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Multifunctional conductive hydrogel for wearable sensor and supercapacitor

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1. Materials

Acrylamide (AM), dopamine (DA), N, N-Methylenebisacrylamide (BIS), and Choline chloride (ChCl) are purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Ethylene glycol (EG) and carboxylated cellulose nanofibers (CCNFs, diameter: 50 nm, length: 1~3 μm) are purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Xylitol (Xy) is purchased from Anhui Zesheng Technology Co., Ltd. Diethylene glycol (DG), glycerol (Gly), ammonium persulfate (APS), sodium hydroxide (NaOH) and ethyl cellulose are purchased from Sinopharm Chemical Reagent Co., Ltd. Active carbon (YEC-8A) (AC) is purchased from Fuzhou Yihuan Carbon Co., Ltd. N-Propanol are purchased from Sinopharm Chemical Reagent Co., Ltd. Acetylene black is purchased from Taiyuan LZY Technology Co., Ltd. Ecoflex is purchased from Smooth-On.

2. Preparation of conductive hydrogels

Preparation of deep eutectic solvents (DESs): ChCl was mixed with DG, Gly, EG, Xy respectively at a fixed molar ratio of 1:2, and then heated and stirred at 100 °C for 2 h to obtain four different DESs, which were labeled as DES_{DG}, DES_{Gly}, $DES_{EG,}$ and DES_{Xy}. The four DESs

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were stored in a dry place for subsequent experiments.

Preparation of DESs-based conductive hydrogels (HDES): HEDS hydrogels were synthesized with modifications from previous reports[1, 2]. Typically, DES and NaOH solution (pH = 11) were uniformly mixed according to the volume ratio of 1:1, and fully stirred. DA was then added to the mixed solution and stirred thoroughly for 30 min to generate PDA. AM, APS, and BIS were further added to the mixed solution and stirred for 10 min, then transferred to a mold (55 mm×15 mm×3 mm) and UV irradiation (365 nm, 7 W) for 30 min to obtain HDES. HDES based on DES_{DG}, DES_{Gly}, DES_{EG}, and DES_{Xy} were marked as $HDES_{DG}$, $HDES_{Gly}$, $HDES_{EG}$, and $HDES_{Xy}$, respectively. $HDES_{EGn}$ based on different contents of DES_{EG} are prepared by changing the volume ratio of DES_{EG} and NaOH solutions. And the volume ratios of DES_{EG} and NaOH solutions of 1:9, 3:7, 5:5, 7:3, and 9:1 are labeled as $HDES_{EG1}$, $HDES_{EG3}$, $HDES_{EG5}$, $HDES_{EG7}$, and $HDES_{EG9}$, respectively. The detailed ingredients of HDES and $HDES_{EGn}$ are shown in **Table S1 and S2.**

In order to avoid the impact of the preparation environment (temperature, humidity, etc.) on the test performance, all hydrogels were placed at room temperature environment (25 °C, 55% humidity) for one day before performing various performance tests.

3. Fabrication of $HDES_{EG}/CCNF_{3\%}$ hydrogel-based strain sensors

Resistive-type strain sensors were fabricated by fixing two copper wires on the edges of both ends of the $HDES_{EG}$/CCNF hydrogel with copper tape. The gauge factor (GF) of strain sensor is defined as follows:

$$GF = \frac{(\Delta R/R_0)}{\varepsilon} \#(1)$$

where $\Delta R/R_0$ is the relative resistance change and ε is the applied strain to the hydrogel.

4. Fabrication of $HDES_{EG}/CCNF_{3\%}$ hydrogel-based capacitive pressure sensors

The $HDES_{EGn}/CCNF_{3\%}$ hydrogel-based capacitive pressure sensor with sandwich structure consists of Ecoflex (55 mm×15 mm×3 mm) as the dielectric layer and $HDES_{EG}/CCNF_{3\%}$ hydrogel (55 mm×15 mm×2.5 mm) as the electrodes. The Ecoflex was placed in the middle of two hydrogels, and then the two copper wires were fixed on one end of the two hydrogels with copper tape, and finally wrapped with 3M HVB tape to obtain the $HDES_{EG}/CCNF_{3\%}$ hydrogel-based capacitive pressure sensor. The sensitivity (S) of the capacitive pressure sensor is defined as follows:

$$S = \frac{(\Delta C/C_0)}{\sigma} \#(2)$$

where $\Delta C/C_0$ is the relative capacitance change and σ is the applied stress to the hydrogel.

