Supplementary Information

Direct ink writing of high-strength and swelling-resistant biocompatible physical-crosslinking hydrogels

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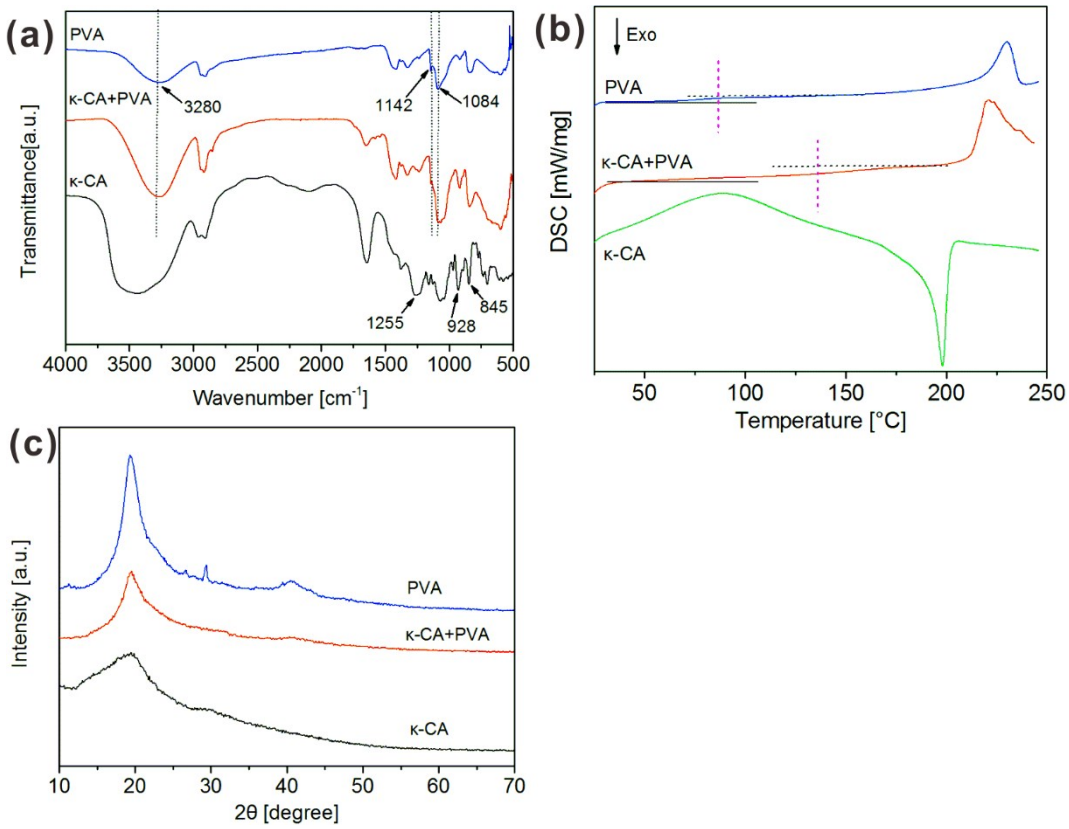

Fig. S1 (a) FT-IR spectra, (b) DSC curves, (c) X-ray diffraction profiles of hydrogels after freezing-thawing routs.

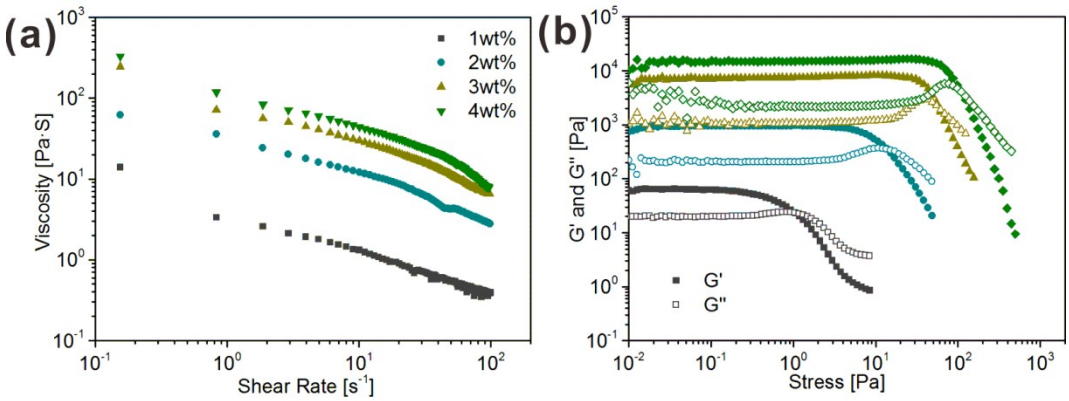

Fig. S2 Rheological properties of κ-CA with different concentrations.

