

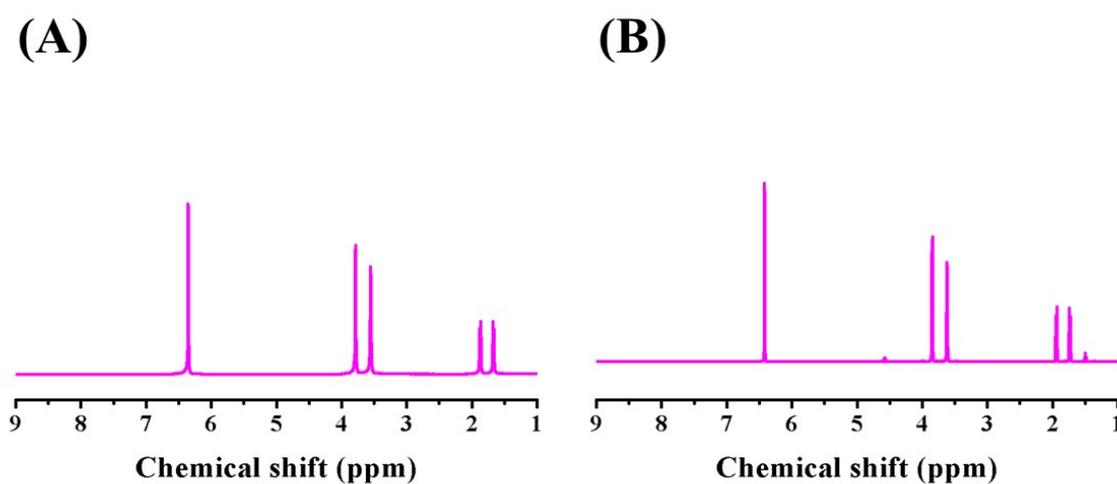
## Electronic Supplementary Information

### Preparing 3D-printable silk fibroin hydrogels with robustness by a two-step crosslinking method

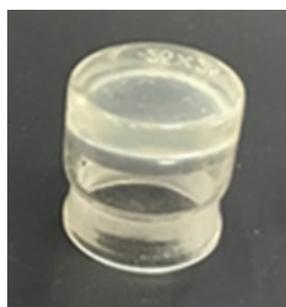
Dafei Gong<sup>a</sup>, Qinrui Lin<sup>b</sup>, Zhengzhong Shao<sup>b</sup>, Xin Chen<sup>b</sup>, Yuhong Yang<sup>a\*</sup>

<sup>a</sup> *Research Center for Analysis and Measurement, Fudan University, 220 Handan Road, Shanghai 200433, People's Republic of China*

<sup>b</sup> *Department of Macromolecular Science, Laboratory of Advanced Materials, Fudan University, 220 Handan Road, Shanghai, 200433, People's Republic of China*



**Figure S1.** (A) <sup>1</sup>H NMR spectrum of carbic anhydride. (B) <sup>1</sup>H NMR spectrum of carbic anhydride treated by trifluoroacetic acid for 14 d.



\* Corresponding authors: E-mail yuhongyang@fudan.edu.cn (Y.H.Y.)

Figure S2. Digital picture of 10 wt% chemically crosslinked RSF hydrogel.

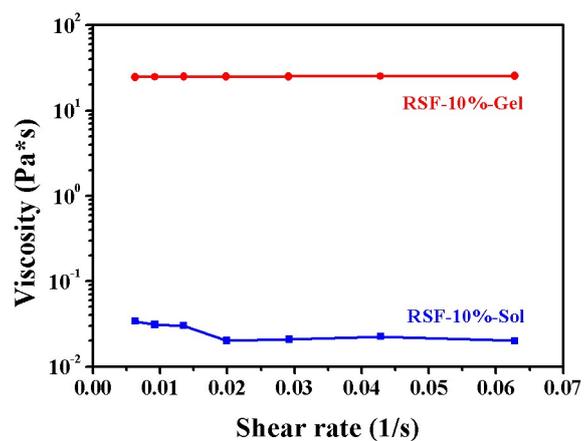


Figure S3. Viscosity of 10 wt% RSF-NB aqueous solution and 10 wt% chemically crosslinked RSF hydrogel.