5. Fabrication of $HDES_{EG}/CCNF_{3\%}$ hydrogel-based supercapacitors

The flexible supercapacitors with sandwich structures consist of two single electrodes and a solid electrolyte, in which the $HDES_{EG}/CCNF_{3\%}$ hydrogel acts as the solid electrolyte. A single electrode composed of a current collector (sliver paste) and an active material layer was prepared on a PET substrate by screen printing technology. First, the silver paste was printed on the PET substrate and dried at 110 °C for 1 h to eliminate the organic solvent content, forming the current collector layer. Then the AC ink was printed on the current collector layer and dried at 80°C for 2h to obtain a single electrode with a square pattern (10 mm×10 mm). AC ink is formulated by evenly mixing AC, acetylene black, and ethyl cellulose solution (5 wt%) at a mass ratio of 75:15:10. The electrode load is 2-3 mg/cm^2. Finally, two electrodes and the $HDES_{EG}$/CCNF hydrogel (10 mm×10 mm× 1mm) were assembled into a sandwich-structured flexible supercapacitor.

6. Mechanical properties test

Mechanical properties were tested by an electric tensile testing machine (ZQ-990LA-5). The test samples were calculated from the actual dimensions of the hydrogel after one day in the mold and the size of the mold is 55 mm×15 mm×3 mm. The breaking strength and the loading-unloading cycle experiments were tested at a speed of 60 mm/min. The compressive strength test was performed at a fixed rate of 10 mm/min.

Toughness (T) is estimated by the area under the stress-strain curves until fracture point by the following equation:

$$T = \int_{\varepsilon_0}^{\varepsilon_0} \sigma(\varepsilon) d\varepsilon \#(3)$$

Where ε_0 and ε correspond to the initial stretch and fracture stretch, respectively.

The dissipated energy (ΔU_i) for the i^{th} cycle, is defined as the area of the hysteresis loop encompassed by the loading-unloading curve, which is calculated by integrating the area under the stress-strain curve:

$$\Delta U_i = \int_{loading} \sigma d\varepsilon - \int_{unloading} \sigma d\varepsilon \#(4)$$

The energy dissipation ratio (σ), measures how efficiently a material dissipates energy and is calculated as below:

$$\delta = \frac{\Delta U_i}{U_i} \times 100\% \#(5)$$

$$\Delta U_i = \int_0^{\sigma_{max}} \sigma d\varepsilon \#(6)$$

where U_i is the elastic energy stored in the materials when it is loaded elastically to a stress σ_{max} in the i^{th} cycle. Young's modulus is calculated from the slope of the initial linear region of the stress-strain curves (10-20% strain).

7. Conductivity test

The conductivity of hydrogels was measured by electrochemical impedance spectroscopy (EIS) in the frequency range of 10^{-2} Hz to 10^{6} Hz by an electrochemical workstation (CHI 760E). The calculation formula is as follows:

$$\sigma = \frac{L}{AR} \#(7)$$

Where L (cm) and A (cm^2) are the thickness and the contact area of hydrogel while R (Ω) is the resistance of the tested hydrogel.

8. Adhesive properties test

Tensile-adhesion test: Two adherends were fixed on the surfaces of two T-shaped metal plates, and the conductive hydrogel (15 mm × 15 mm × 2.5 mm) was placed between the adherends. The T-shaped metal plate was fixed by the clamps of the electric tensile testing machine. Adhesion tests were performed after one minute of adhesion. The calculation formula is as follows:

$$\sigma = \frac{F}{S} \#(8)$$

Where F and S are the axial force and the contact area between hydrogel and adherend respectively.

Lap-shear test: The hydrogel (10 mm×10 mm×1 mm) adheres between two adherends, and the shear strength of the hydrogel is measured under the action of axial force after two hours of adhesion. The calculation formula refers to formula (6). Where F and S are the axial force and the contact area between hydrogel and adherend respectively.

