

Supplementary file

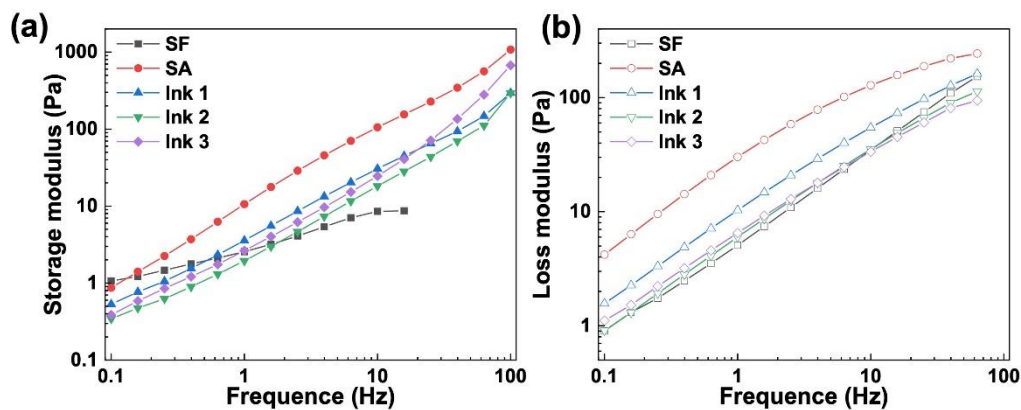


Figure S1. Modulus-frequency curves of extrusion printing inks based on silk fibroin/sodium alginate mixture, silk fibroin (15 wt%) and sodium alginate (3 wt%). (a) Storage modulus-frequency curve, (b) Loss modulus-frequency curve.

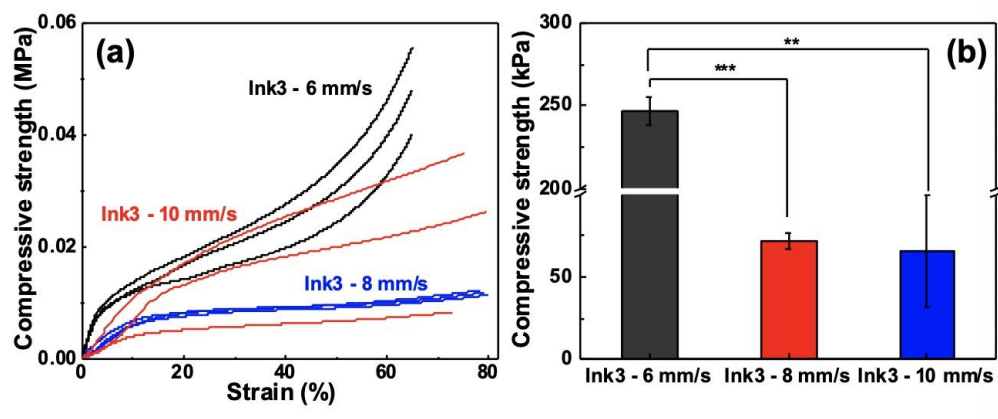


Figure S2. (a) Compressive stress-strain curves of SF scaffolds from ink 3 at various extrusion speeds. (b) Derived compressive modulus from the initial linear region 1% to 3% of the curves in (a). Significant differences are denoted as: * for $p < 0.05$; ** for $0.01 < p < 0.05$; *** for $0.001 < p < 0.01$.

