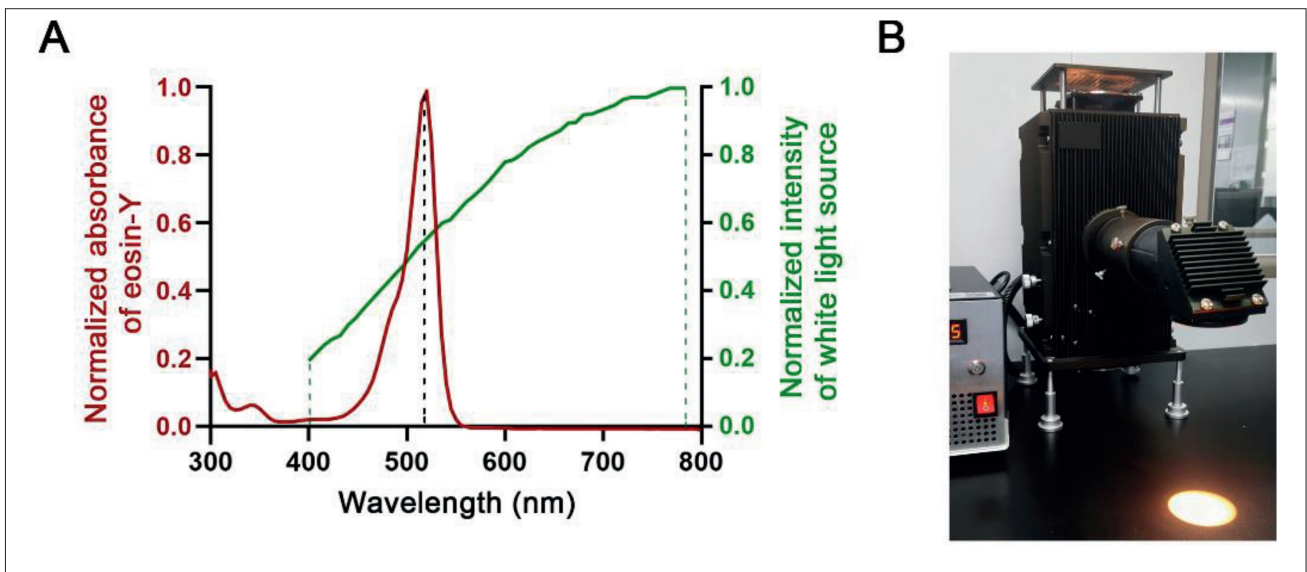


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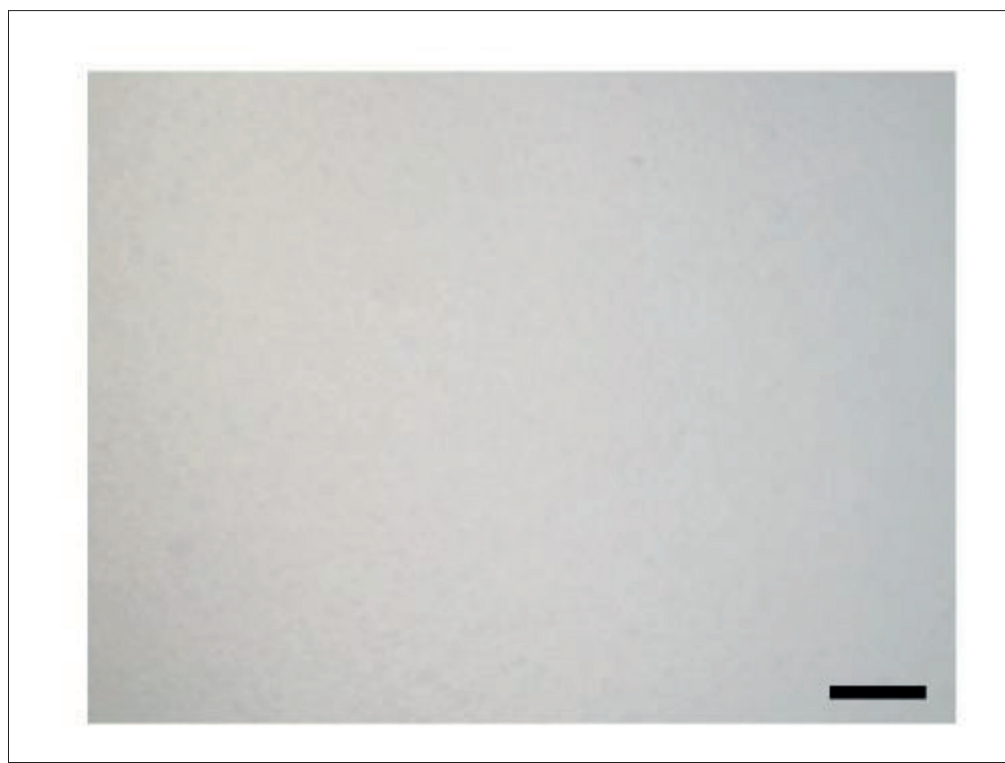
Bioprinting with superelastic and fatigue-resistant bioinks for large-sized tissue delivery

