

## Dityrosine-Inspired Photocrosslinking Technique for 3D Printing of Silk Fibroin-Based Hydrogel Scaffolds

Yi Huang<sup>1,2,3</sup>, Guangdong Sun<sup>1</sup>, Lingling Lv<sup>1</sup>, Yongqiang Li<sup>1,3</sup>, Dapeng Li<sup>4</sup>, Qinguo Fan<sup>4</sup>, Juming Yao<sup>2\*</sup>, Jianzhong Shao<sup>1\*</sup>

<sup>1</sup> Engineering Research Center for Eco-Dyeing and Finishing of Textiles, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou, Zhejiang, 310018, P. R. China.

<sup>2</sup> School of Materials Science and Engineering, Zhejiang Sci-Tech University, Hangzhou, Zhejiang, 310018, P. R. China.

<sup>3</sup> Zhejiang Sci-Tech University Tongxiang Research Institute, Tongxiang, Zhejiang, 314500, P. R. China.

<sup>4</sup> Department of Bioengineering, University of Massachusetts Dartmouth, North Dartmouth, Massachusetts, 02747, USA.

“\*”denotes co-corresponding authors: Juming Yao (yaoj@zstu.edu.cn, 86-571-86843618) & Jianzhong Shao (jshao@zstu.edu.cn, 86-571-86843610)

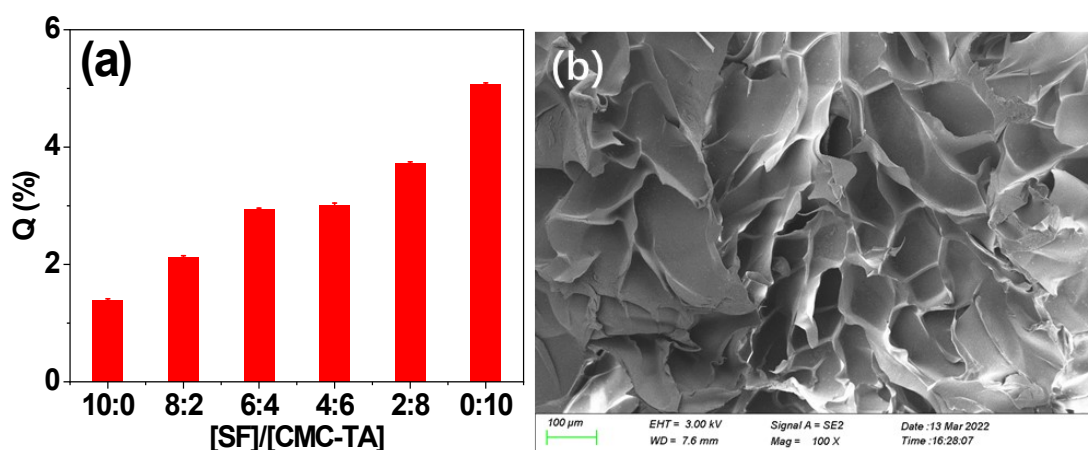


Figure S1. Water absorbency (a) of photocrosslinked SF hydrogels prepared with different mass ratio of SF and CMC-TA; and the microstructures (b) of SF/CMC-TA (6/4) hydrogel ( $[Ru(II)]/[KPS] = 1:40$ ;  $[Ru(II)] = 0.05$  mM)

