Supporting Information

Constructing self-healing flexible supercapacitors via graphene oxide synergistic multi-network polymer-supramolecular hydrogel electrolyte

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Experimental section

S1. Materials

Acrylamide (AM, 99.0%), carboxymethyl chitosan (CMCS，99.0%), polyethylene glycol (PEG, 99.0%.), N, N'-methylenebis acrylamide (MBA, 98%), potassium persulfate (KPS, 98.5%.), Sulfuric acid (H_2SO_4, 1 M), graphene oxide (GO, experimental preparation). All chemicals were analytical grade and used without further purification.

S2 Preparation of the PAM/CMCS/PEG/GO hydrogel

PAM/CMCS/PEG/GO hydrogel was prepared as follows: in 10 mL of 1 mol L^{-1} sulfuric acid (H_2SO_4) solution, 0.2 g CMCS and 1 g PEG were added and stirred uniformly for 1 h to form a homogeneous solution. Subsequently, 2.7 g AM was added to the solution in the presence of appropriate amounts of MBA and KPS, and stirring was continued for 1 h until complete dissolution. Finally, GO with different mass fractions (3 wt%, 5 wt%, 7 wt%) was added to the solution, stirred until a homogeneous solution was formed and immediately poured into a circular Petri dish and put into an oven at 60 ℃ for 30 min to polymerize the PAM/CMCS/PEG/GO hydrogel electrolyte film with physical cross-linking and chemical cross-linking.

S3. Material characterization

Fourier transform infrared spectroscopy (FT-IR, Digilab Merlin FTS 3000) was used to evaluate the chemical structure of hydrogels in the range of 500-4000 cm^{-1}. The morphology of the hydrogels was observed by scanning electron microscopy (SEM, FE-SEM, Ultra Plus,) The crystal structure of the material was determined by X-ray diffraction (XRD, D/Max-2400, physics) equipped with Cu Ka radiation (k=1.5418 A).

S4. Mechanical properties measurement

The hydrogel tensile test was carried out using AGS-X universal testing machine (AGS-X100 N Shimadzu, Japan), and the hydrogel sample (20×15×2mm) was tested with a tensile rate of 20 mm min^{-1}. Compression tests of the hydrogel were performed on the AGS-X universal test machine.

S5 Fabrication of the FSC

The 16 mg of activated carbon (AC), 2 mg of acetylene black and 2 mg of polyvinylidene fluoride (PVDF) were dispersed in N-methyl-2-pyrrolidone (NMP) to form uniform slurry. Then, the slurry was coated on nickel foams (2 cm × 1.5 cm) with the average mass of 8 mg, and dried at 60℃ for 8 h. Finally, a symmetric SC with sandwich structure (AC/ PAM/CMCS/PEG/GO hydrogel electrolyte /AC) was fabricated based on AC as electrode materials, PAM/CMCS/PEG/GO hydrogel as electrolyte.

S6. Electrochemical properties measurement

The electrochemical performance of the assembled SC is tested by electrochemical workstation (CHI660D, Shanghai Chenhua, China). Cyclic voltammetry (CV) was performed at different scanning rates (10~100 mV s^{-1})

and constant current charge-discharge (GCD) tests were performed at different current densities (0.3~3A g^{-1})

The specific capacitance of SC is calculated according to the following formula:

$$C_A = 4I \times \frac{\Delta t}{\Delta V}$$

Δt is the discharge time (h), I is the current density (A g^{-1}) and ΔV voltage range (V). The energy density (E_A, Wh kg^{-1}) and power density (P_A, W kg^{-1}) are calculated by the following formula:

$$E_A = \frac{CV2}{4}$$

$$P_A = \frac{EA}{\Delta t}$$

The electrochemical impedance spectroscopy (EIS) was conducted using an electrochemical workstation (CHI660D, Shanghai Chenhua, China) within the frequency range of 10^{-2} to 10000 Hz. The calculation formula is as follows:

$$\sigma = 1000\ L / (R \times S)$$

where L is the thickness of the hydrogel electrolyte(cm), *S* is the area of the hydrogel electrolyte (3

cm^2), R denotes the measured resistance.

