

Supporting information

Bioadhesive and Electroactive Hydrogels for Flexible Bioelectronics and Supercapacitors Enabled by Redox-Active Core-Shell PEDOT@ZIF System

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1. Materials

Dopamine hydrochloride, 4,5-Dichloroimidazole, 3,4-ethoxylene dioxy thiophene was purchased from Sigma-Aldrich (USA). Acrylamide (AM), Zinc acetate dihydrate, Methanol, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, acrylamide, Ammonium persulfate (APS), Ethanol, N, N-methylenebisacrylamide (BIS), and N, N, N', N'-tetramethylethylenediamine (TMEDA) were purchased from Kelong (Chengdu, China).

2. Methods

2.1 Preparation of polydopamine modified ZIF-71 (PZIF-71)

The preparation process of ZIF-71 has been reported previously¹. Firstly, 2 mg ml⁻¹ methanol solution of zinc acetate was mixed in 12 mg ml⁻¹ methanol solution of 4,5-Dichloroimidazole under stirring for 30 min. Then, the mixture solution was centrifuged at 10000 rap⁻¹ with methanol to remove the excess reactants for twice. Secondly, 0.1 g of dopamine was dissolved in Tris-HCl solution (pH=8.5) for 30 min of pre-polymerization process. Then, the ZIF-71 was added into the resulting pre-polymerization solution. After 12 h of polymerization, the solution was centrifuged at 8000 rap⁻¹ with RO water for three times. The dopamine modified ZIF-71 was obtained and was denoted as PZIF-71.

2.2 Preparation of PEDOT@PZIF-71 core-shell nanoparticles

The as-prepared PZIF-71 and EDOT was dissolved into ethanol under vigorously stirring. Then, FeCl_3 solution was added dropwise into the PZIF-71/EDOT solution. The mixture was stirred for 24 h under ice bath for the polymerization of EDOT and assemble on the surface of PZIF-71. The final core-shell nanoparticles were obtained after centrifuging and washing the mixture with RO water several times, which was denoted as PEDOT@PZIF-71. Different mass ratio of EDOT and PZIF-71 of PEDOT@PZIF-71 nanoparticles were also prepared and the details were list in Table S1.

Table S1 Different stoichiometry and composition of a series of nanoparticles

EDOT:PZIF-71 (Mass ratio)	4,5- Dichloroi midazole (mg)	Zinc acetate dihydrate (mg)	DA (mg)	EDOT (μ L)	FeCl ₃ ·H ₂ O (g)	methanol (mL)	Tirs-HCl (mL)	Ethanol (mL)
1:3	160	110	100	76	2	10	20	40
1:2	160	110	100	152	4	10	20	40
1:1	160	110	100	228	6	10	20	40
2:1	160	110	100	304	8	10	20	40
3:1	160	110	100	380	10	10	20	40

2.3. Preparation of various hydrogels

The hydrogels were prepared according to the following procedure. AM, ammonium persulfate (APS), N, N-methylenebisacrylamide, and TMEDA were added in a breaker placed in an ice bath. The PEODT@PZIF-71/PAM hydrogel was synthesized after stirring the reaction mixture for 10 min. Hydrogels with different mass ratios of PEODT@PZIF-71 to AM were prepared. The compositions of the hydrogels are listed in Table S2.

Table S2 Compositions of the hydrogels.

Hydrogels	ZIF/AM (wt.%)	PEDOT/AM (wt.%)	PEDOT@PZIF				TMEDA (μ L)	Water (mL)
			/AM (wt.%)	AM (g)	APS/AM (wt.%)	BIS/AM (wt.%)		
PAM	0	0	0	2.6	2	0.2	10	10
ZIF-71/PAM	0.75	0	0	2.6	2	0.2	10	10
PEDOT/PAM	0	0.75	0	2.6	2	0.2	10	10
0.25% PEDOT@PZIF- 71/PAM	0	0	0.25	2.6	10	0.2	10	10
0.5% PEDOT@PZIF- 71/PAM	0	0	0.5	2.6	10	0.2	10	10
0.75% PEDOT@PZIF- 71/PAM	0	0	0.75	2.6	10	0.2	10	10
1% PEDOT@PZIF- 71/PAM	0	0	1	2.6	10	0.2	10	10
1.25% PEDOT@PZIF- 71/PAM	0	0	1.25	2.6	10	0.2	10	10

2.4 Preparation of PEDOT@PZIF-71/PAM hydrogel-based supercapacitor: Two pieces of same size PEDOT@PZIF-71/PAM hydrogel was used as both positive and negative electrodes for supercapacitor. One piece of fiber membrane (pre-soaked in 1 M Na₂SO₄) was used as the separator.

3. Characterization

3.1. Characterization of PEDOT@PZIF-71 core-shell nanoparticles

The morphologies of the PEDOT@PZIF-71 were observed via scanning electron microscopy (SEM, JSM 6390, JEOL, Japan) and transmission electron microscopy (TEM, Tecnai-F30, FEI, USA).