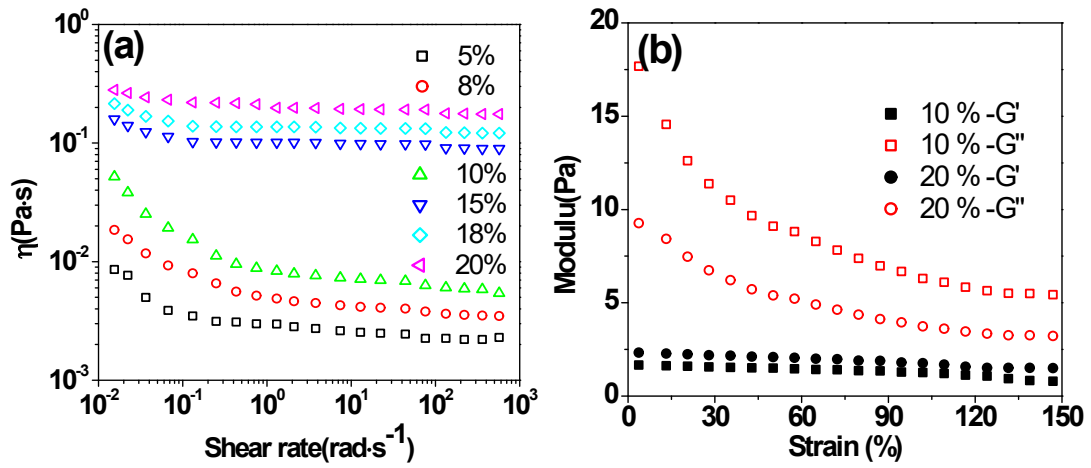


Figure S2. Shear viscosity (a) and dynamic modulus (b) of silk fibroin solution

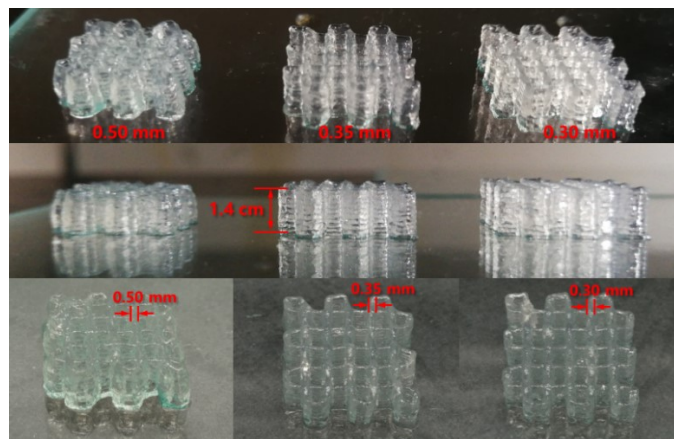


Figure S3. 3D printed XG hydrogel with three needle sizes

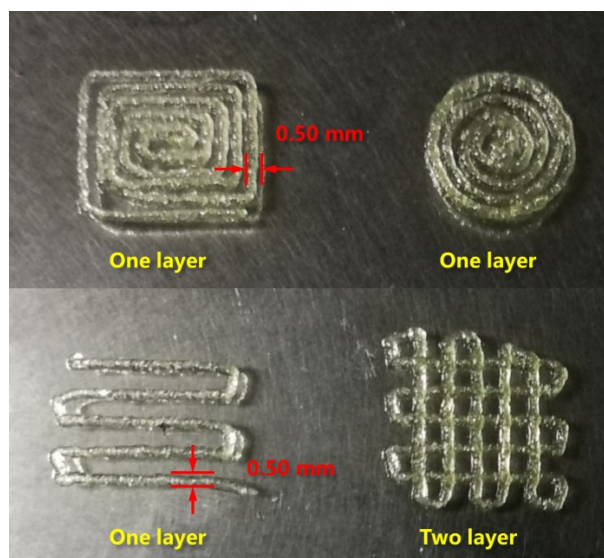


Figure S4. Extrusion printing of single and double layers of SF/XG gels (needle aperture 0.50 mm)

Table S1. Optimized printing parameters for SF/XG hydrogels

Needle size/ mm	Dispense gap/ mm	Moving speed/ (mm·sec <sup>-1</sup> )	pneumatic pressure/ PSI
0.50	3.5	1.5	3.3
0.35	3.2	1.5	4.7
0.30	3.0	1.5	10.1