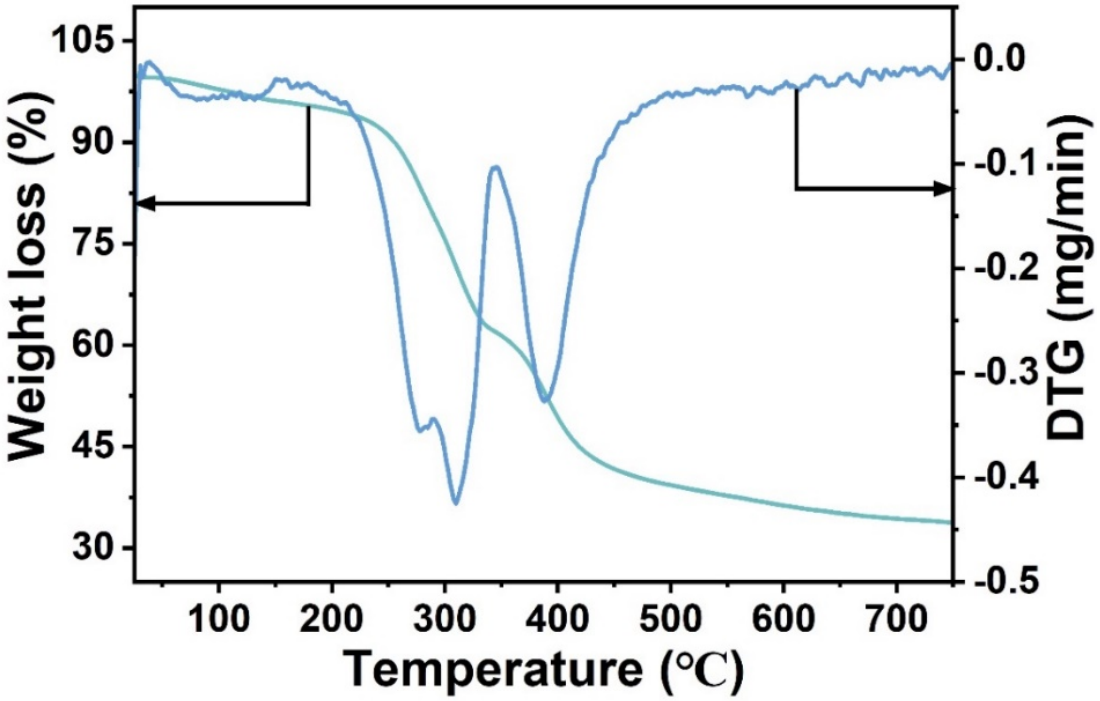

Fig. S1 TGA and DTG diagram of PAM/CMCS/PEG/GO hydrogel.