9. . Characterization of Supercapacitors

The electrochemical performance of the assembled supercapacitor is tested by CV (scanning rate range from 5 to 100 mV/s), GCD (current density between 1 and 10 mA/m^2), and EIS (1×10^{-2}Hz to 1×10^{6} Hz, 5 mV). The voltage window for CV and GCD tests is set from 0 to 1 V. The device is tested for cycling stability at a current density of 5 mA/m^2.

The single electrode-specific capacitance (C_S) is determined using equation (7):

$$C_S = \frac{I\Delta t}{S\Delta V} \#(9)$$

where I (mA) is the current, Δt (s) is the discharge time, S is the area of single-electrode, and ΔV (V) is the voltage change.

Table S1 Composition of HDES

Abbreviation	DES	AM (g)	APS (g)	BIS (mg)	DA (mg)	H_2O (mL)	DES (mL)
$HDES_{DG}$	DES_{DG}	2.5	0.25	6	5	5	5
$HDES_{Gly}$	DES_{Gly}	2.5	0.25	6	5	5	5
$HDES_{EG}$	DES_{EG}	2.5	0.25	6	5	5	5
$HDES_{Xy}$	DES_{Xy}	2.5	0.25	6	5	5	5

Table S2 Composition of $HDES_{EG}$

Abbreviation	AM (g)	APS (g)	BIS (mg)	DA (mg)	H_2O (mL)	DES_{EG} (mL)
$HDES_{EG1}$	2.5	0.25	6	5	9	1
$HDES_{EG3}$	2.5	0.25	6	5	7	3
$HDES_{EG5}$	2.5	0.25	6	5	5	5
$HDES_{EG7}$	2.5	0.25	6	5	3	7
$HDES_{EG9}$	2.5	0.25	6	5	1	9

Table S3 Composition of $HDES_{EG}/CCNF_{n\%}$

Abbreviation	CCNFs/AM wt.%	AM (g)	APS (g)	BIS (mg)	DA (mg)	H_2O (ml)	DES (ml)
$HDES_{EG}/CCNF_{1\%}$	1	2.5	0.25	6	5	5	5
$HDES_{EG}/CCNF_{2\%}$	2	2.5	0.25	6	5	5	5
$HDES_{EG}/CCNF_{3\%}$	3	2.5	0.25	6	5	5	5
$HDES_{EG}/CCNF_{4\%}$	4	2.5	0.25	6	5	5	5

Table S4 Performance comparison of $HDES_{EG}$/CCNF with other research

Self-Adhesion	Conductivity (mS/cm)	elongation at break	Minimum working temperature	Reference
Yes	0.231	>1200%	—	[3]
No	1.2	>600%	-20 °C	[4]
Yes	0.22	178%	—	[5]
No	0.58	<350%	—	[6]
No	0.003	>650%	—	[7]
No	0.064	>500%	-18 °C	[8]
Yes	0.65	<1500	—	[9]
No	1.7	>450%	-20 °C	[10]
Yes	—	7300%	-10 °C	[11]
No	0.4	1920%	—	[12]
No	0.21	<100%	—	[13]
Yes	0.99	>400%	-20 °C	**This work**

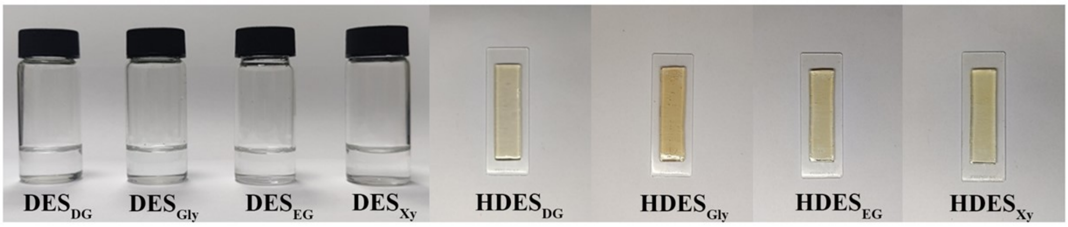

Figure S1 Optical images of four DESs and corresponding hydrogels.

