

## Supplementary Materials

# GOx/Hb Cascade Oxidized Crosslinking of Silk Fibroin for Tissue-Responsive Wound Repair

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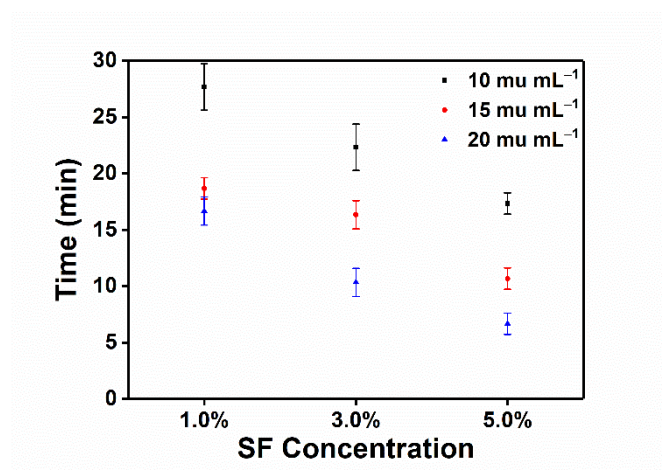
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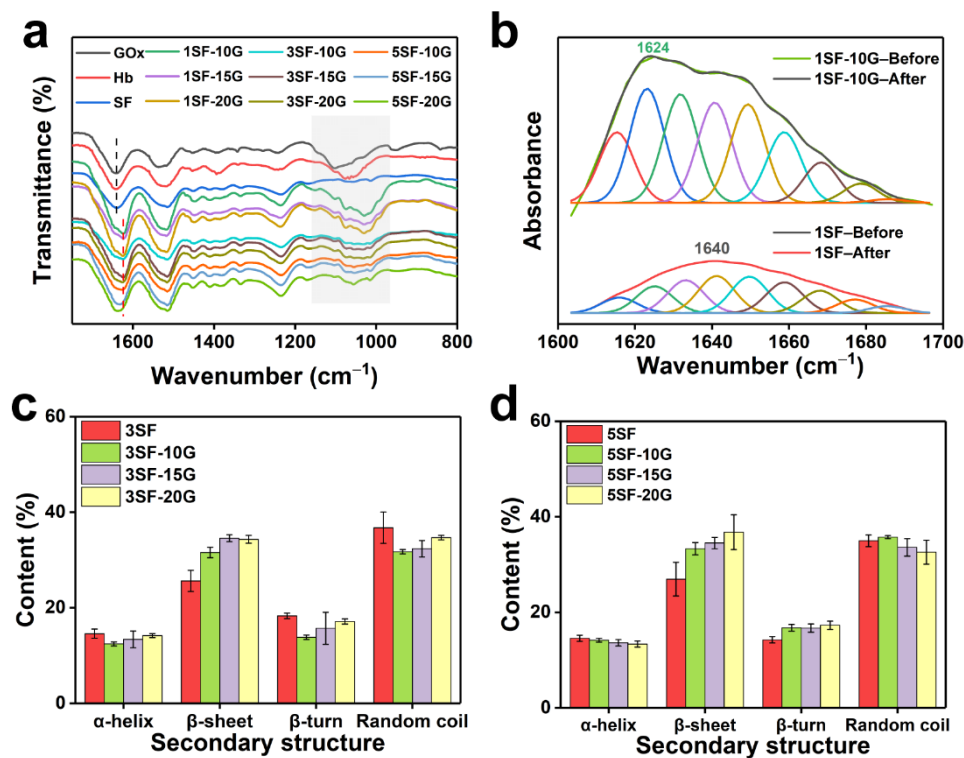
## Results and Discussion