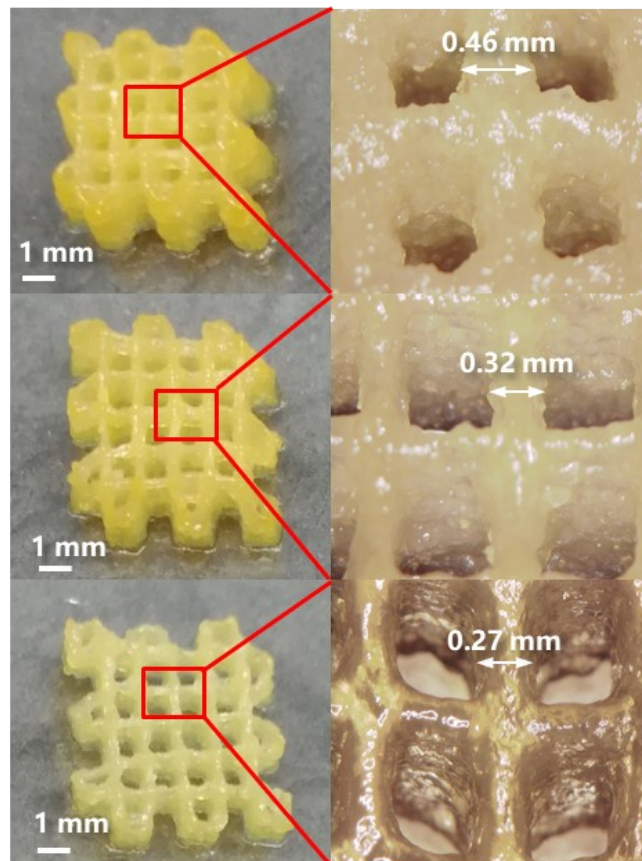


Figure S5. Printed SF/XG composite hydrogel with 3D network structure and its local enlarged drawings.

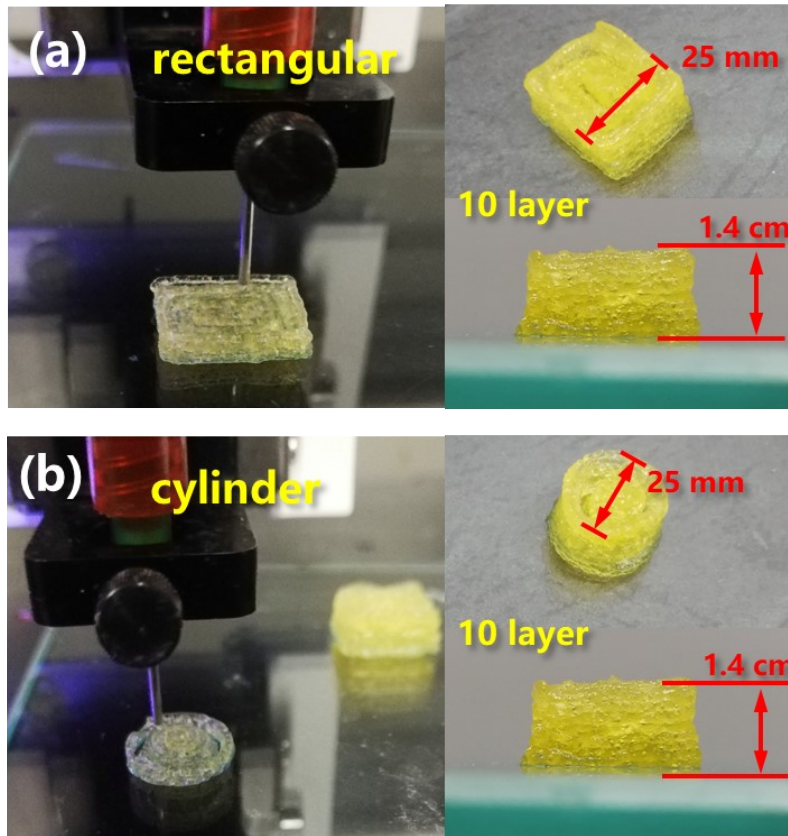


Figure S6. Printing process of cuboid (a) and cylinder (b) SF/XG composite gel and its basic form.