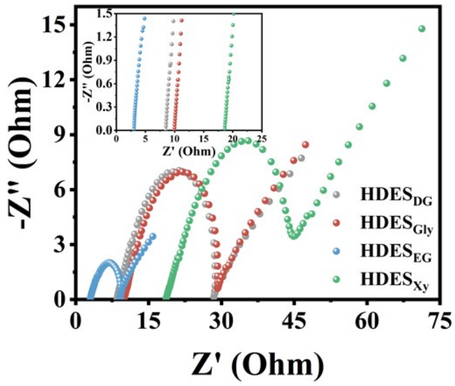

Figure S2 Electrochemical impedance spectroscopy of $HDES_{DG}$, $HDES_{Gly,}$ $HDES_{EG}$ and $HDES_{Xy.}$

Figure S3 Optical image of $HDES_{EG9}$

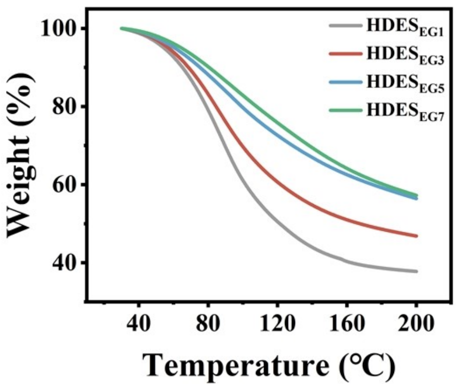

Figure S4 Thermogravimetric analysis curve of HDESEGn (n = 1, 2, 3, 4).

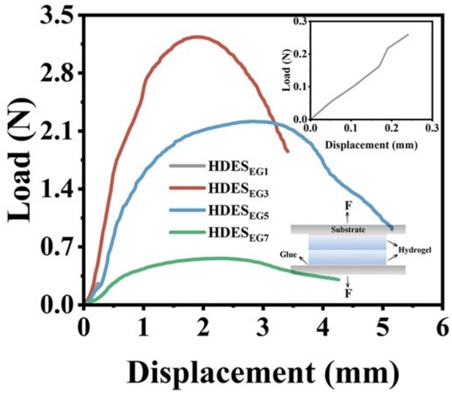

Figure S5 The load-displacement curves of $HDES_{EGn}$ (n = 1, 3, 5, 7).

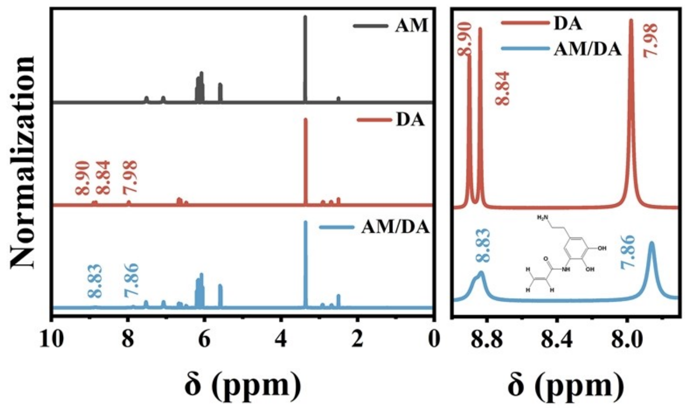

Figure S6 The ^{1}HNMR spectra of AM, DA and mixture in dimethyl sulfoxide, and the possible structure of complexation.

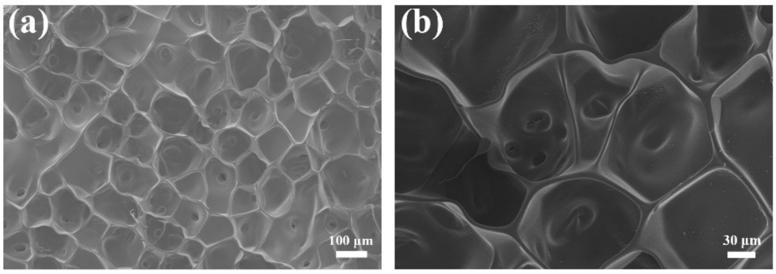

Figure S7 (a, b) SEM image of $HDES_{EG5}$ under different magnifications.