Supplementary File

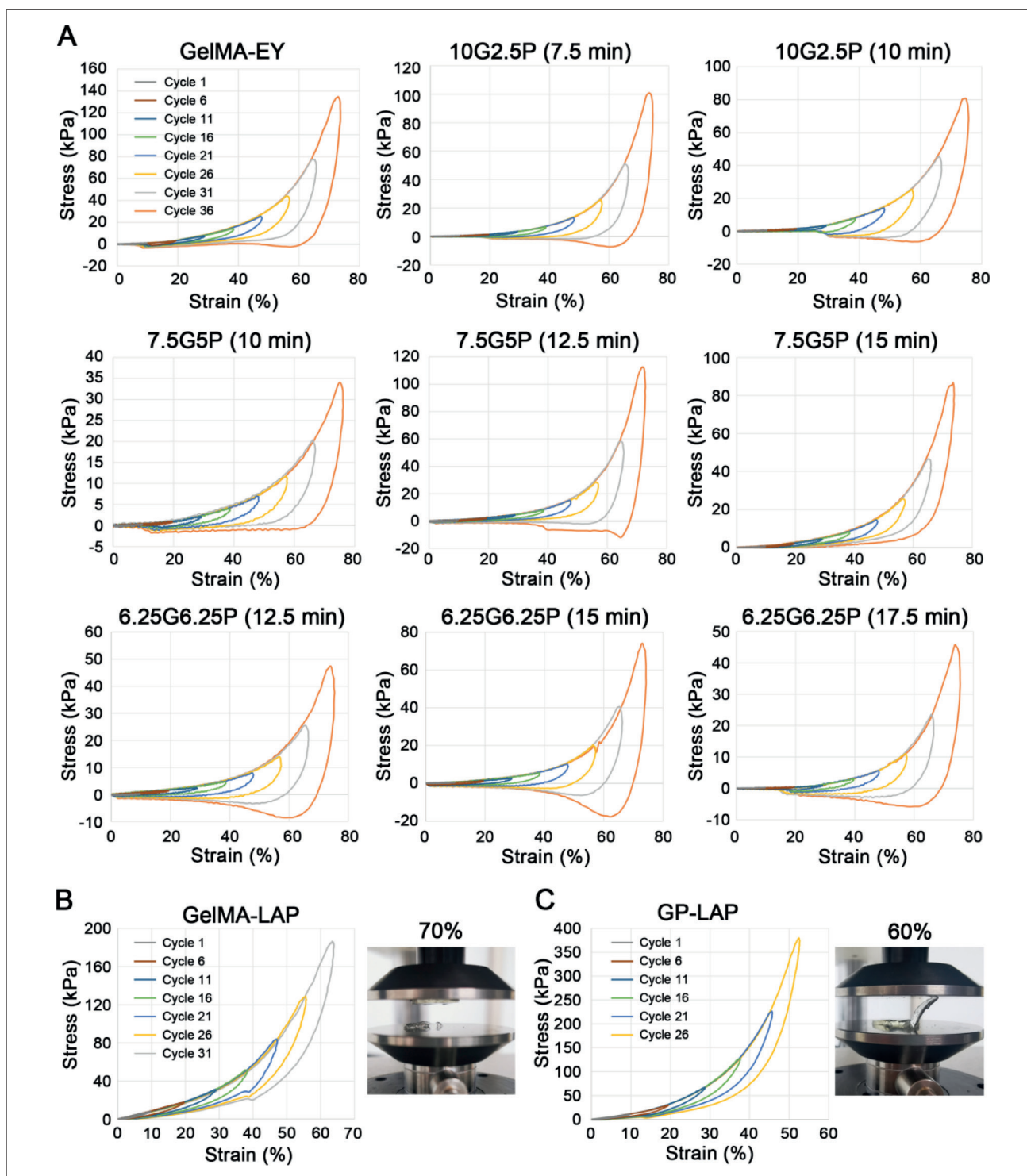
(A) Supplementary figures and tables



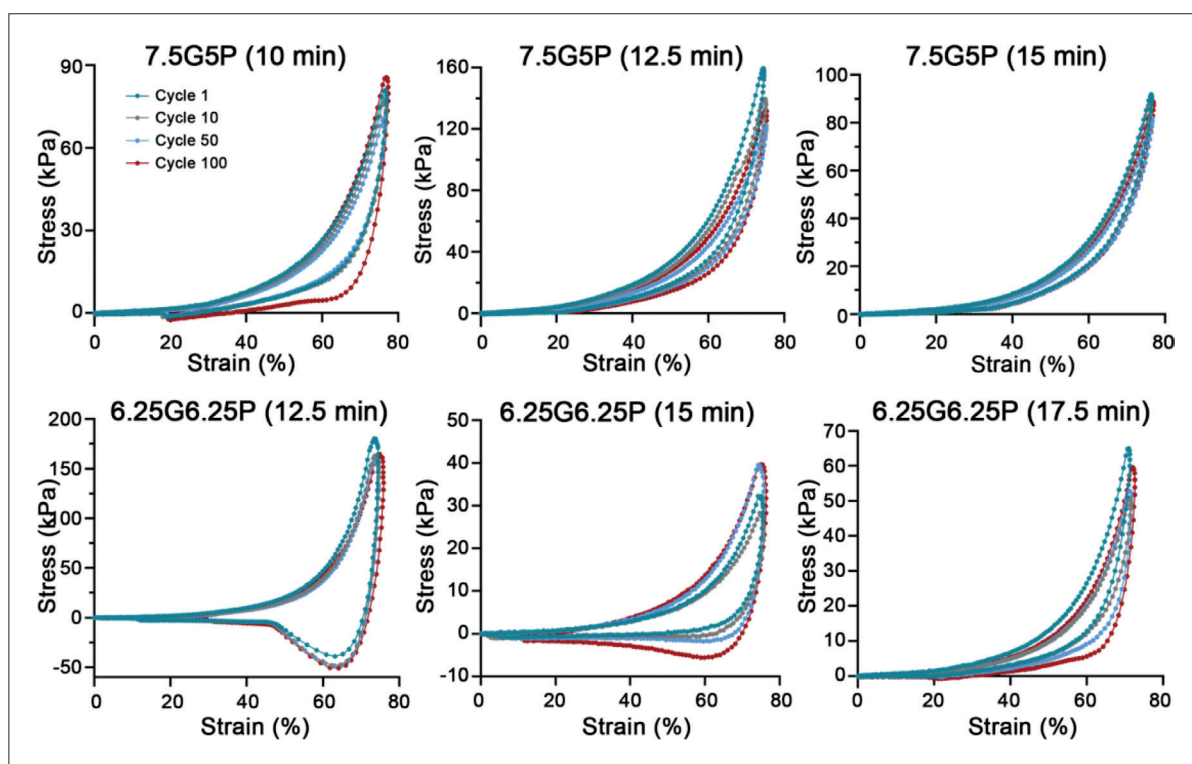
**Figure S1.** Illustration of the white light source in this study. (A) The normalized absorbance curve of eosin-Y (EY; red) and the intensity curve of the white light