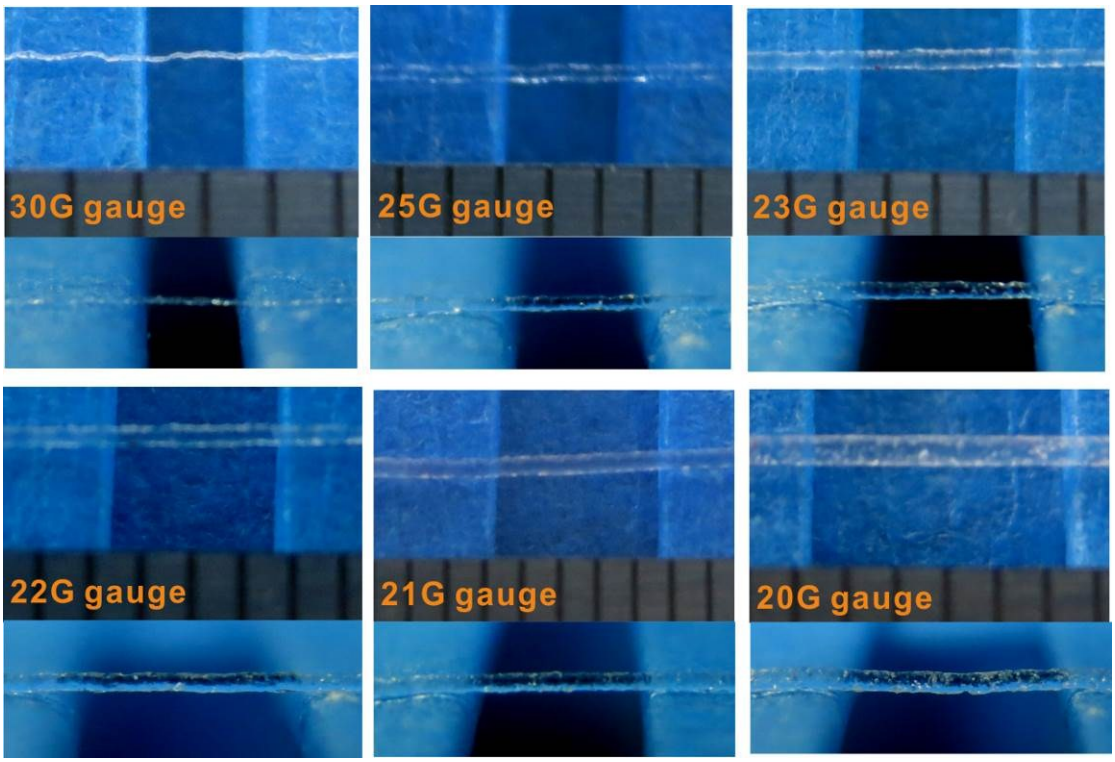

Fig. S3 Span length of hydrogel filaments extruded from different nozzles (e.g. different diameters).