**Table S1.** Concentrations of each ingredient in SF hydrogels.

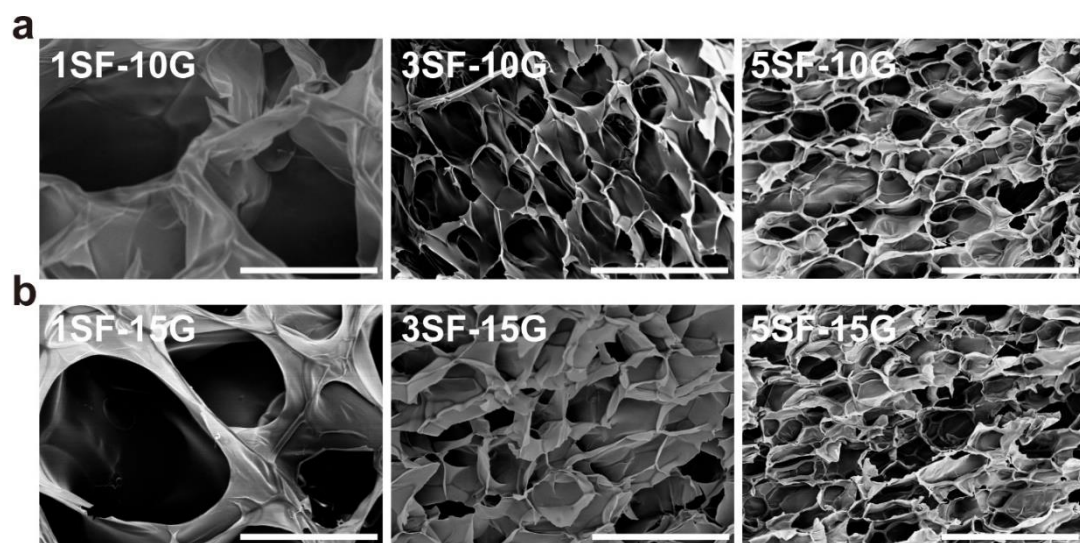
Sample	SF	Glucose	GOx	Hb
1SF-10G	1.0% w/v	4.5 mg mL <sup>-1</sup>	10 mu mL <sup>-1</sup>	3 mg mL <sup>-1</sup>
1SF-15G			15 mu mL <sup>-1</sup>	
1SF-20G			20 mu mL <sup>-1</sup>	
3SF-10G	10 mu mL <sup>-1</sup>			
3SF-15G	15 mu mL <sup>-1</sup>			
3SF-20G	20 mu mL <sup>-1</sup>			
5SF-10G	10 mu mL <sup>-1</sup>			
5SF-15G	15 mu mL <sup>-1</sup>			
5SF-20G	20 mu mL <sup>-1</sup>			



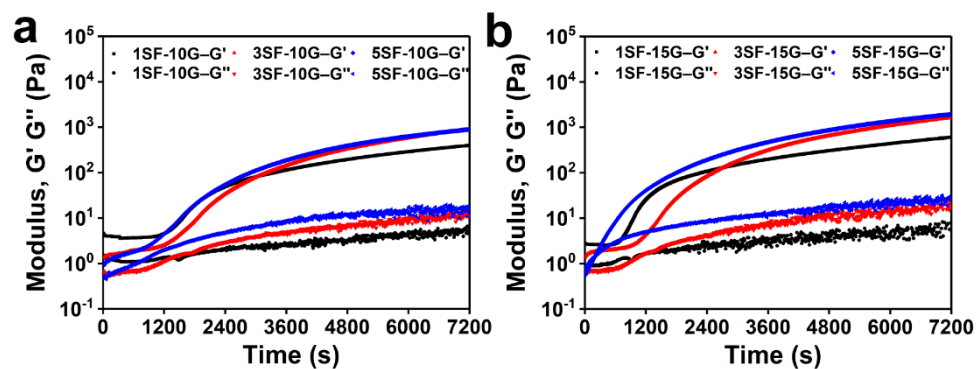
**Figure S1.** Gelation times of varying SF and GOx concentration at 37 °C. Error bars represent the mean  $\pm$  standard deviation (s.d.); n = 3.



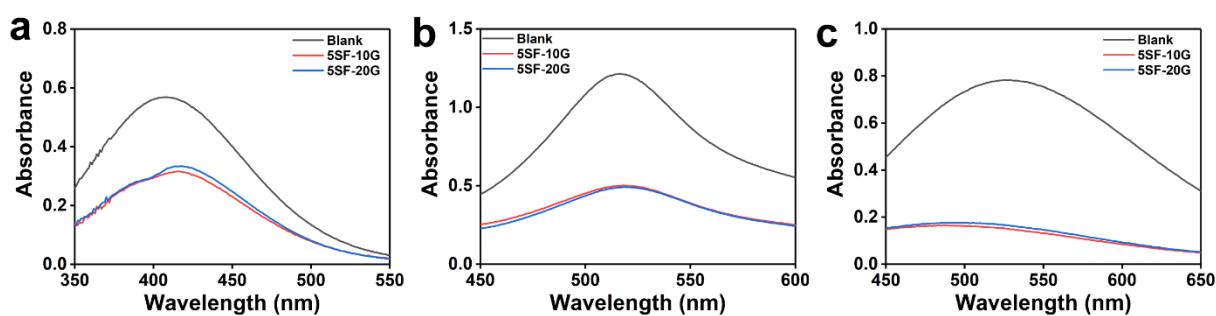
**Figure S2.** Mechanism of SF hydrogel formation. (a) FTIR spectra of GOx, Hb, SF hydrogels. (b) Peak fitting diagram of 1SF, 1SF-10G were performed using a PeakFit v4.12. (c, d) The results of second structure of SF hydrogels by peak fitting, Error bar represent mean  $\pm$  s.d.;  $n \geq 3$ .