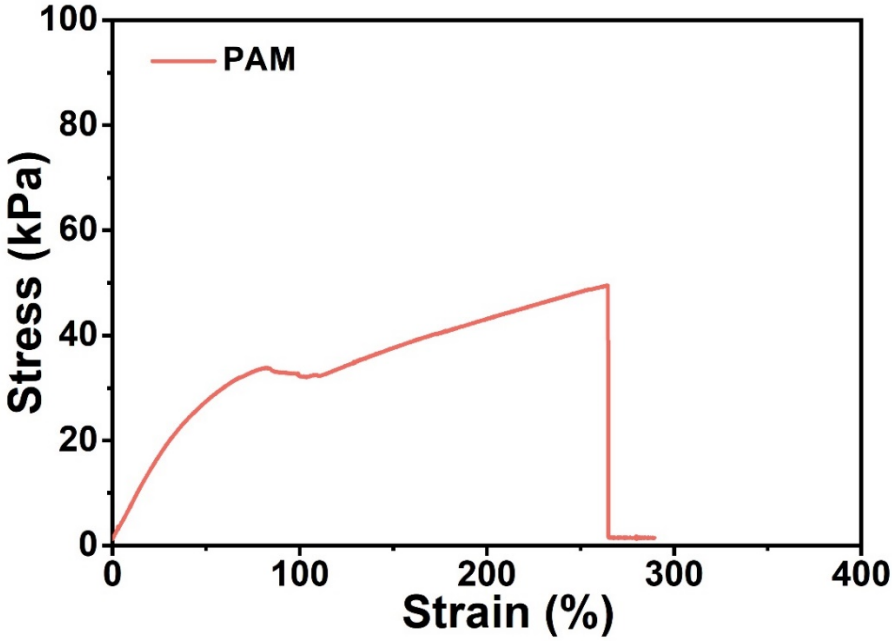

Fig. S2 Tensile stress-strain curves of PAM hydrogel.