source (green). (B) The tungsten halogen white light source used in this study.



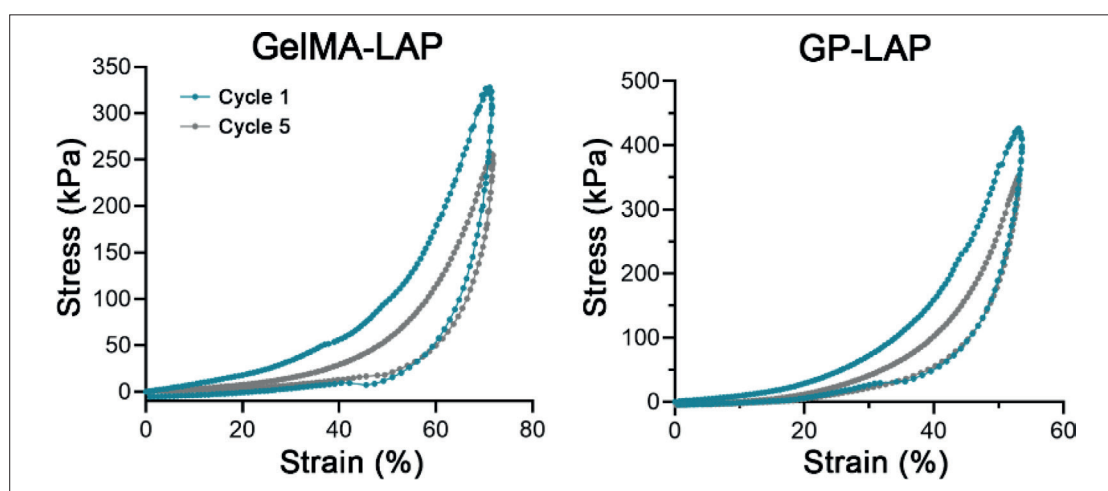
**Figure S2.** Microscopic image of gelatin methacryloyl/poly(ethylene glycol) diacrylate (GP) after material mixing and photocrosslinking. Magnification: 100×. Scale bar: 100  $\mu$ m.



