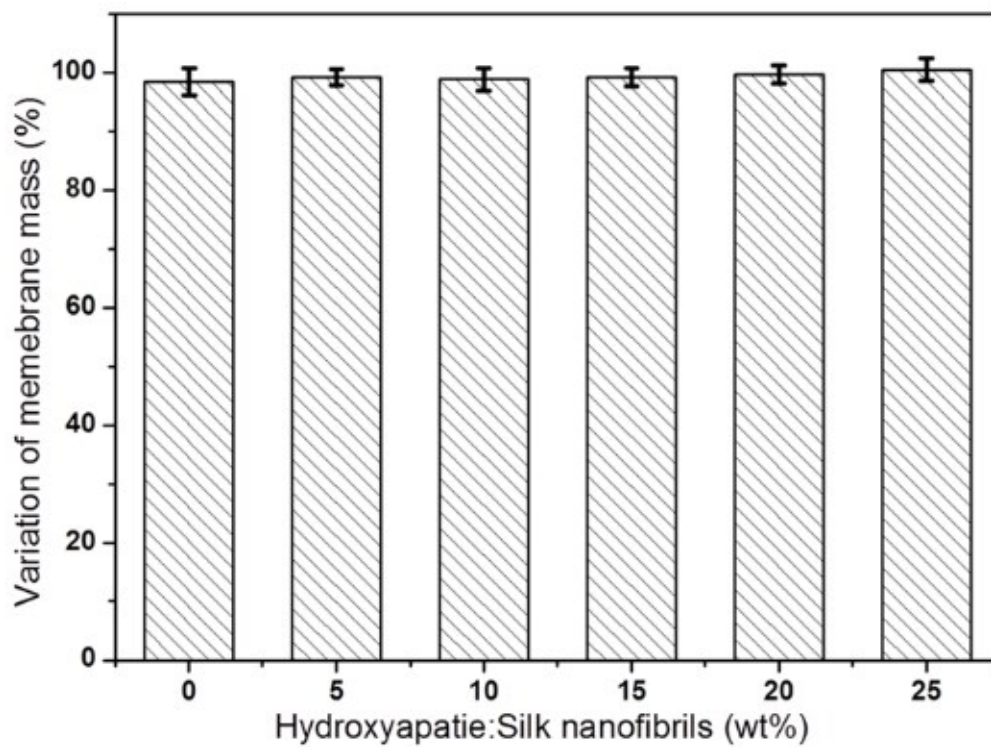


Fig. S9. The weight remaining ratio of the hybrid films with different compositions after the incubation in PBS (pH = 7.2, 37°C) for 7 days.

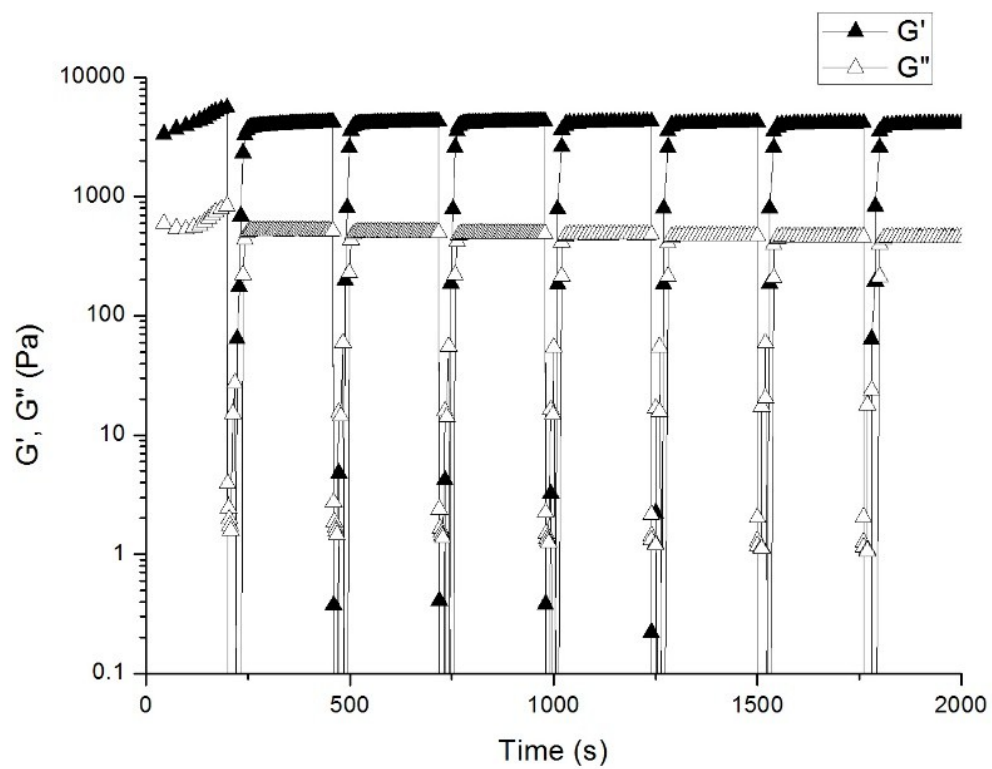


Fig. S10. Shear recovery test of SF nanofibril/nanoHAP hydrogel with 125 mmol L^{-1} NaCl at $37 \text{ }^\circ\text{C}$ after immersing in PBS for 7days.

Table S1. The solid content of SF nanofibril/nanoHAP hydrogels (mass ratio of nanoHAP and SF nanofibril = 0.05)

NaCl concentration (mmol L ⁻¹)	25	50	75	100	125
Solid content (wt%)	1.32±0.06	1.77±0.04	2.10±0.05	2.46±0.10	2.73±0.11

Table S2. The solid content of SF nanofibril/nanoHAP hydrogels after immersing in PBS for 7 days (pH=7.2, 37°C, NaCl 150mmol/L, mass ratio of nanoHAP and SF nanofibril = 0.05)

NaCl concentration (mmol L ⁻¹)	25	50	75	100	125
Solid content (wt%)	1.34±0.03	1.63±0.05	2.15±0.05	2.64±0.07	2.90±0.06