3D hollow-structured hydrogels with editable macrostructure, function, and mechanical properties induced by segmented adjustments

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Supplementary Figures

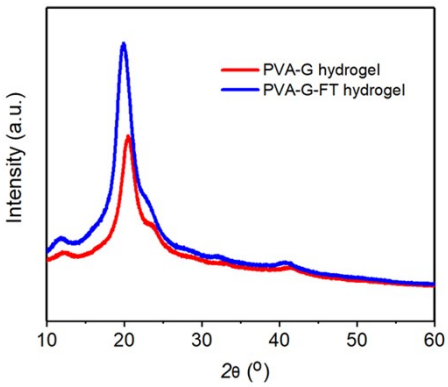

Figure S1. X-Ray Diffraction (XRD) patterns of PVA-G and PVA-G-FT hydrogels.

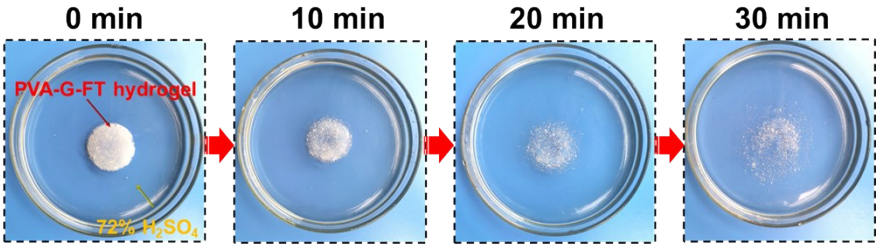

Figure S2. The autonomous degradation process of PVA-G-FT hydrogel in 72% H_2SO_4 solution.

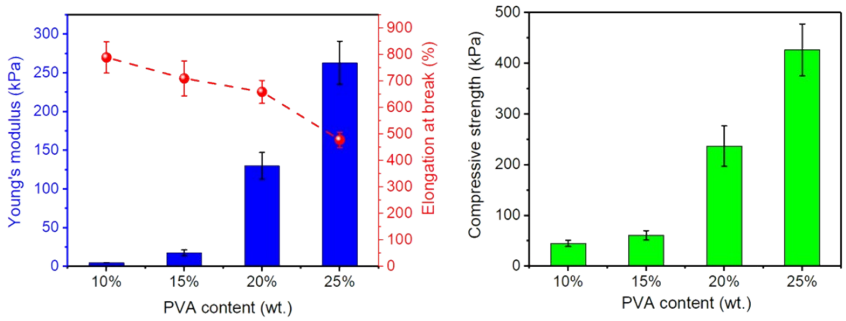

Figure S3. The Young's modulus, elongation at break, and compressive strength of PVA-G-FT hydrogels with various PVA contents.

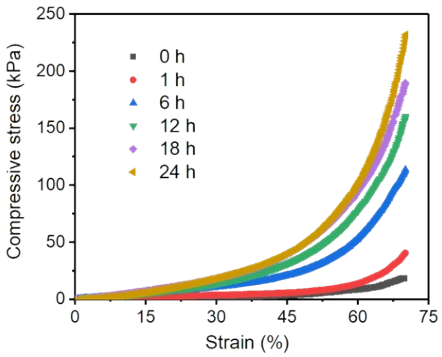

Figure S4. Typical compressive stress-strain curves of PVA-G-FT hydrogels treated with different freezing times.

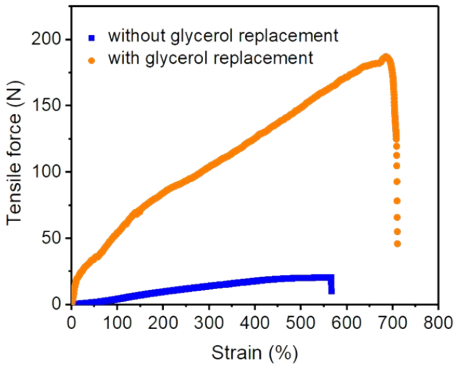

Figure S5. Tensile force−strain curve for PVA-G-FT hydrogel tube with or without glycerol replacement.