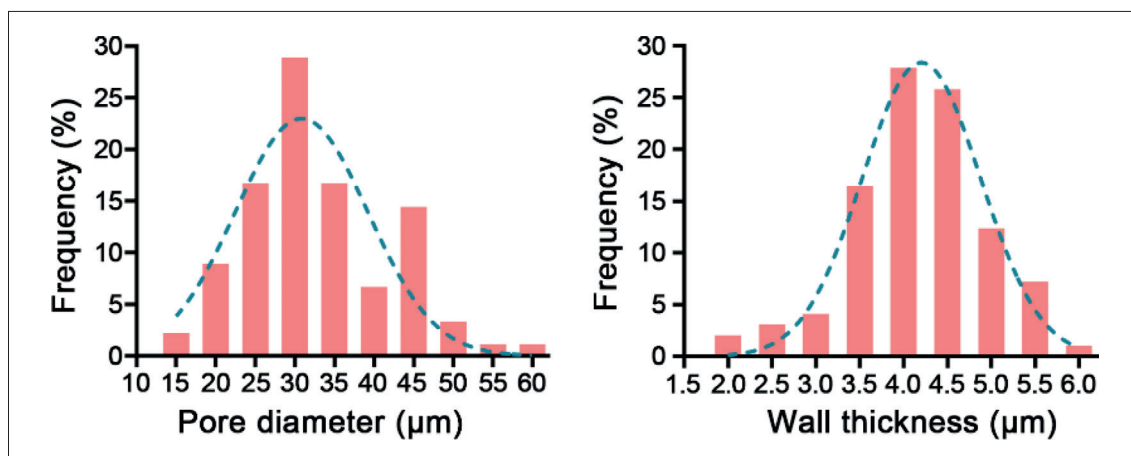
**Figure S3.** Compression tests for fully crosslinked GelMA and GP under EY and LAP photoinitiator systems. (A) GelMA (12.5%) and GP under the EY system with white light-induced crosslinking. (B) GelMA (12.5%) under LAP system with UV light-induced crosslinking. (C) GP (10G2.5P) under LAP system with UV light-induced crosslinking. Images of the failed (right in B) GelMA-LAP and (right in C) GP-LAP samples. Abbreviations: GelMA: Gelatin methacryloyl; and GP: Gelatin methacryloyl/poly(ethylene glycol) diacrylate; LAP: Lithium phenyl-2,4,6-trimethylbenzoylphosphinate; EY: Eosin-Y; and UV: Ultraviolet.



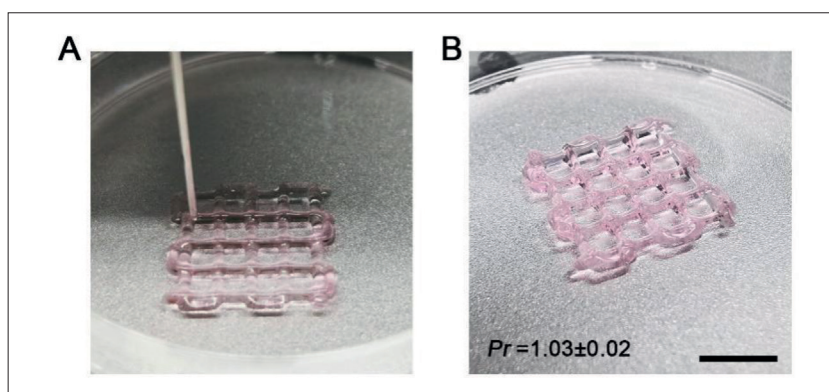
**Figure S4.** Hysteresis curves from fatigue tests on GP-EY under 100 cyclic loading compressions at 80% strain. Abbreviations: GP: Gelatin methacryloyl/poly(ethylene glycol) diacrylate; and EY: Eosin-Y.