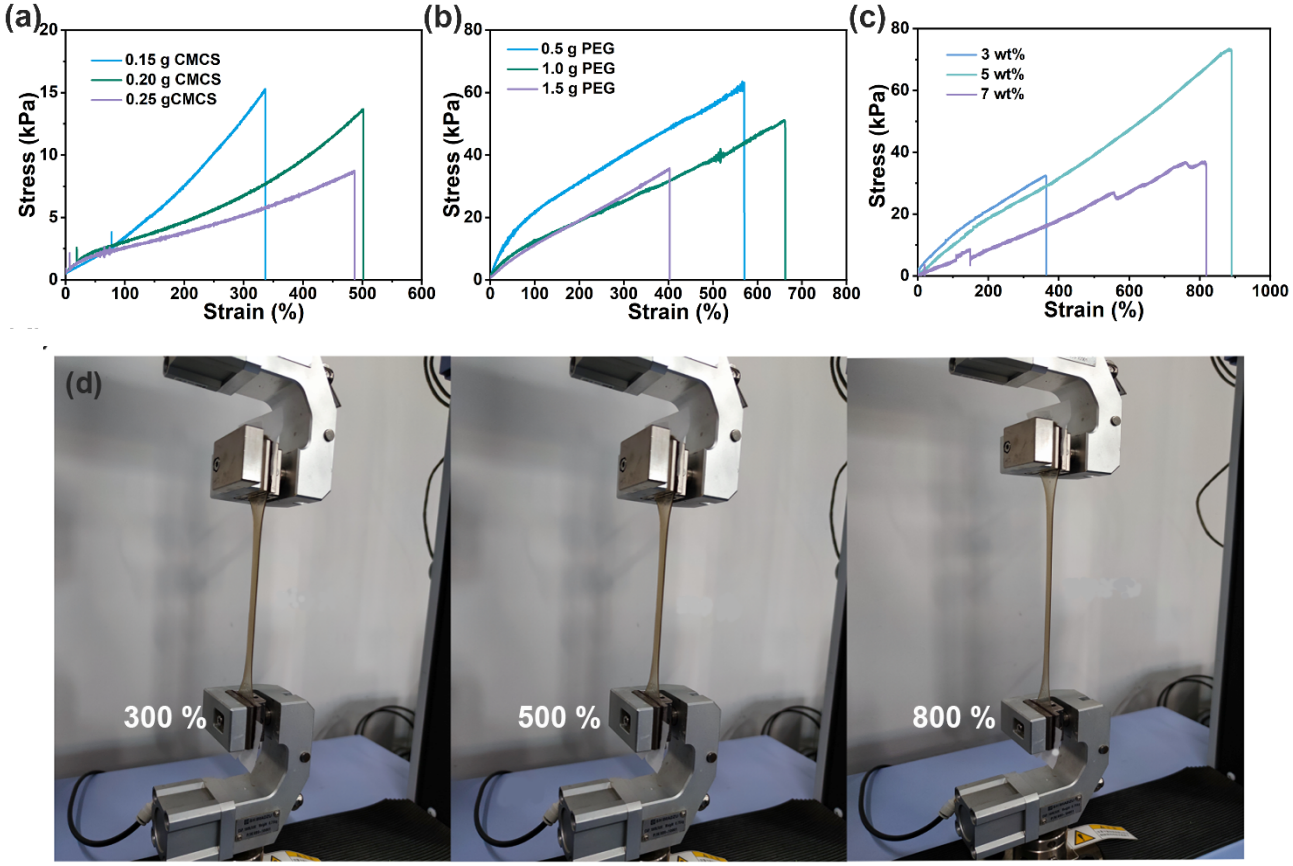

Fig. S3 Tensile stress-strain curves of (a) PAM/CMCS hydrogel with different CMCS contents, (b) PAM/CMCS/PEG hydrogel with different PEG contents, (c) PAM/CMCS/PEG/GO hydrogel with different GO contents, (d) Schematic diagram of tensile properties of PAM/CMCS/PEG/GO hydrogel.