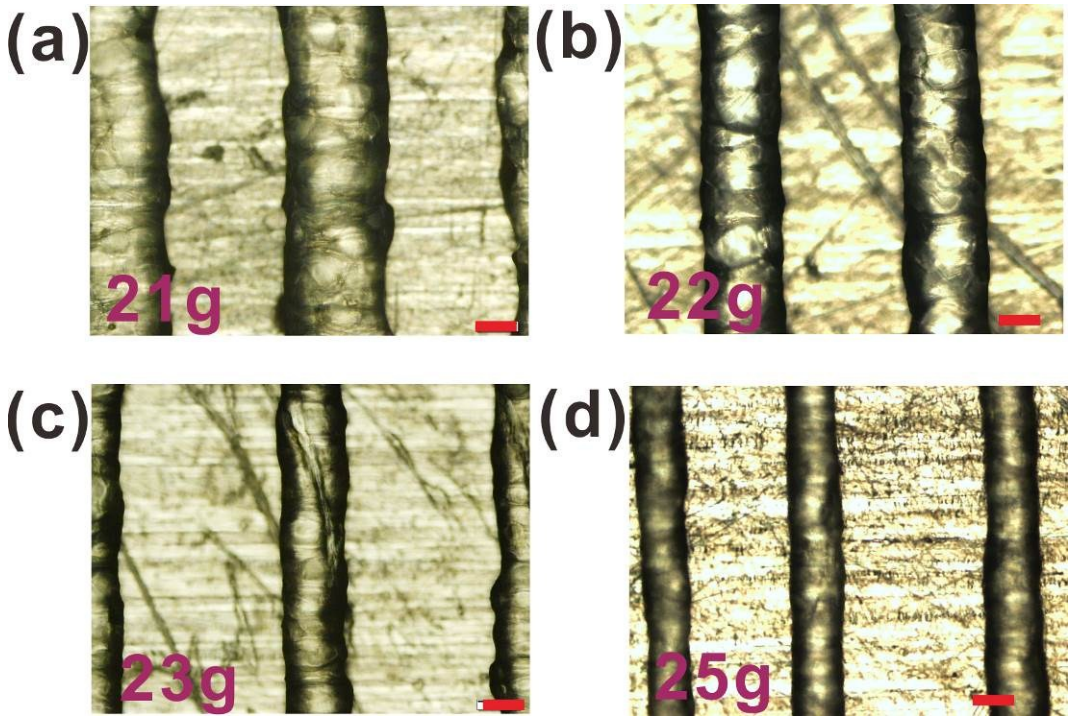

Fig. S4 Photomicrographs of the real filaments printed by different diameter nozzles. The scale bars are 200 μm.

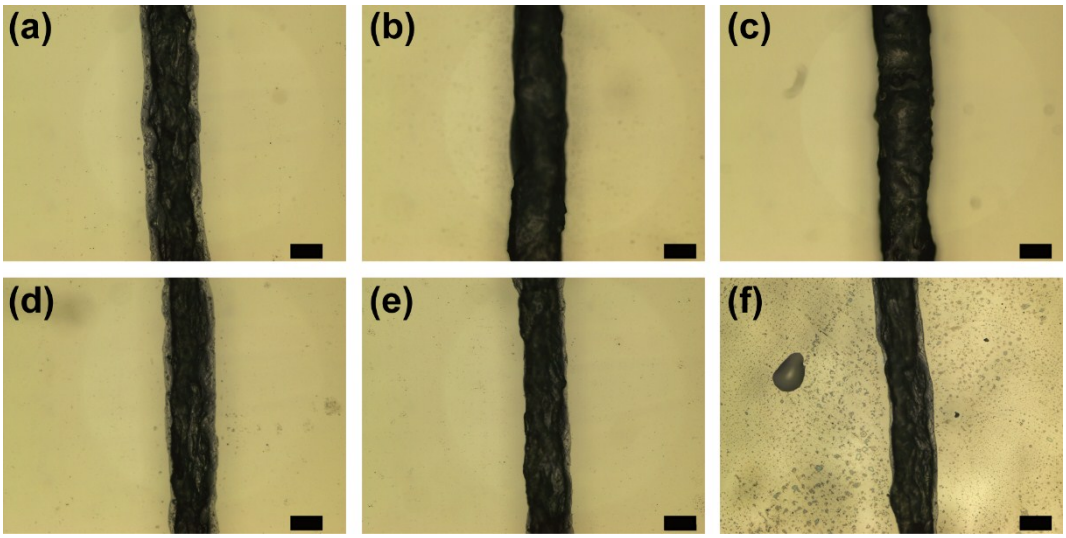

Fig. S5 Photomicrographs of the real filaments printed under different freezing-thawing cycles. (a) Initial filament and (b)-(f) the 1-5 cycles of freezing-thawing routes. The scalebars are 200 μm.