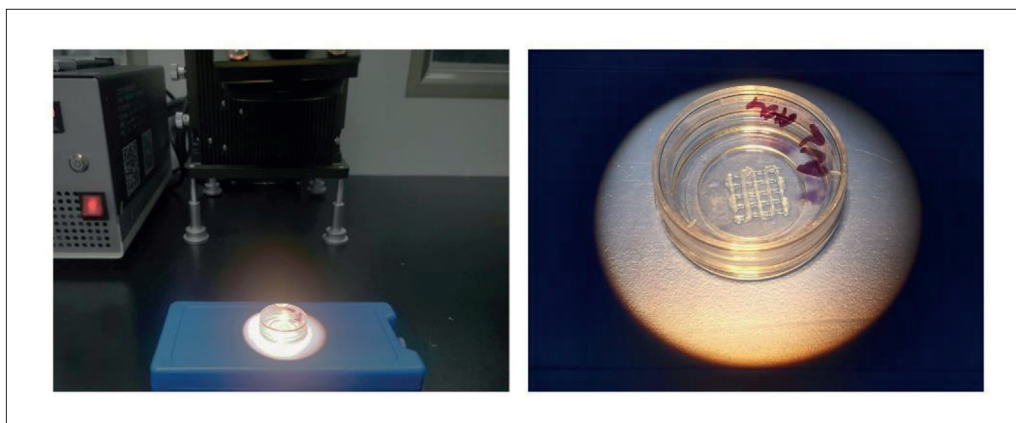
**Figure S5.** Hysteresis curves from fatigue tests on GelMA-LAP and GP-LAP under 5 cyclic compressions at 70% and 60% strain, respectively. Abbreviations: GelMA: Gelatin methacryloyl; GP: Gelatin methacryloyl/poly(ethylene glycol) diacrylate; and LAP: Lithium phenyl-2,4,6-trimethylbenzoylphosphinate.



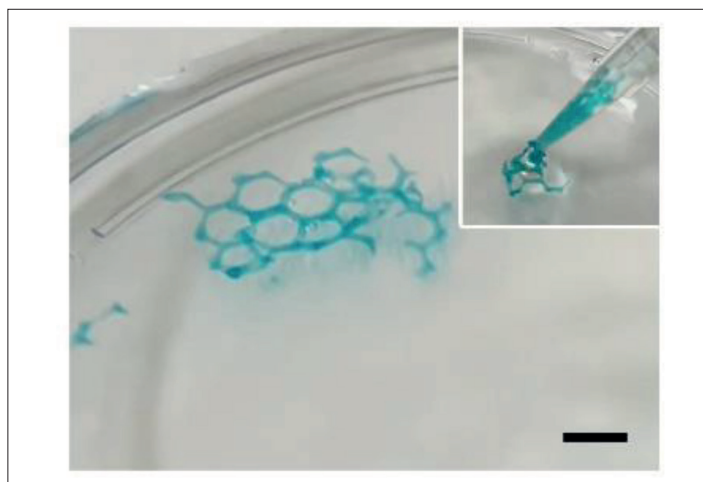
**Figure S6.** Semi-quantitative analysis and the corresponding fitted curves of pore diameter and wall thickness distribution of gelatin methacryloyl/poly(ethylene glycol) diacrylate (GP) hydrogel. The data was obtained based on more than 60 macropores from three independent random scanning electron microscopy (SEM) images.



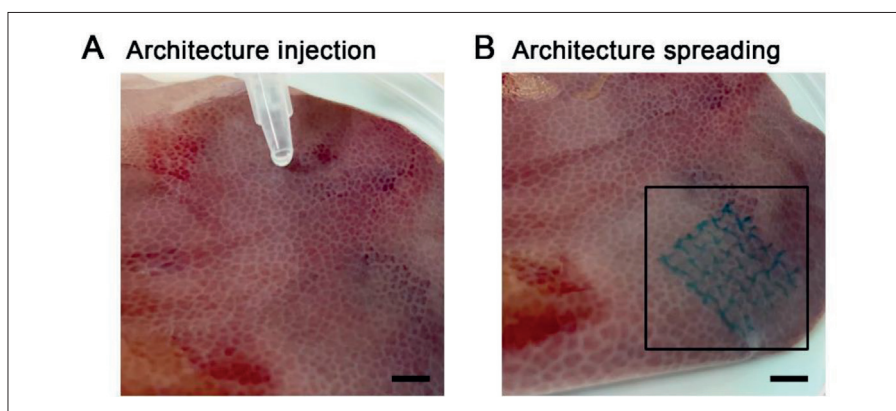
**Figure S7.** Shape fidelity assessment of the printed 10G2.5P hydrogel. (A) Macroscopic image of the hydrogel during micro-extrusion 3D printing. (B) Macroscopic image of the grid architecture after photocrosslinking for shape fidelity assessment. Bioink printability ( $Pr$ ) was calculated based on six independent images with more than 30 channels. Scale bar: 5 mm (B).