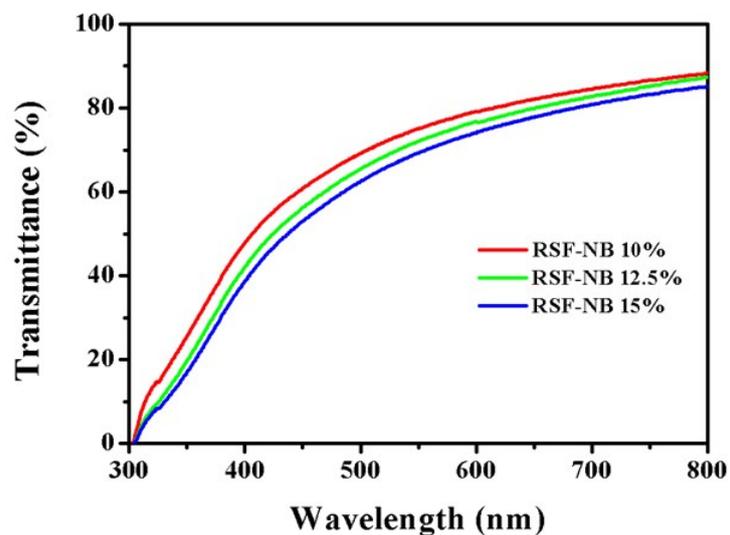
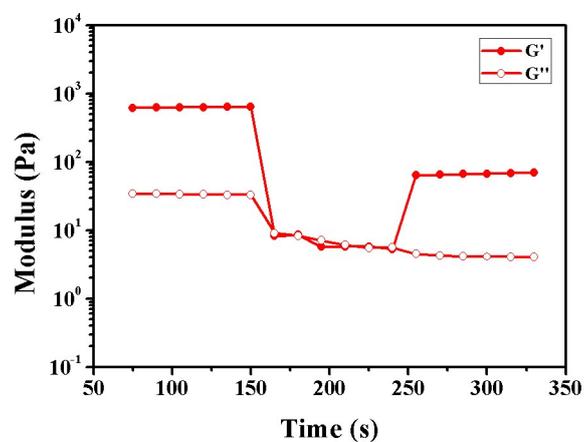
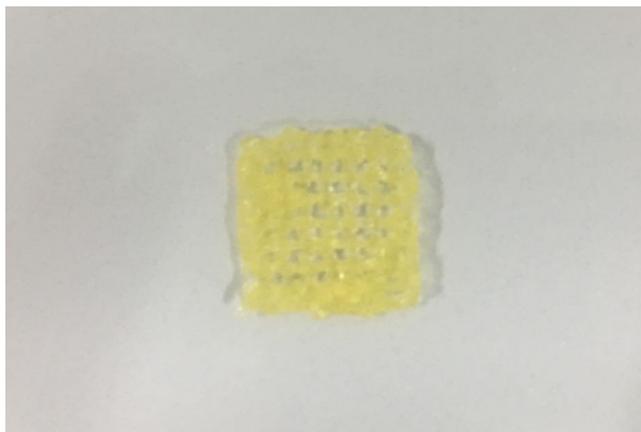