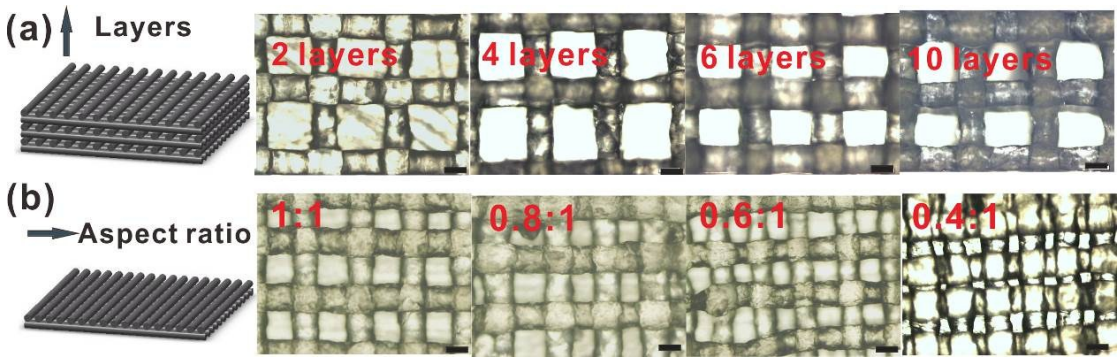

Fig. S6 (a) Following the vertical, printed woodpile-structured hydrogel scaffolds with different layers. (b) Following the horizontal, printed grids with different aspect ratios. The scalar bars are 200 μm.

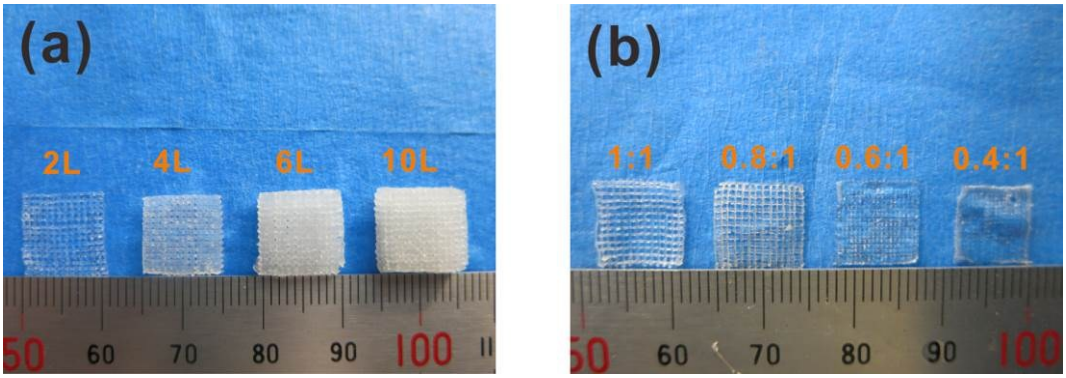

Fig. S7 The digital images of hydrogel grids with different layers (a) and aspect ratios (b).