Experimental section

1. The preparation procedure of hydrogels

1.1 First, 2.5 g PVA-1799(Aladdin Industrial Corporation) was completely dissolved in 10 g of water, and then 3 mL of borax solution (5 wt%, Aladdin Industrial Corporation) was added to the above solution to obtain PVA hydrogel. Next, 2.5 g PVA-1799 was completely dissolved in a mixed solvent of 9 g of water and 1g of glycerol, and then 3 mL of borax solution (5 wt%) was added to the above solution to obtain PVA-G hydrogel (where PVA content is 20 wt%).The PVA-G hydrogel was frozen at -30 ℃ for 24 h and then thawed to obtain PVA-G-FT hydrogel. Among them, the PVA-G hydrogel was coated on different templates and then subjected to a freezing -thawing method to obtain hollow hydrogels of different shapes (unless otherwise stated, the preparation of the hollow hydrogel follows the above method and formula). Note, the various PVA contents and freezing time were applied to obtain PVA-G-FT hydrogels with different strengths. The PVA-G-FT hydrogel tube was soaked in glycerol for 3 hours to obtain an antifreeze and anti-dryness tube.

1.2 Firstly, some multi-wall carbon nanotubes (CNTs, Aladdin Industrial Corporation)/ proanthocyanins (PC, Shanghai Macklin Biochemical Co., Ltd) and 2.5 g PVA-1799 was completely dissolved in a mixed solvent of 9 g of water and 1g of glycerol, and then 3 mL of borax solution (5 wt%) was added to the above solution to obtain CNTs-PVA-G/PC-PVA-G hydrogel. The obtained hydrogel was frozen at -30 ℃ for 24 h and then thawed to obtain CNTs-PVA-G-FT/PC-PVA-G-FT hydrogel.

Table S1. The content of various hydrogels

Code	PVA (g)	Glycerol (g)	Water (g)	Borax solution (5 wt%)	PC/PVA	CNTs/PVA
PVA	2.5	0	10	3 mL	0	0
PVA-G	2.5	1	9	3 mL	0	0
PVA-G-FT	2.5	1	9	3 mL	0	0
CNTs-PVA-G-FT	2.5	1	9	3 mL	0	0.05/0.1/0.15
PC-PVA-G-FT	2.5	1	9	3 mL	0.05	0

2. Characterization of hydrogels and pure hydrogel tube

The X-ray diffraction (XRD) patterns of PVA-G and PVA-G-FT hydrogels were measured on a Rigaku Ultima IV (Japan) diffractometer, using Cu Kα radiation. Tensile tests were performed on a digital tensile machine (KJ-1065B, Kejian Instrument Co. Ltd, Dongguan, China), with a loading rate of 30 mm/min. The tensile stress (T) was calculated as T= F/S, where F is the tensile load and S is the cross-sectional area. Young's modulus of the hydrogel was calculated from the slope of the 0-20% strain region in the tensile stress-strain curve. Cylindrical hydrogel specimens were used for

the compression tests. The compressive stress (t) was calculated as t = f/s, where f is the compressive load and s is the original area of the sample. The crosshead speed during compression was maintained at 10 mm/min. The compressive modulus of the hydrogel was calculated from the slope of the 0-20% strain region in the compressive stress-strain curve.

3. Characterization of functional hydrogel tubes

The freezing temperature of the hydrogels were investigated using a differential scanning calorimetry (DSC 214, Netsch). The cooling cycle was carried out from 20 °C to −45 °C at a rate of 5 °C/min. The conductivity of hydrogels was measured by an LCR meter (TH 2832), the applied voltage is 1 V and the measuring frequency is 1 kHz. The conductivity (σ) was calculated using the following equation, $\sigma = L/RA$, in which R is the resistance, L and A are the materials' length and cross-sectional area, respectively. The PC-PVA-G-FT hydrogel samples were irradiated using 808 nm NIR laser (Shengzhen) with a photothermal power of 2.5 W. The distance between the light source and the hydrogel surface was 15 cm. FLIR (USA) was applied to provide thermal imaging technology. First, the PVA-G and PVA-G-FT hydrogel tubes are cut into thin slices along the radial direction. Then, observe the wall thickness of the gel tube through an optical microscope (Axio-Imager LSM-800, Germany).

4.Application of hollow CNTs-PVA-G-FT(CNTs/PVA=0.15) hydrogel

The conductive hydrogel ring (d=8 cm and 1cm) can be used as a strain sensor for

monitoring the motion signals (recorded by LCR meter). Specifically, the sensor is wrapped directly on the arm and finger of an adult to receive electric-signals generated by human movement (pressure and strain).

The conductive hydrogel ring (d=8 cm) can be used as a bioelectrode to collect electrophysiological signals (EMG and ECG) of the human body in a quiet state using a multichannel physiological signal acquisition and process system.

All tests are performed at room temperature.