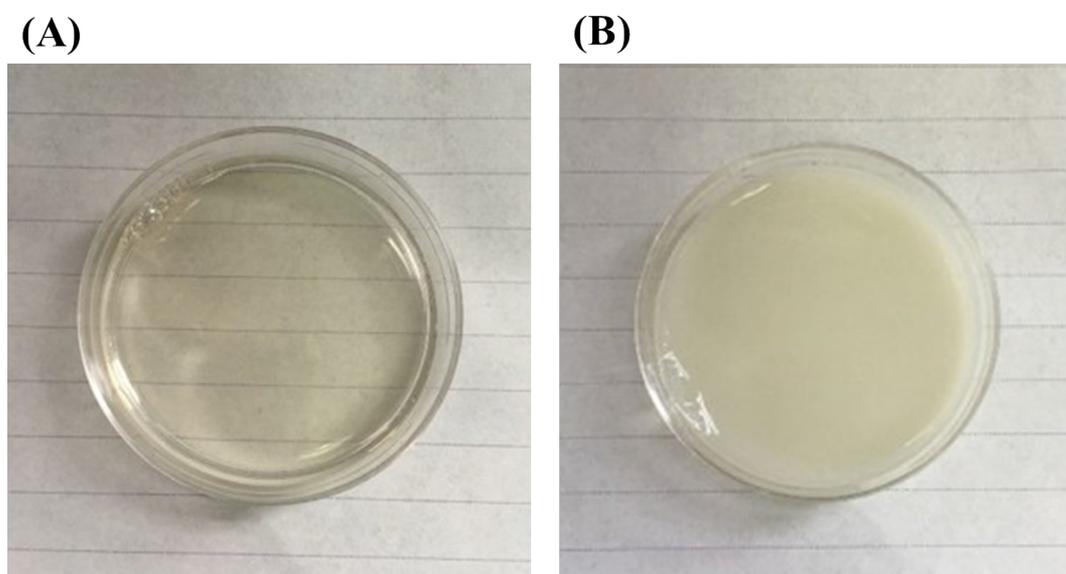
Figure S4. Transmittance spectra of RSF-NB solutions with different concentrations.



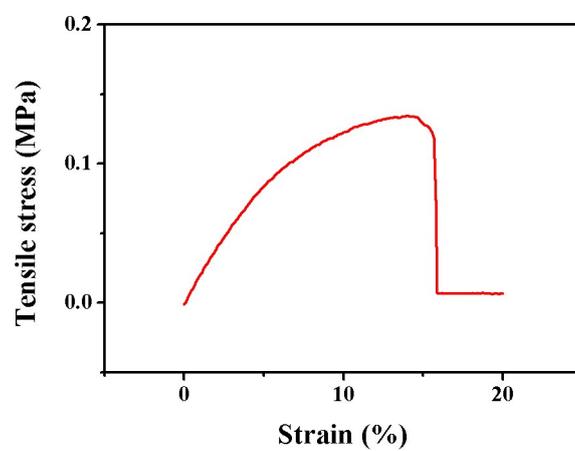
**Figure S5.** Shear-thinning behaviour of 10 wt% chemically crosslinked RSF hydrogel.



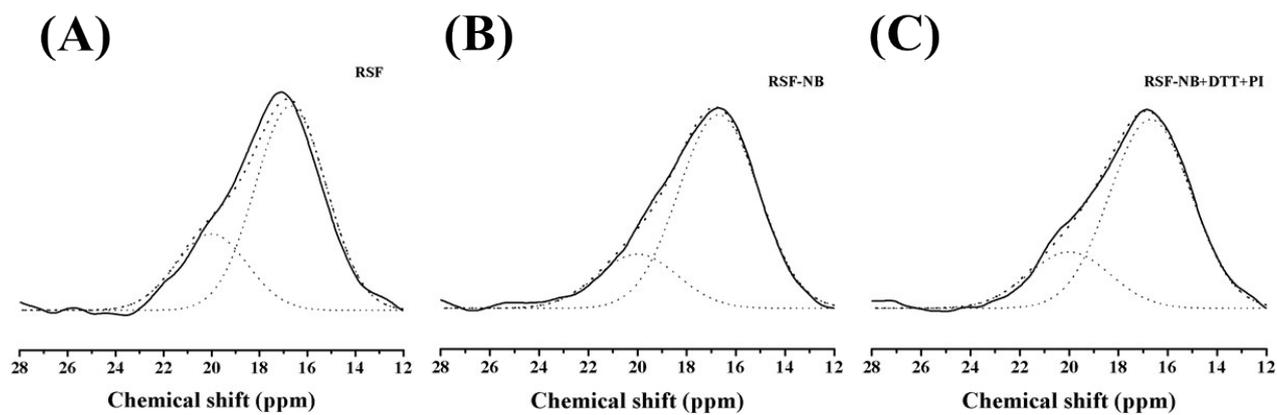
**Figure S6.** Digital photo of a 3D printed chemically crosslinked RSF hydrogel dyed with curcumin.