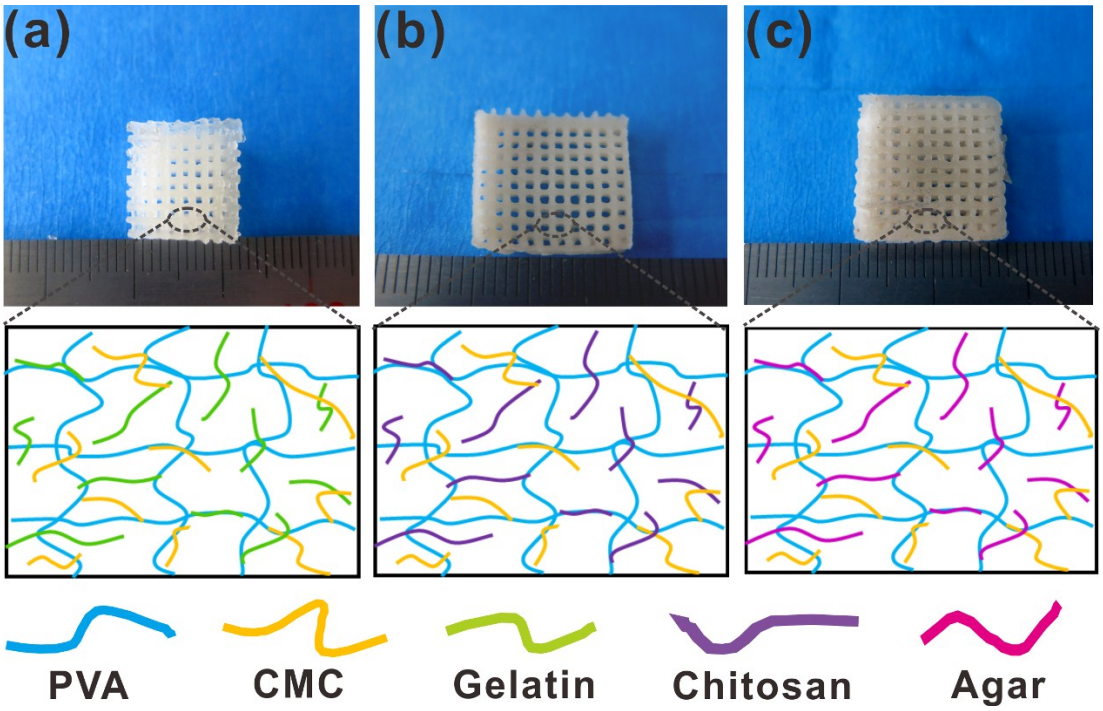

Fig. S8 3D printing of physical cross-linking hydrogels with different natural occurring macromolecules.

(a) PVA/gelatin/carboxymethyl cellulose (CMC), (b) PVA/chitosan/CMC, and (c) PVA/agar/CMC.