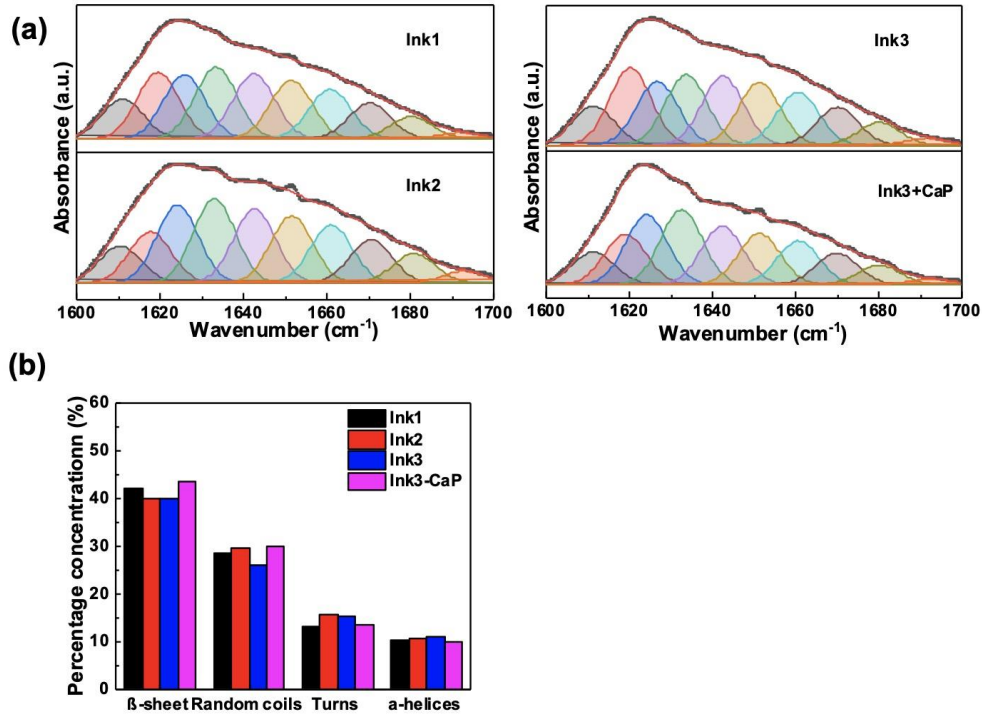


Figure S3. (a) FTIR spectra of silk fibroin scaffolds from mixed inks and sodium alginate and (b) the peak convolution results from the Amide I band.

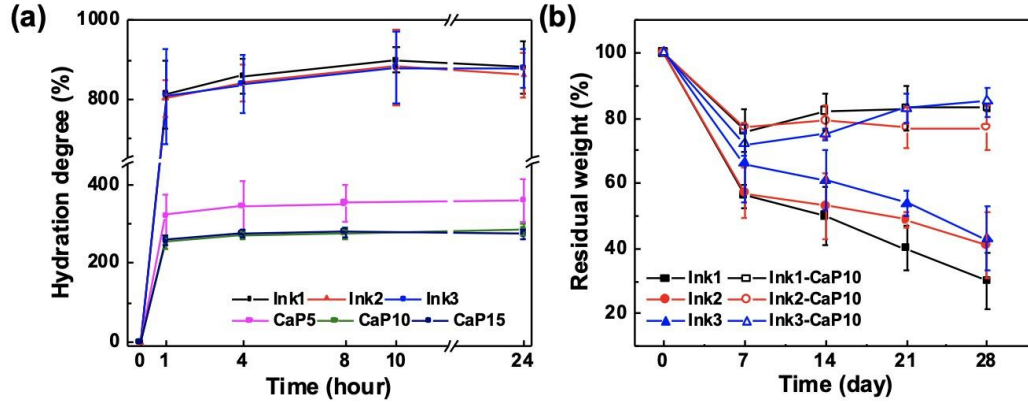


Figure S4. Water retention and in vitro degradation behaviour of SF scaffolds. (a) water content and time relationship curve, (b) porosity of ink printing brackets with different formulas (significant difference analysis: * $p < 0.05$, ** $0.01 < p < 0.05$, *** $p < 0.01$)

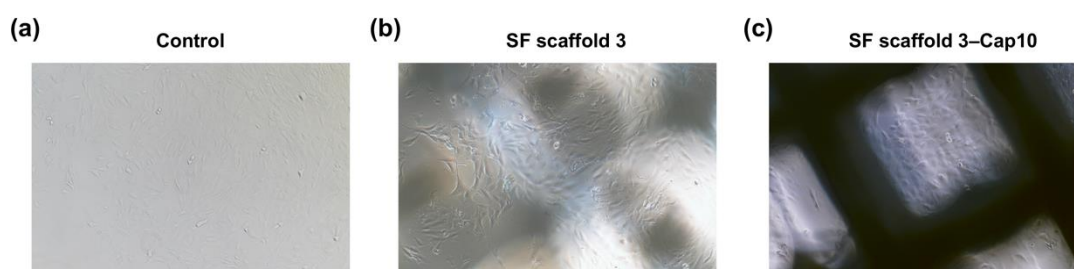


Figure S5. The cell number and morphology co-cultured with DMEM medium(a), SF scaffold 3(b) and SF scaffold 3-cap10 (c) on day 5.

Table S1. Crystalline phase analysis after post-mineralization of calcium phosphate in SF scaffolds using $\text{Ca}(\text{CH}_3\text{COO})_2 / (\text{NH}_4)_2\text{HPO}_4$ solutions for co-precipitation

Parameter		Crystal size			Crystalline phases
		Shape	Length	Thickness	
Organic	pH	4-5	10-20 μm	< 1 μm	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
		7-8	5-10 μm		$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
		10-11	< 2 μm		$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, CaHPO_4
Water	pH	4-5	6-10 μm	< 1 μm	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$
		7-8	3-8 μm	< 1 μm	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, CaHPO_4
		10-11	< 2 μm	< 1 μm	Amorphous, CaHPO_4
Temperature	50 $^\circ\text{C}$	Plate/Lamella	Length < 2 μm Thickness < 1 μm	< 1 μm	CaHPO_4
		Particle	Diameter 1-2 μm		
	80 $^\circ\text{C}$	Plate/Lamella	Length < 2 μm Thickness < 1 μm	< 1 μm	CaHPO_4
		Particle	Diameter 3-5 μm		

Table S2. Conformational content of printed scaffolds from different inks before and after mineralization

Conformation	SF Scaffold 1 from Ink 1	SF Scaffold 2 from Ink 2	SF Scaffold 3 from Ink 3	SF10-SA1.0-CaP5
Silk I	61.3%	51.5%	47.9%	48.0%
Silk II	38.7%	48.5%	52.1%	52.0%