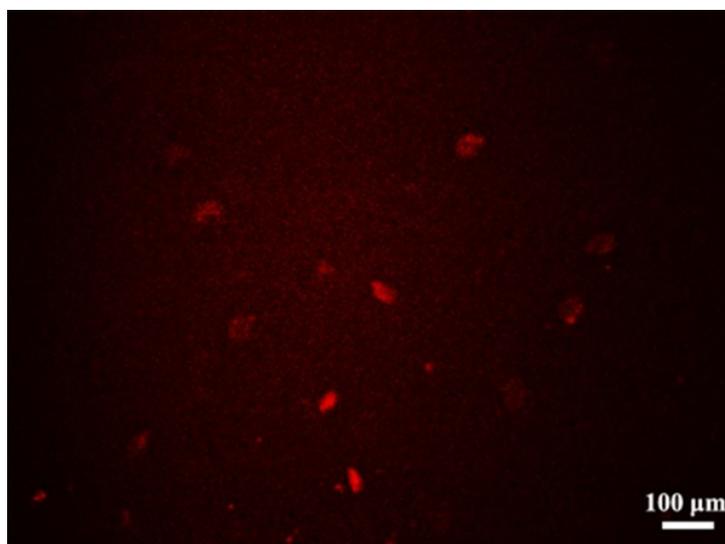
**Figure S7.** (A) Digital picture of chemically crosslinked RSF hydrogel. (B) Digital picture of double-network RSF hydrogel.



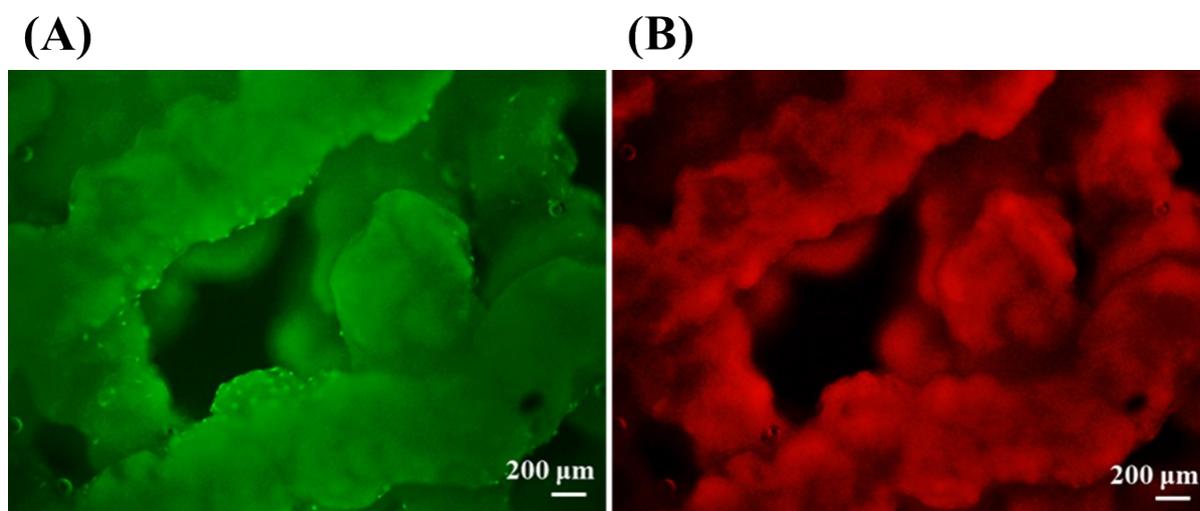
**Figure S8.** Representative tensile curve of 10 wt% double-network RSF hydrogel.



**Figure S9.**  $^{13}\text{C}$  NMR spectra and simulated ones of (A) RSF solution, (B) RSF-NB solution, (C) precursor solution.



**Figure S10.** Fluorescence microscope image of L929 cells incubated on the surface of chemically crosslinked hydrogel for 24 h.



**Figure S11.** (A, B) Fluorescence microscope images of L929 cells incubated in 3D printed double-network RSF hydrogel for 3 days with live/dead assay.