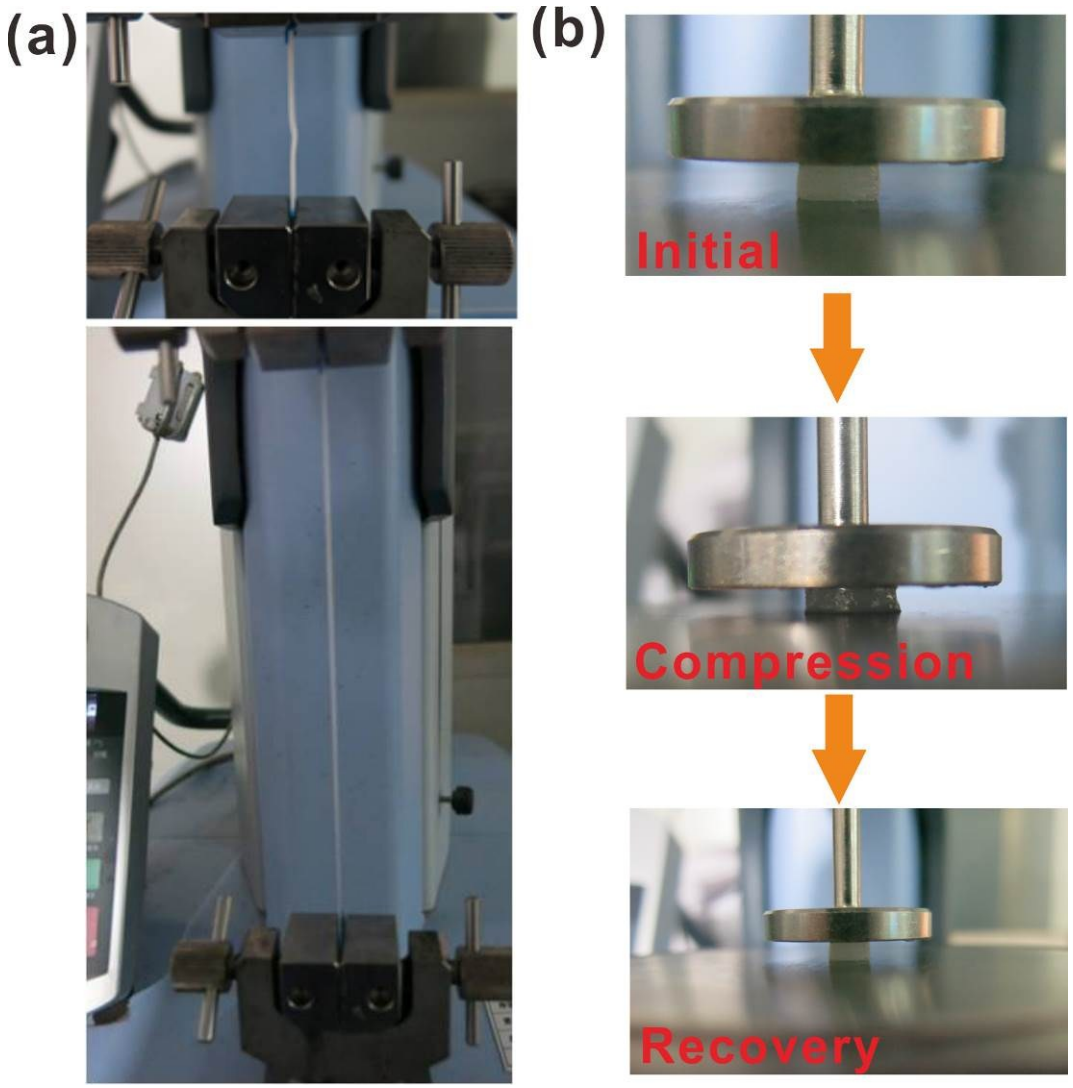

Fig. S9 Tensile test and compression test of hybrid hydrogels.

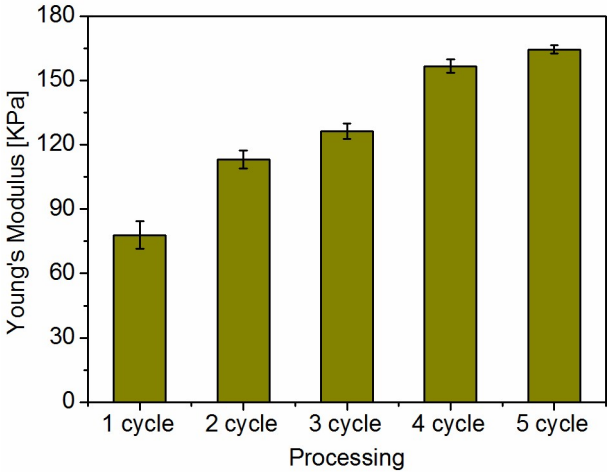

Fig. S10 The correspording Young' s moduli of hydrogels with different postprocessing.

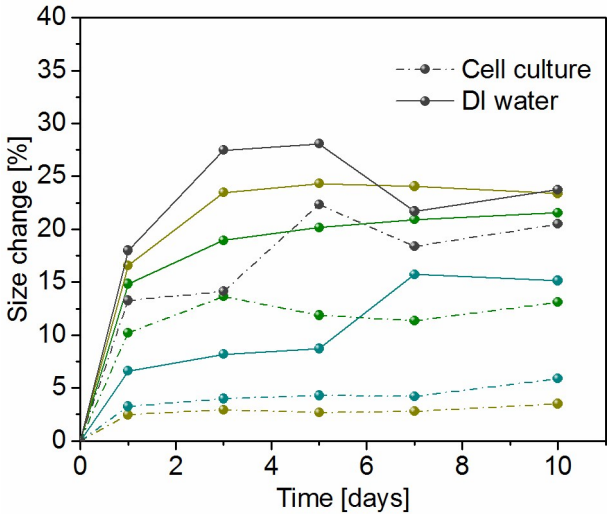

Fig. S11 The size change of filaments immersing in DI water and cell base at different incubation time.

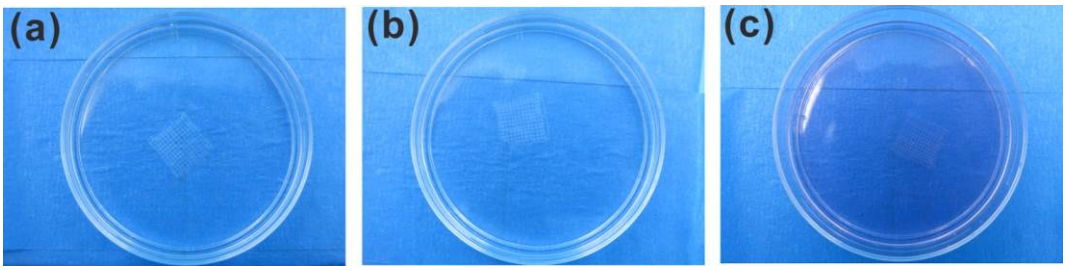

Fig. S12 The printed two-dimensional networks were immersed in DI water at initial (a) and 10 days (b); in cell culture 10 days (c).