The zeta potentials of the various nanomaterials were determined by carrying out electrophoretic light scattering measurements using a Zeta-sizer (Malvern, UK).

The surface area of pristine ZIF-71, PEDOT and PEDOT@PZIF-71 was measured via N₂ absorption-desorption isotherms at 77.35 K by ASAP 2460 system. All samples were degassed at 120 °C for 4 h under a N₂ flow prior to measurements. The surface area was then determined by standard multipoint Brunauer-Emmett-Teller (BET) and Langmuir models utilizing MicroActive for ASAP 2460 Version 2.01.

The catechol groups of PZIF-71 and PEDOT@PZIF-71 was monitored by XPS analysis. A monochromatic Al K α X-ray excitation source was used at 15 KV and 150 W. the C1s spectra at the binding energy of 285 eV was set as the reference.

Nanoparticle tablets were prepared using a tableting machine to measure the conductivity of the nanoparticles. The electrical conductivities of various nanoparticle tablets (R = 15 mm, H = 1 mm) were measured using a four-probe resistivity test system (Jingge, Suzhou, China).

3.2. Characterization of hydrogels

Morphologies of the various hydrogels. The as-prepared hydrogels were freeze-dried at -80 °C. The cross-section of the hydrogels was observed by SEM (JSM 6300, JEOL, Japan).

Mechanical properties of the various hydrogels. The mechanical performances of the hydrogels were evaluated by a universal test machine (Instron 5567, USA) according to the published procedures². The tensile tests of the hydrogel (width: 25 mm, length: 5mm, thickness: 2 mm) were carried out at an extension speed of 20 mm min⁻¹. The fracture energy of the specimens was tested by the standard single-edge notch test³. The crosshead speed was 2 mm s⁻¹ and the specimens were fixed between clamps with a gauge length of 5 mm. The thickness and width of the specimens were 2 and 25 mm, respectively. Two specimens (one notched and the other unnotched) were pulled during the test. The unnotched specimen was pulled to obtain the stress-strain curve, whereas the notched one was used to determine the critical extension ratio (λc), at which cracks expanded. A notch of 5-mm length was introduced in the middle of the notched specimen. The fracture energy (J m⁻²) was calculated using Eq. S1, proposed by Greensmith for elastomers⁴:

$$Gc = \frac{1}{B} \left[\frac{\partial (\Delta U)}{\partial a} \right] = 2 \frac{\pi}{\sqrt{\lambda c}} a w_0 \quad (\text{Equation S1})$$

where a is the length of the crack and λc is the extension ratio at which cracks expand in the single-edge notch tests.

Adhesive strengths of the hydrogels. The adhesive strengths of the PAM, PEDOT/PAM, ZIF-71/PAM, and PEDOT@PZIF-71/PAM hydrogels were measured by performing tensile adhesive tests based on a previously reported procedure⁵. Hydrogels with a bonded area of $25 \times 25 \text{ mm}^2$ were applied to the surfaces of the specimens. The samples were pulled to failure at a crosshead speed of 5 mm min^{-1} using a universal testing machine (Instron 5567, USA) equipped with a 100 N-load cell under ambient conditions until their detachment.

Cytocompatibility of the hydrogels. The cytocompatibility of the PAM, PEDOT/PAM, ZIF-71/PAM, PEDOT@PZIF-71/PAM hydrogels (D: 8 mm, H: 2 mm) was evaluated by C2C12 cells (Stem Cell Bank, Chinese Academy of sciences) according to our previous reported studies⁶. Briefly, the samples were purified by repeatedly deswelling in pure ethanol and swelling in PBS, at least three cycles. They were further sterilized by 75% ethanol for a week. The various hydrogels were placed into 48-well cell plate. C2C12 cells (5×10^4) were seeded onto the surface of the hydrogel and cultured in cell incubator for 2 h to allow the cell adhesion. after that, 1 mL DMEM supplemented with 10% fetal bovine serum were added into the cell plate. Then, a multi-channel cell electrostimulation (ES) device developed in-house was used to carry out the ES experiments of the cells. The ES experiments were carried out when the cells were seeded on the hydrogels after 1 day. Various ES voltages (0, 300, and 600 mV) were applied on the cells for 30 min every day. After 7 days of stimulation, the proliferation was assayed to examine the electrical response of C2C12 on the hydrogels. Cell proliferation was evaluated by MTT assay. Calcein AM staining was used to observe the cell viability on the hydrogels. In addition, the focal adhesion formation was assessed by rabbit monoclonal antibody to vinculin (ab196454, Abcam, UK) and 4,6-diamidino-2-phenylindole (DAPI, Abcam, UK) after three days' culture. The cells were examined using a confocal laser scanning microscope (CLSM, Leica, Germany).