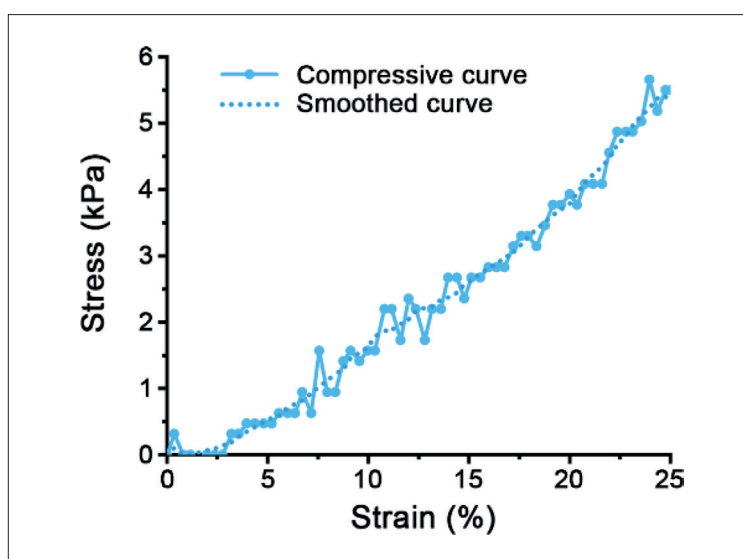
**Figure S8.** White light-induced crosslinking of 3D-printed architectures. The image of the photocrosslinking process with the white light source (left), and the image of bioprinted architectures during photocrosslinking with lid of the petri dish closed (right).



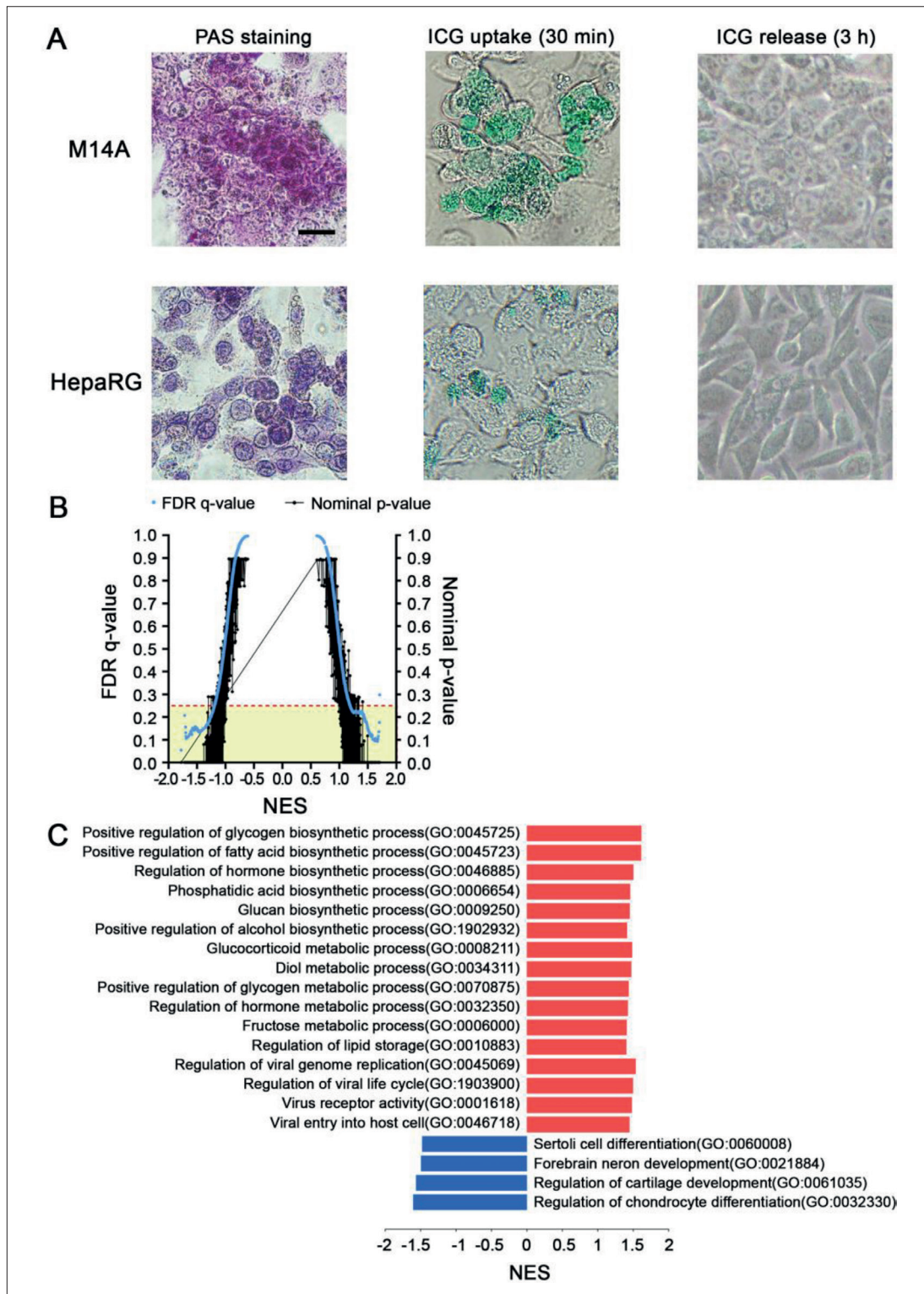
**Figure S9.** Injection of honeycomb architectures through dispensing needles with an inner diameter of 1 mm resulted in structural damage and filament fracture. Scale bar: 5 mm.