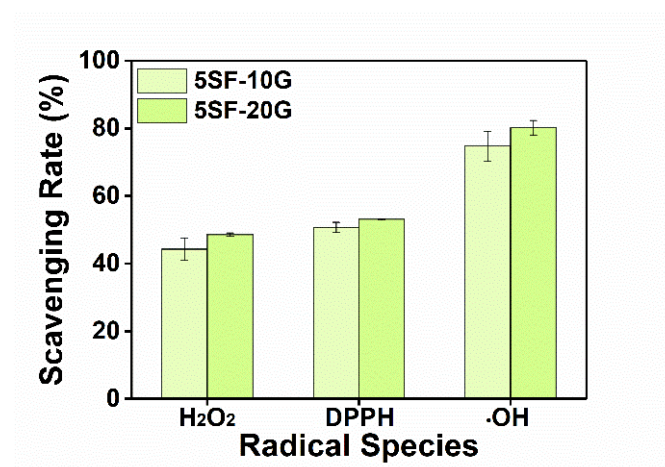
**Figure S3.** Characterization of hydrogel morphology. The 3D porous structure of SF hydrogel (a) SF/glucose/GOx (10  $\mu\text{M}$  mL $^{-1}$ )/Hb, (b) SF/glucose/GOx (15  $\mu\text{M}$  mL $^{-1}$ )/Hb with different SF concentration. Scale bars are 50  $\mu\text{m}$ .



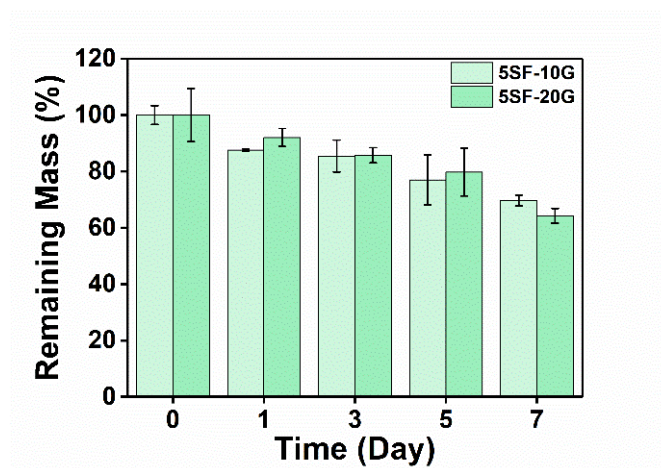
**Figure S4.** Rheological properties of SF hydrogels under different enzymatic systems. The storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of (a) SF/glucose/GOx ( $10\mu\text{mL}^{-1}$ )/Hb and (b) SF/glucose/GOx ( $15\mu\text{mL}^{-1}$ )/Hb hydrogels.



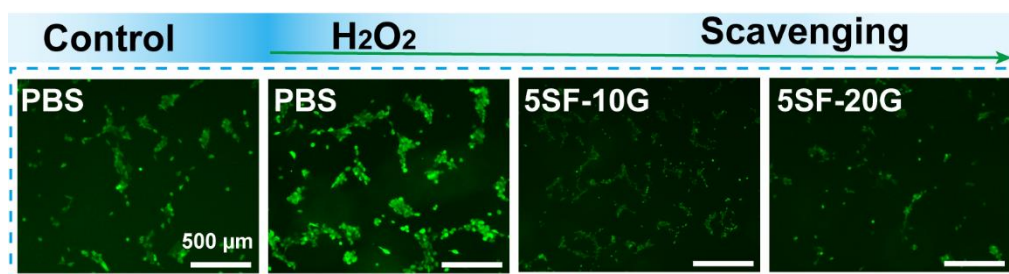
**Figure S5.** UV-vis spectra of (a)  $\text{H}_2\text{O}_2$ , (b) DPPH and (c)  $\cdot\text{OH}$  after being scavenged by the SF hydrogels for one hour.