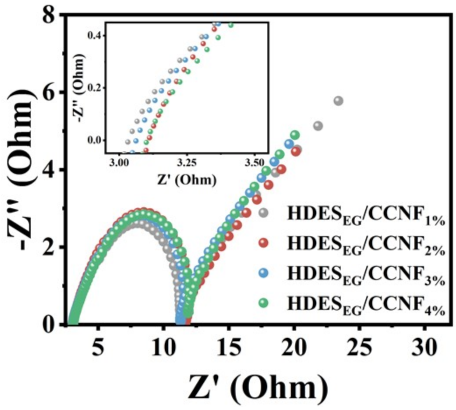

Figure S8 Electrochemical impedance spectroscopy of HDES/CCNF$_{n\%}$ (n = 1, 2, 3, 4).

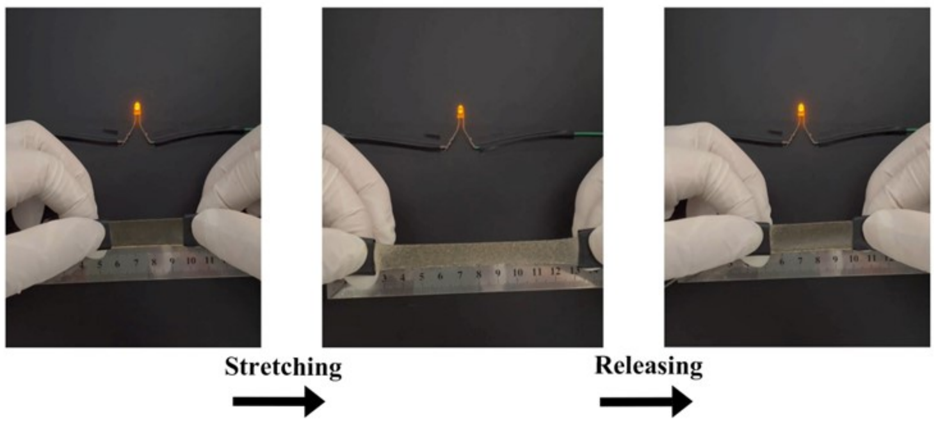

Figure S9 Optical photograph of brightness change of LED lamp integrated with hydrogel during the stretching/release of HDES$_{EG}$/CCNF$_{3\%}$.

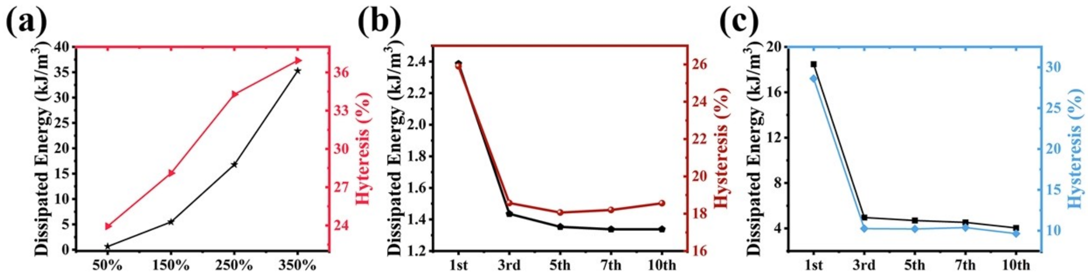

Figure S10 (a) Dissipated energy at different strains under a single loading-unloading cycle (50%, 150%, 250%, 350%). (b) Dissipated energy corresponding to different loading-unloading cycles for stretching without time interval at 100% strain. (c) Dissipated energy corresponding to different loading-unloading cycles for stretching without time interval at 300% strain.

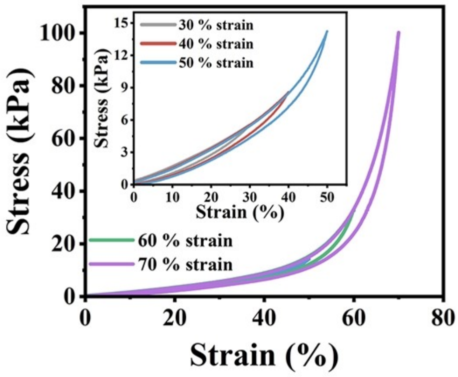

Figure S11 Compressive strength of $HDES_{EG}/CCNF_{3\%}$ hydrogels at 30-70% strain.