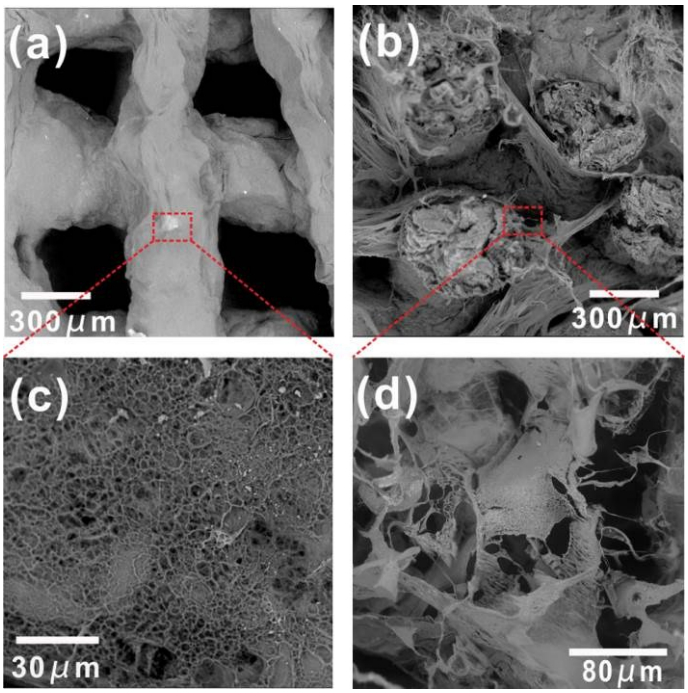

Fig. S13 SEM images of hydrogel scaffolds. (a) Surface morphology and (b) cross-section morphology. (c) and (d) the corresponding magnifications.

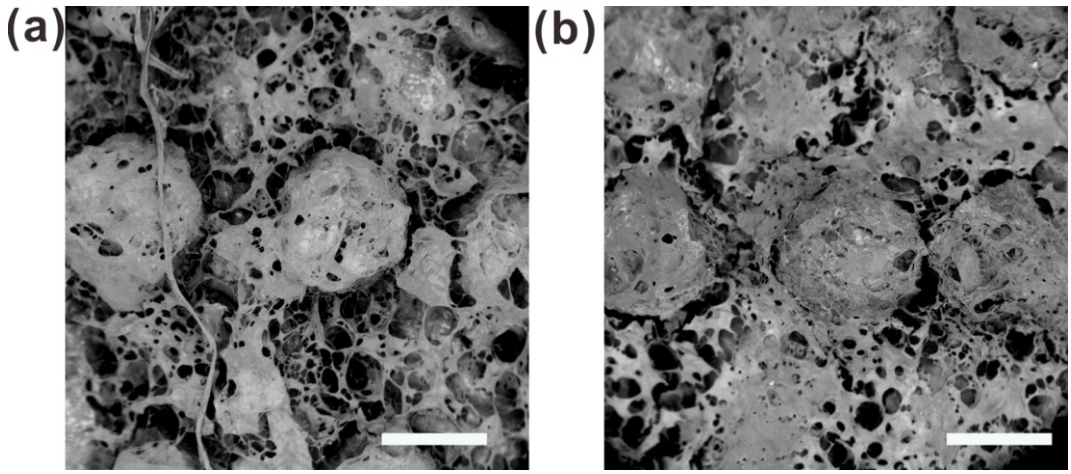

Fig. S14 SEM images of extra side of hydrogel scaffolds with cell attachment at 3 days (a) and 7 days (b) respectively. The scale bars are 200 μm.