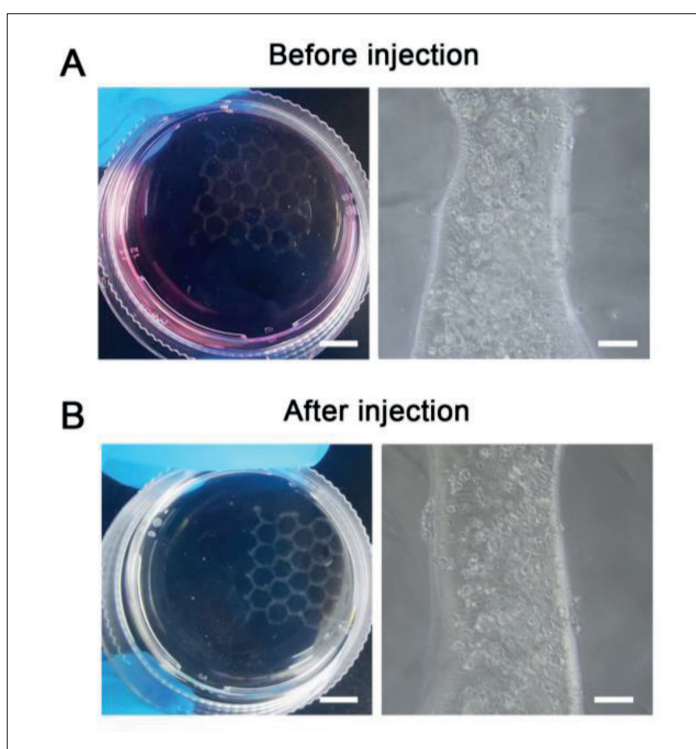
**Figure S10.** Simulation experiment for *in vivo* injection. The large-sized architectures (sinusoidal mesh) were (A) injected and (B) spread on the pork liver surface. Scale bars: 5 mm.



**Figure S11.** Compressive stress-strain curve and the corresponding smoothed curve of 10G2.5P under 10 min light exposure.



**Figure S12.** Phenotype and function evaluation of M14A compared to HepaRG in planar culture. (A) Typical images of glycogen storage with PAS staining (red-violet), ICG uptake (green), and release of M14A and HepaRG cells. (B) The NES-significance chart (M14A vs. HepaRG;  $n = 3$ ). (C) GSEA analysis of significantly enriched gene sets of M14A vs. HepaRG ( $n = 3$ ). Gene sets with absolute values of NES  $\geq 1$  and FDR  $q$ -value  $< 0.25$  are listed. Scale bar: 25  $\mu\text{m}$ . Abbreviations: PAS: Periodic acid-Schiff; ICG: Indocyanine green; FDR: False discovery rate; NES: normalized enrichment score; and GSEA: Gene set enrichment analysis.