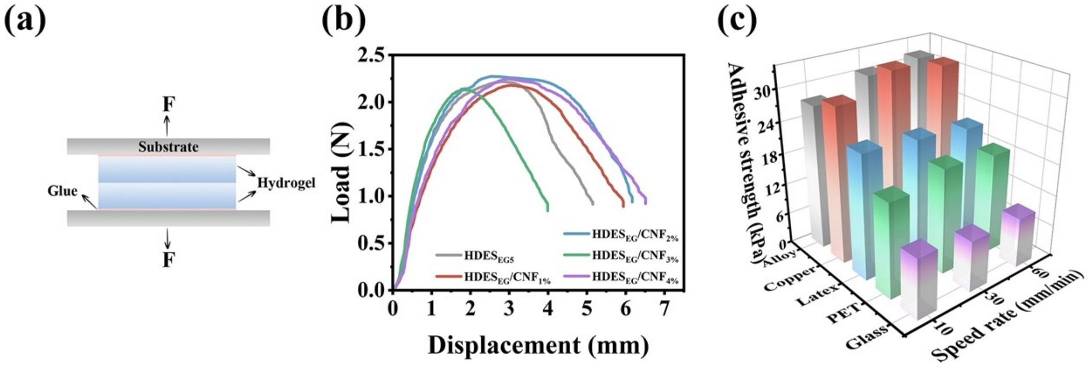

Figure S12 (a) Schematic diagram of tentile-adhesion test. (b) The load-displacement curve of $HDES_{EG}/CCNF_{n\%}$ (n = 1, 2, 3, 4). (c) The adhesive strength of $HDES_{EG}/CCNF_{3\%}$ under different speed rates.

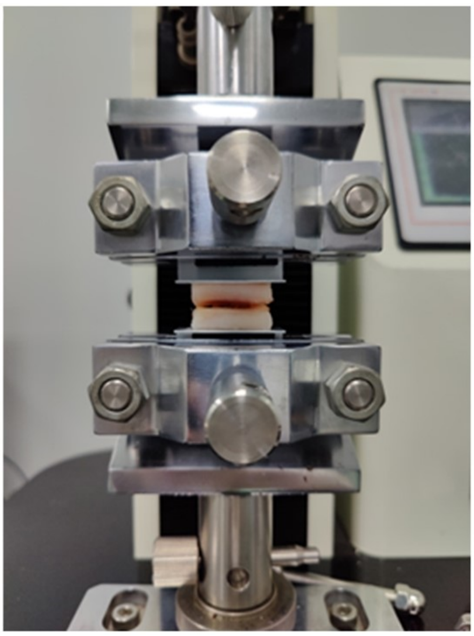

Figure S13 Optical image of the adhesion strength test on pig skin.