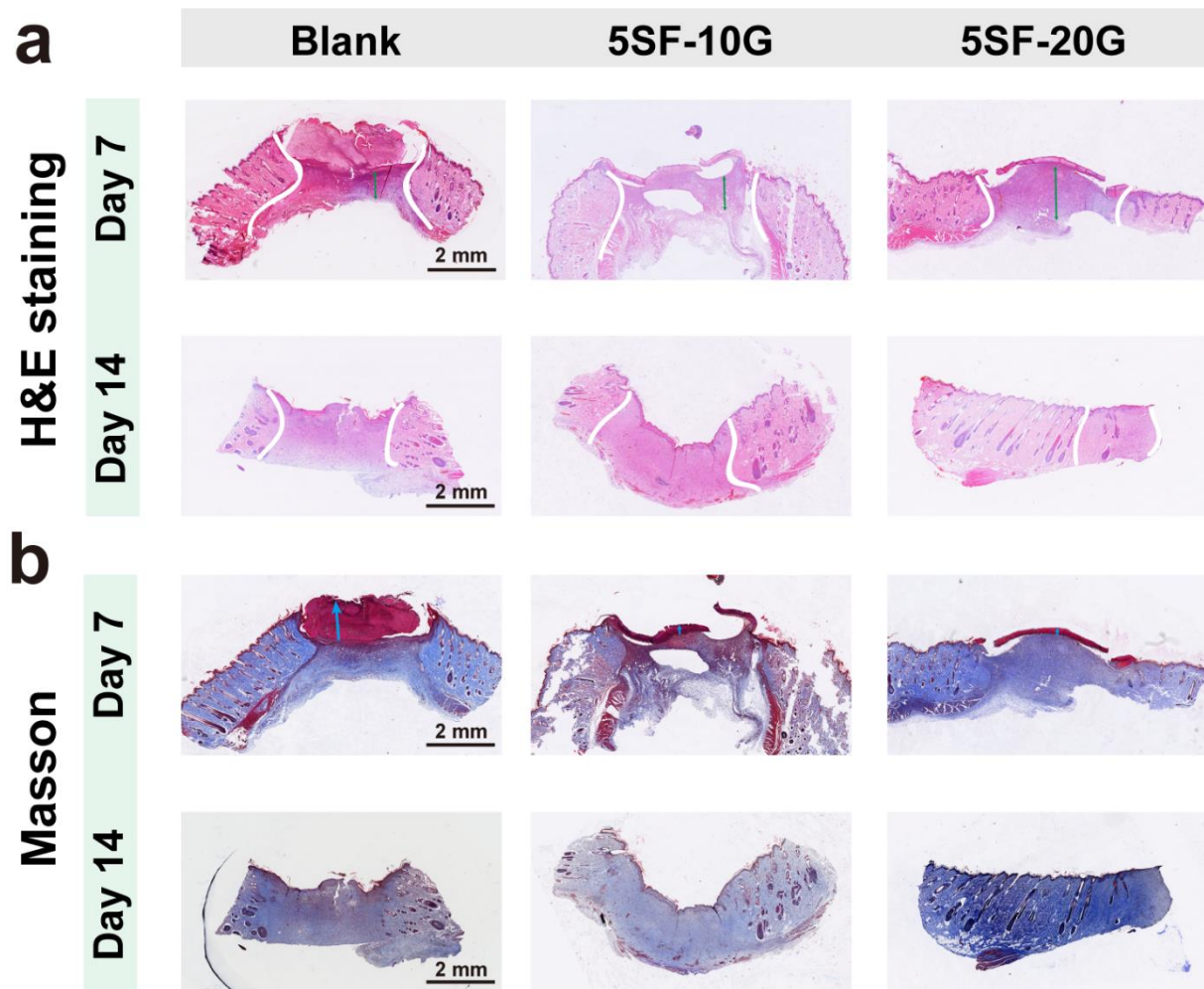
**Figure S6.**  $\text{H}_2\text{O}_2$ , DPPH and  $\cdot\text{OH}$  scavenging rate of the SF hydrogels (5SF-10G, 5SF-20G). Error bar represent mean  $\pm$  s.d.;  $n \geq 3$ .



**Figure S7.** Mass Remaining of silk hydrogels after enzymatic degradation. Error bar represent mean  $\pm$  s.d.;  $n \geq 3$ .