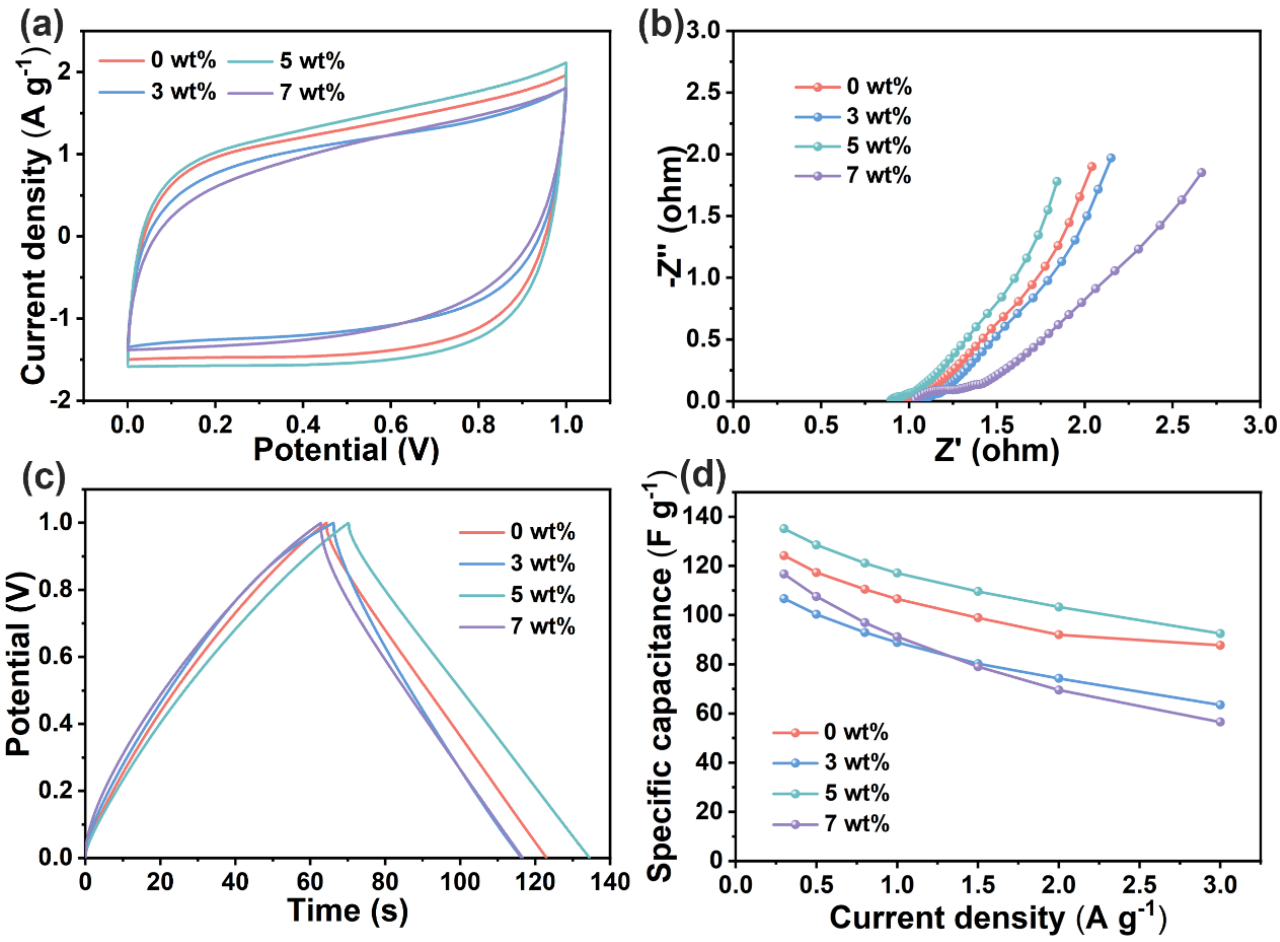

Fig. S4 PAM/CMCS/PEG/GO hydrogel-based SCs of different GO contents (a) CV curves at sweep speed of 50 mV s^{-1}, (b) EIS diagram, (c) GCD curves s at current density of 0.5 A g^{-1}, (d) Specific capacitance curves.

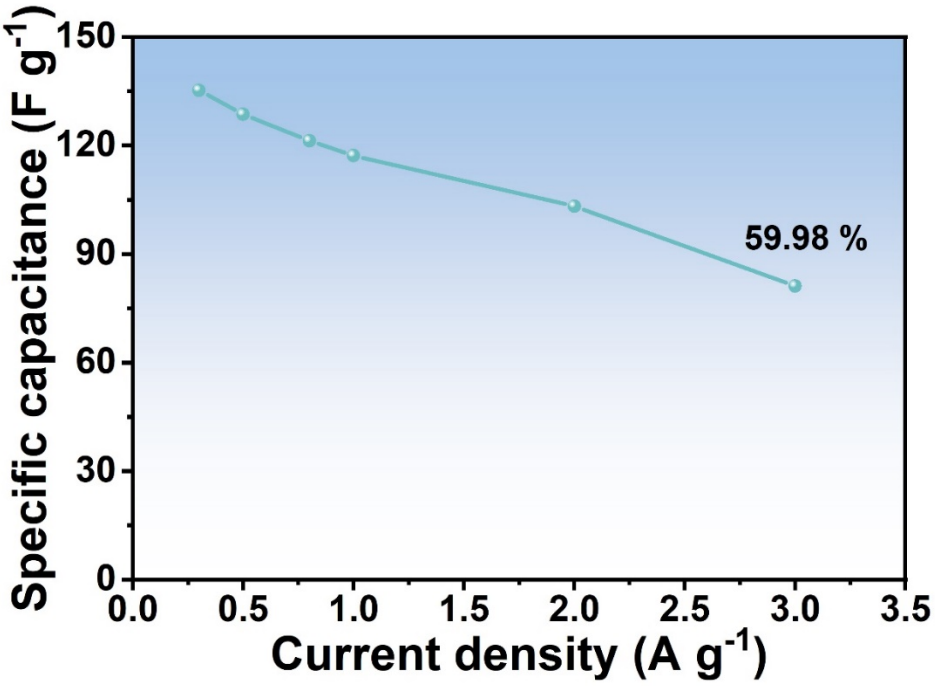

Fig. S5 Specific capacitance of PAM/CMCS/PEG/GO hydrogel-based FSC at different current densities.