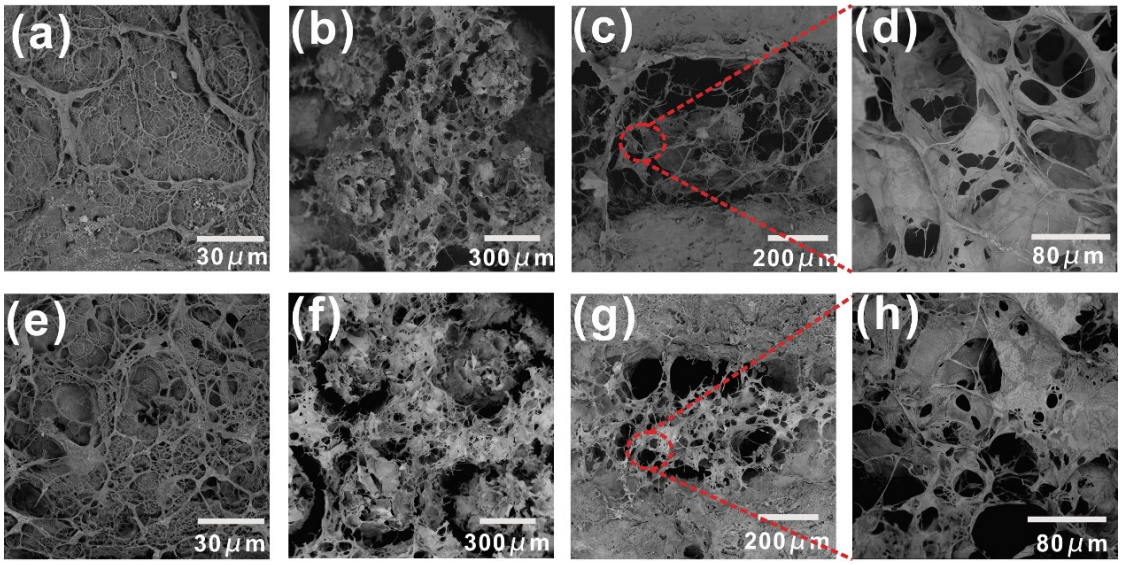

Fig. S15 SEM images of L929 fibroblast seeded on the woodpile-structured scaffolds at 3 days (top) and 7 days (bottom) respectively.

Table S1 The simulation of relationship between filament size and moving speed.

Equation form		**$Y=Intercept+B_1X+B_2X^2$**		
(Moving speed)				
Needle	R2	**Intercept (σ)**	**B_1 (σ)**	**B_2 (σ)**
25g	0.98	584.47(33.62)	-108.58(15.01)	8.52(1.59)
23g	0.90	682.88(70.46)	-109.26(32.31)	8.06(3.55)
22g	0.90	874.01(89.24)	-159.82(38.68)	12.72(3.93)
21g	0.96	1280.22(99.84)	-237.58(43.56)	16.79(4.52)

Table S2 The simulation of relationship between filament size and extrusion flux.

Equation form		**$Y=Intercept+B_1X+B_2X^2$**		
(Extrusion flux)				
Needle	R2	**Intercept (σ)**	**B_1 (σ)**	**B_2 (σ)**
25g	0.99	198.24(17.04)	143.63(72.33)	82.93(62.21)
23g	0.99	285.64(13.27)	326.44(56.64)	-74.48(49.58)
22g	0.98	318.63(22.80)	365.92(97.77)	-133.91(91.13)
21g	0.92	415.96(37.40)	476.35(160.27)	-204.84(143.09)

Movie S1 The fluid transportant of printed banched tube.

Experimental section

Materials

Carboxymethylcellulose (CMC) sodium salt was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd. Chitosan (deacetylation: 85%) was purchased from J&K Scientific Ltd. Gelatin and agar were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemical agents were directly used without any purification.

Ink preparation

The CMC (15 wt%) was dissolved into DI water at 60 °C with vigorous strring. The PVA solution (10 wt%) and CMC solution were mixed with the volume ratio of 1. The gelatin (10 wt%) was dissolved into DI water at 50 °C with vigorous strring and then cooled to RT. The chitosan (15 wt% of PVA+CMC solution) and agar (10 wt% PVA+CMC solution) were added into the mixed solution (PVA+CMC) with vigorous stirring respectively. The gelatin gel (10 wt% of PVA+CMC solution) was blended into the mixture (PVA+CMC) with with vigorous stirring. Finally, all above of hybrid hydrogel inks were kept overnight at RT.