**Figure S13.** The macroscopic and microscopic images of cell-laden architectures (A) before injection and (B) after injection. Scale bar: 5 mm (A, left; B, left), 100  $\mu$ m (A, right; B, right).

**Table S1. Antibodies used in this study**

Antibodies	Company	CAS number	Dilution
Primary			
HNF4A	Perseus Proteomics, Japan	PP-K9218-00	1:50
ALB	Abcam, UK	ab207327	1:200
MRP2	Abcam, UK	ab172630	1:200
Secondary			
Anti-rabbit IgG (H+L), F(ab') <sub>2</sub> Fragment (Alexa Fluor 488 Conjugate)	Cell Signaling Technology, USA	4412S	1:1000
Anti-mouse IgG (H+L) F(ab') <sub>2</sub> Fragment (Alexa Fluor 488 Conjugate)	Cell Signaling Technology, USA	4408S	1:1000

Table S2. Composition and mechanical properties of GelMA/PEGDA mixtures used in previous reports

Material type	Composition	PEGDA M <sub>w</sub> (Da)	Photoinitiator	Maximum strain (%)	Maximum stress (kPa)	Superelasticity	Fatigue resistance	Ref.
GelMA	10% GelMA	-	LAP	60	100	No	No	15
	10% GelMA	-	I2959	60	10	No	No	29
	5% GelMA	-	LAP	55	100	No	No	32
GelMA/ PEGDA mixture	10G5P	575	LAP	52	130	No	No	15
	10G5P	< 500	I2959	47	70.6	No	No	29
	5G10P	8000 (PEG)	LAP	80	60	No	No	32
	10G10P	2000 (PEG)	LAP	78	900	Yes	No	33
	10G5P	700	I2959	63	75	No	No	42
	10G2.5P	Not mentioned	LAP	50	52	No	No	43
	7.5G2.5P	700	EY	50	20	No	No	44
This work	10G2.5P	6000	EY	80	192	Yes	Yes	-

Abbreviations: GelMA: Gelatin methacryloyl; PEGDA: Poly(ethylene glycol) diacrylate; M<sub>w</sub>: Molecular weight; PEG: Poly(ethylene glycol); I2959: Irgacure 2959; LAP: Lithium phenyl-2,4,6-trimethylbenzoylphosphinate; and EY: Eosin-Y.

Table S3. Experimental settings for mechanical property studies

Photoinitiator	Material composition	Exposure time (min)
EY	12.5GelMA	10
	10G2.5P	7.5; 10; 12.5
	7.5G5P	10; 12.5; 15
	6.25G6.25P	12.5; 15; 17.5
LAP	12.5GelMA	0.5
	10G2.5P	0.5

Abbreviations: GelMA: Gelatin methacryloyl; LAP: Lithium phenyl-2,4,6-trimethylbenzoylphosphinate; and EY: Eosin-Y.

Table S4. Injection capacity of large-sized architectures with disparate repetitive units

Inner diameter (mm)	Comparable sizes in clinic	Honeycomb	Semi-re-entrant honeycomb	Re-entrant honeycomb	Sinusoidal mesh	Lozenge grid	Curved mesh
5	7F (catheter)	✓	✓	✓	✓	✓	✓
4	6F (catheter)	✓	✓	✓	✓	✓	✓
3	4F (catheter)	✓	✓	✓	✓	✓	✓
2	12G (needle)	✓	✓	✓	✓	✓	✓
1.5	14G (needle)	✓	✓	✓	✓	✓	✓
1	17G (needle)	✗	✗	✗	✗	✗	✗

✓: Samples remained integral, with little filament fracture; and ✗: Samples were damaged, with obvious filament fracture.

**(B) Supplementary videos**

**Video S1.** Recording of cyclic compression tests on gelatin methacryloyl/poly(ethylene glycol) diacrylate-eosin-Y (GP-EY) hydrogel.

**Video S2.** Recording of the cyclic pinch of circular ring structures.

**Video S3.** Large-sized architectures with disparate repetitive units injected through 2 mm needles with complete structural integrity and recovery.

**Video S4.** Large-sized architectures with disparate repetitive units injected through 1.5 mm needles with complete structural integrity and recovery.

**Video S5.** Injection of sinusoidal mesh-printed samples onto the surface of the pork liver.

**Video S6.** Large-sized cell-laden architectures after a 16-day culture (honeycomb patterns) injected through 1.5 mm needles with complete structural integrity and recovery.