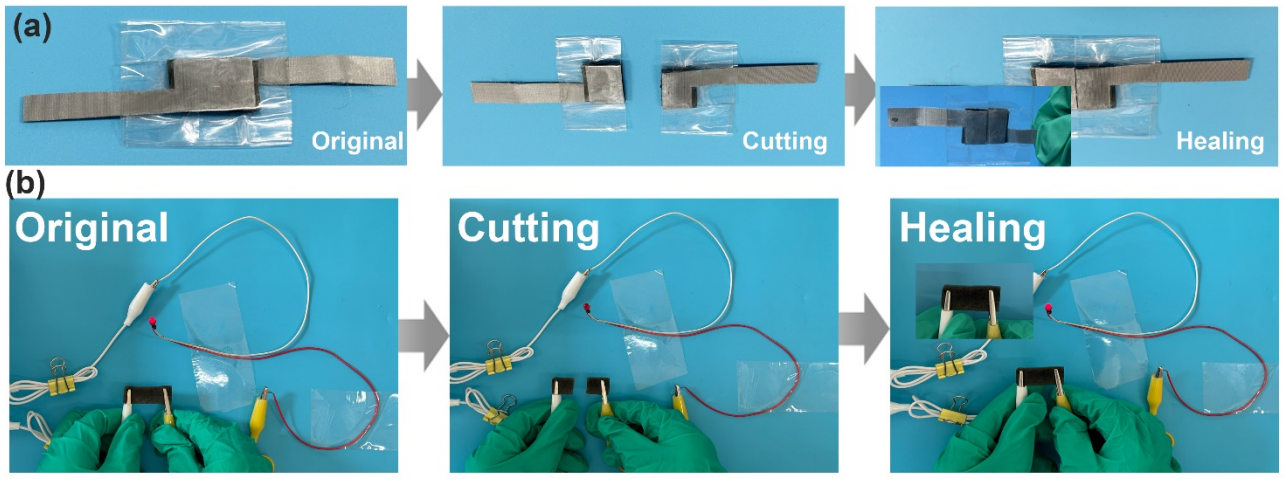

Fig. S6 (a) Digital photographs of self-healing process, (b) Optical pictures of self-healing and electrical conductivity of the PAM/CMCS/PEG/GO hydrogel electrolyte.

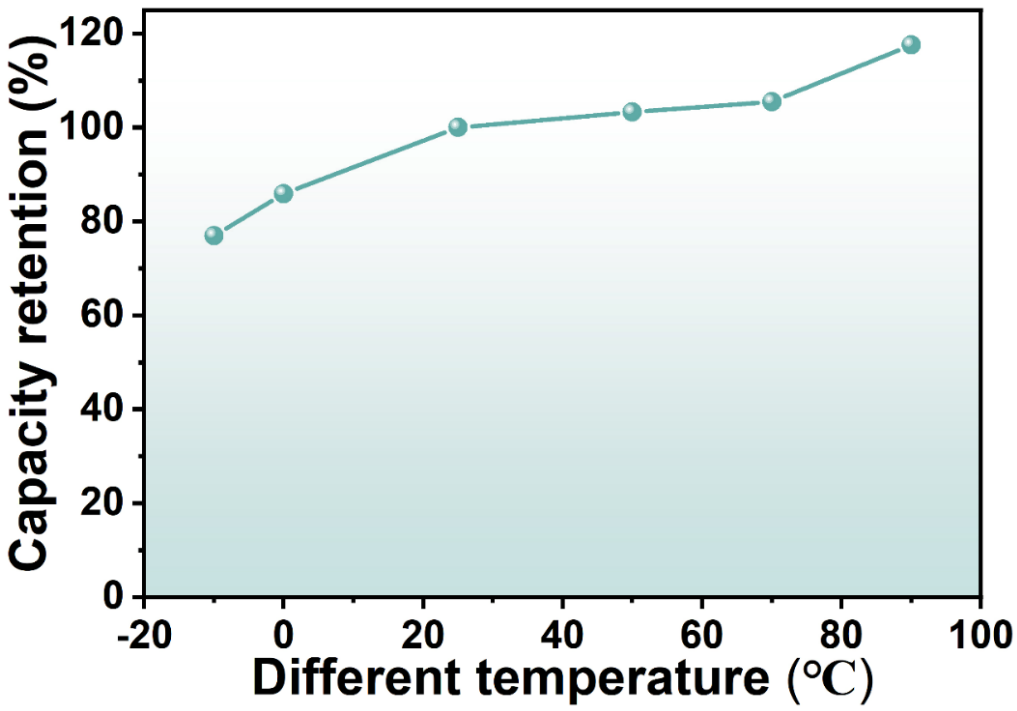

Fig. S7 Capacitance retention rate of PAM/CMCS/PEG/GO hydrogel-based SCs at different temperatures.