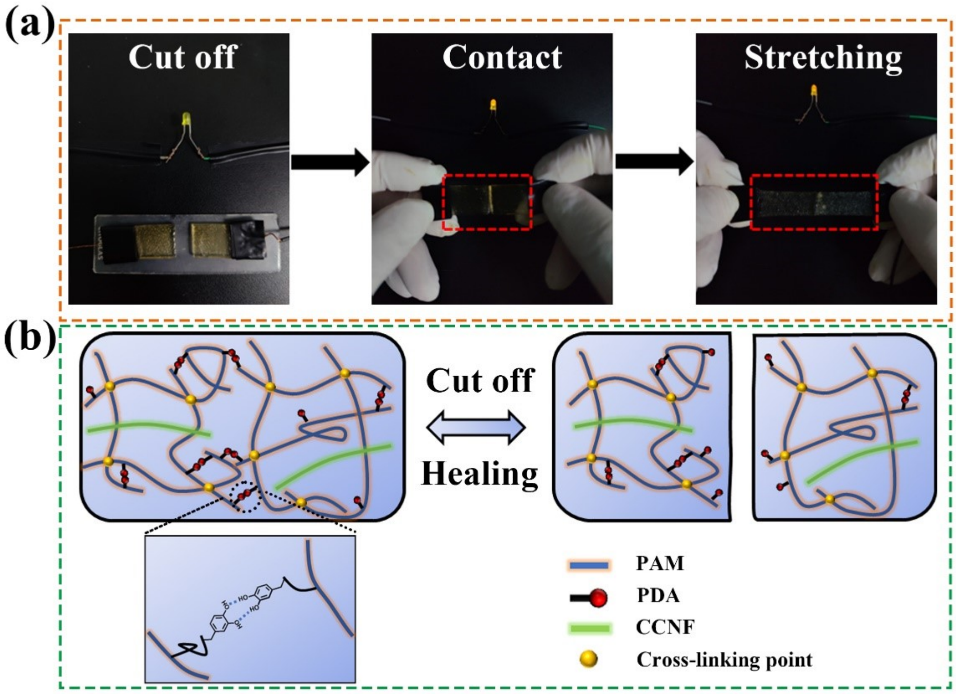

Figure S14 (a) Optical photograph of the brightness change of the LED lamp integrated with the hydrogel when the hydrogel is cut off, contacted and stretched. (b) Schematic diagram of the self-healing mechanism of the $HDES_{EG}/CCNF_{3\%}$.

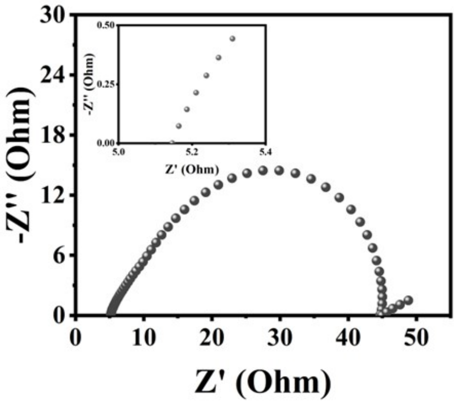

Figure S15 The EIS of hydrogel after freezing for 15 days.

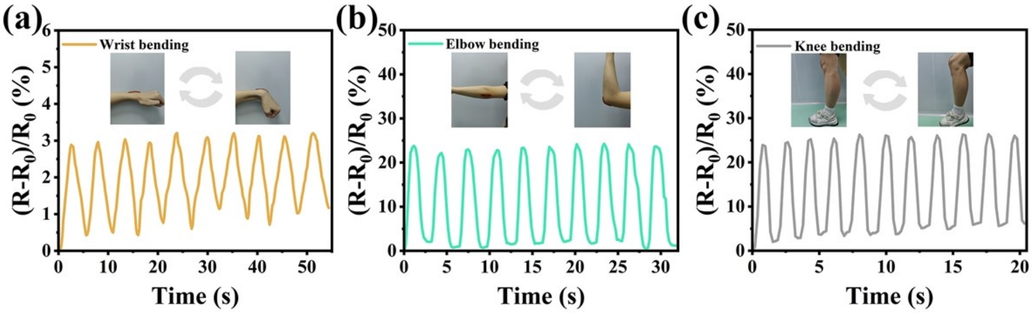

Figure S16 Application of DES_{EG}-CCNF hydrogel-based strain sensors in joint motion monitoring: (a) Wrist movement, (b) arm movement and (c) knee movement.

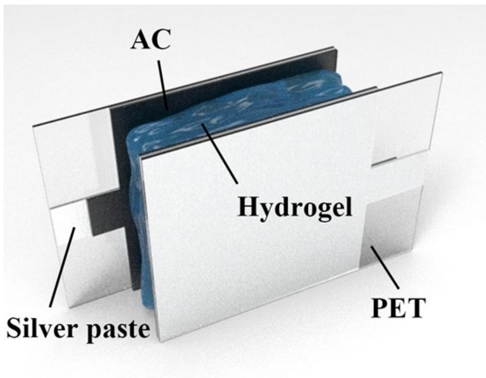

Figure S17 Schematic diagram of assembled supercapacitor with the hydrogel as a solid electrolyte.

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