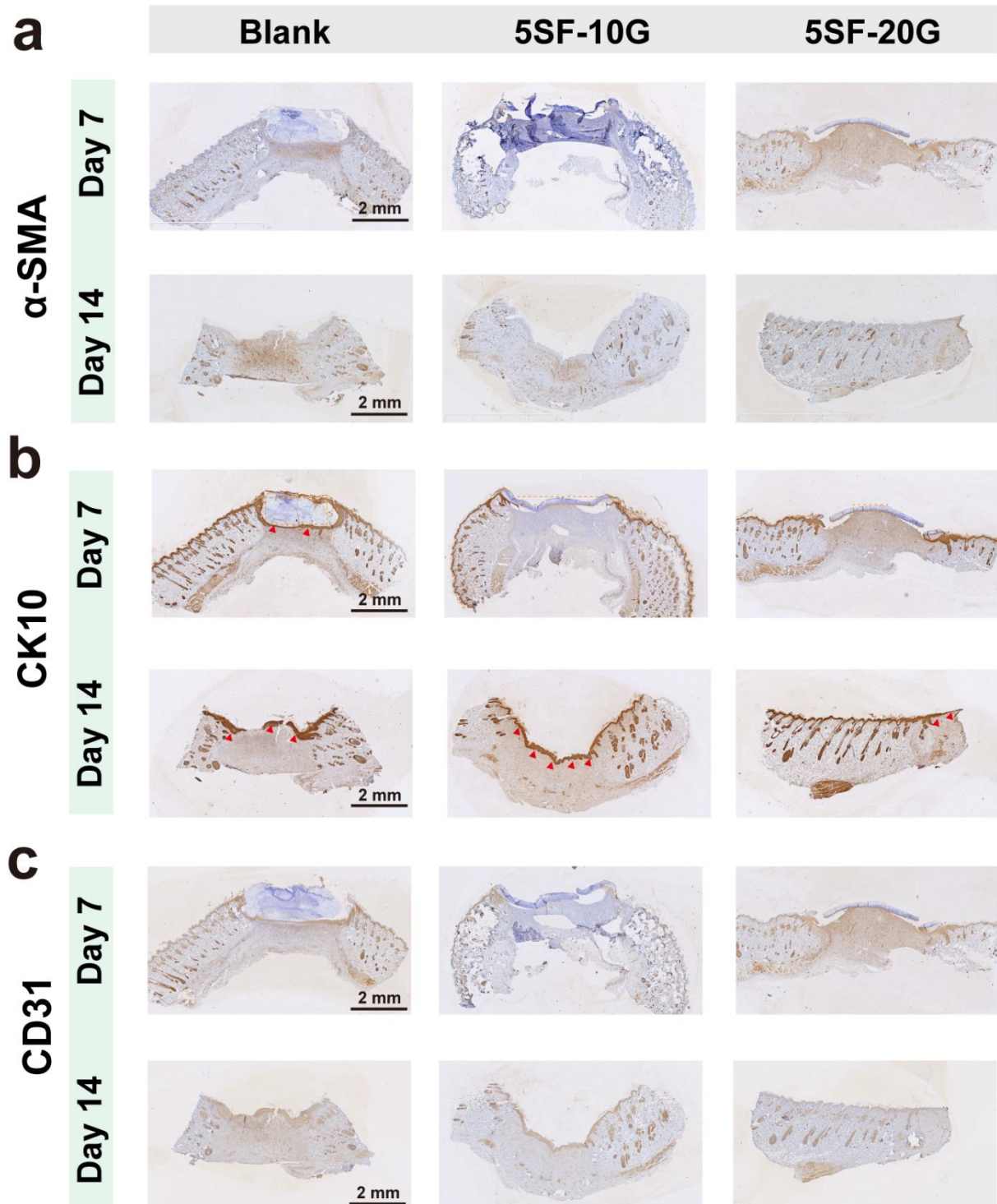


**Figure S8.** The oxidative stress in cells incubated with SF hydrogels (5SF-10G and 5SF-20G) was monitored via a ROS probe (DCFH-DA). Scale bar are 500  $\mu$ m.



**Figure S9.** Wound healing abilities of SF hydrogels. (a) H&E staining of the wound tissues on Days 7 and 14. White solid lines and green double-headed arrows represent the range and thickness of granulation tissue (b) Masson's trichrome staining of the wound tissues on Days 7 and 14. Blue arrows represent the residual scab, Scale bar are 2 mm.





**Figure S10.** Wound healing abilities of SF hydrogels. (a)  $\alpha$ -SMA staining, showing myofibroblasts on days 7 and 14. (b) CK10 staining, showing keratin in skin on days 7 and 14, orange dotted frames and red triangles indicated the negative and positive expression of keratin, respectively. (c) CD31 staining images, representing the extent of vascularization on days 7 and 14. Scale bars are 2 mm.