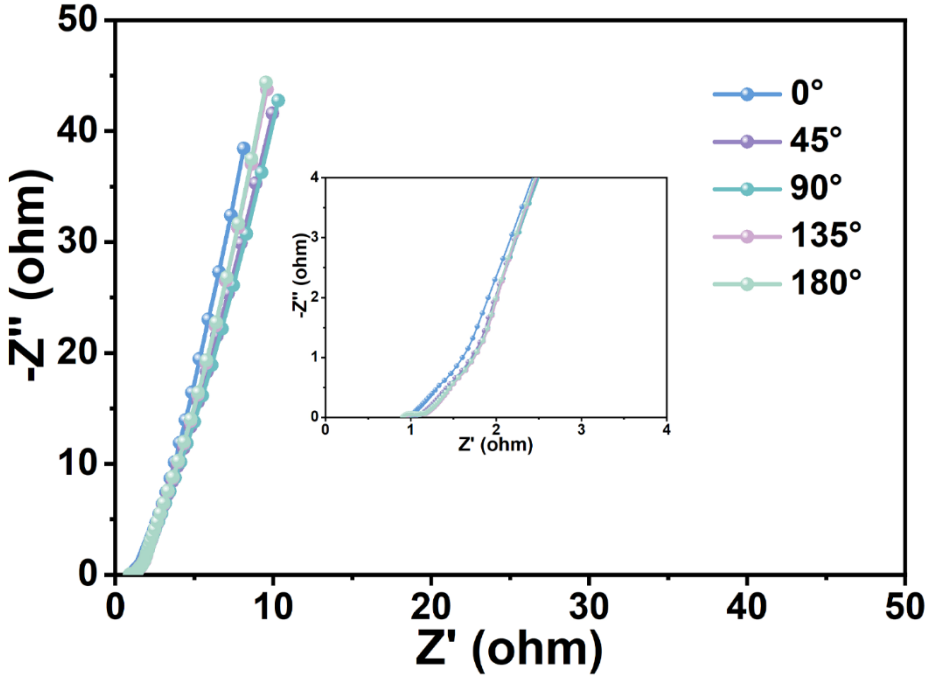

Fig. S8 EIS diagram of PAM/CMCS/PEG/GO hydrogel-based SCs under different bending angles.

Table S1. Comparison of electrochemical performance of capacitor with previous reports.

Materials	P_A	E_A	Refs.
PAM/CMCS/PEG/GO	150 W kg^{-1}	4.7 Wh kg^{-1}	This work
PVA/Agar/EMIMBF	150 W kg^{-1}	4 Wh kg^{-1}	[S1]
Li-AG/PAM	48 W kg^{-1}	1.75 Wh kg^{-1}	[S2]
MGO/PAM	100 W kg^{-1}	9.8 Wh kg^{-1}	[S3]
PAM/β-CD/EMIMBF4-0.6	120 W kg^{-1}	6.83 Wh kg^{-1}	[S4]
PL-Proline	125 W kg^{-1}	5.1 Wh kg^{-1}	[S5]
5PA/Gly-2OHE	164 W kg^{-1}	3.2 Wh kg^{-1}	[S6]
PAM-HPC-0.4	72 W kg^{-1}	4.7 Wh kg^{-1}	[S7]
GCHME-KI	75 W kg^{-1}	2.3 Wh kg^{-1}	[S8]

Table S2. Comparison of the self-healing efficiency and ionic conductivity of our device with recently reported gel-based supercapacitors.

Materials	Healing times	Healing efficiency (%)	Ionic conductivity (mS cm^{-1})	Refs.
PAM/CMC/Ag/$ZnSO_4$	5	95 %	23.1	[S9]
B-PVA/KCl/GO	5	90.5 %	47.5	[S10]
PVA/PA-PANI	5	80 %	46.5	[S11]
Fe-DPCL	7	86 %	30	[S12]
AA/Betaine/$ZnCl_2$	5	88.3 %	-	[S13]
PVA/Agar/$EMIMBF_4$/Li_2SO_4	5	80 %	45	[S14]
PVA/ Gly/ H_2SO_4	10	48.5 %	66.8	[S15]

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