In vivo evaluation of the biocompatibility of the hydrogels. All the animal experiments were performed according to the protocols approved by the local ethical committee and the laboratory animal administration rules of China. The surgical procedures were carried out as reported previously⁶. For biocompatibility studies, four New Zealand white rabbits of either gender (about 3 kg) were sedated with pentobarbital (3 wt.%, 40 mg kg^{-1}) and a section of fur on their back was shaved. The four parallel sterilized PAM, PEDOT/PAM and PEDOT@PZIF-71/PAM hydrogels (D = 5 mm, H = 3 mm, total 12 samples) were separately implanted into different subcutaneous muscle spaces. On the 14th day after the surgery, the subcutaneous

muscle tissues surrounding the samples were harvested. The harvested muscle tissues were fixed in a 10 % neutral buffered formalin solution for 24 h and were stained with hematoxylin and eosin (H&E) for evaluating the biocompatibility of the hydrogels.

Conductivity of the hydrogels. The conductivity of the hydrogels was measured using a two-probe method on an electrochemical system (CHI 660, Chenghua, China) according to a previously reported procedure⁷. In brief, the hydrogels (R = 7.5 mm, L = 10 mm) were placed between two parallel titanium electrodes, which were connected by an electrical loop. Electrical currents (I) of 0.001, 0.002, 0.003, 0.004, and 0.005 A were applied to the hydrogel and the electrical potentials (V) were recorded. The conductivities σ of the hydrogels were calculated using equation S2.

$$\sigma = \frac{IL}{V * \pi R^2} \text{ (Equation S2)}$$

where L and R are the length and diameter of the hydrogels, respectively.

3.3 Electrochemical characterization

Electrochemical characterization of as-prepared nanoparticles

The cyclic voltammetry (CV) measurements of the ZIF-71, PEDOT and PEDOT@PZIF-71 nanoparticles were carried out on an electrochemical analytical system (Chi 660E, Chenhua, China) in a three-electrode system. The nanoparticles coated on a nickel foam were used as the working electrode, and Pt and Ag/AgCl (KCl sat.) were used as the counter and reference electrodes, respectively. A NaSO₄ solution (0.1 M, pH = 7.4) was used as the electrolyte. A CV scan rate of 5 mV s⁻¹ was used under the potential window from 0 to 1 V (vs. Ag/AgCl). The galvanostatic charge-discharge (GCD) test of PEDOT@PZIF-71 nanoparticles were conducted at various current density from 0.001 A to 0.01 A with the potential window between 0 to 1 V.

Electrochemical characterization of as-prepared hydrogel supercapacitor.

The electrochemical performance of as-prepared PEDOT@PZIF-71/PAM hydrogel supercapacitor was measured in a two-electrode system using the same electrochemical analytical system, CV was conducted at room temperature within the potential range from -0.2 to 1 V, with the scanning rate at 5, 10, 20, 50 and 100 mV s⁻¹. The GCD testing was performed within the potential range from 0 to 1 V. The gravimetric specific capacitance C_{sp} (F g⁻¹) of as-

prepared samples was calculated from its galvanostatic charge-discharge curves according to equation S3:

$$C_{sp} = \frac{It}{m\Delta V} \quad (\text{Equation S3})$$

where I is the constant current, m is the total mass of the active materials, ν is the scan rate, and ΔV is the width of the voltage window.

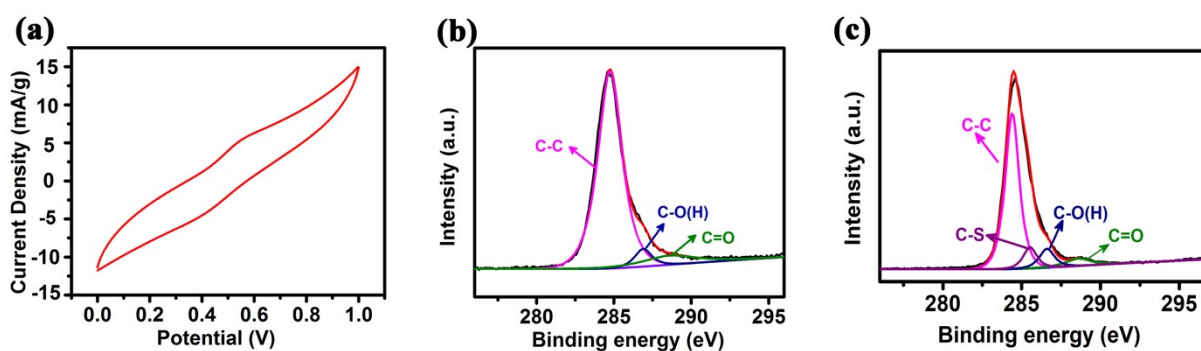


Fig. S1. (a) CV analysis of PEDOT-PZIF-71. XPS spectrums of (a)PZIF-71 and (b) PEDOT@PZIF-71

Table S3 Peak species, binding energies and peak area ratio of the high-resolution C1s spectra of PZIF-71 and PEDOT@PZIF-71 NPs

Functional Groups	C-C	C-S	C-O	C=O
Binding Energy(eV)	284.5	285.2	286.6	288.6
PZIF-71	87.25%	0%	4%	8.75%
PEDOT@PZIF-71	80.8%	7.3%	7.5%	4.4%

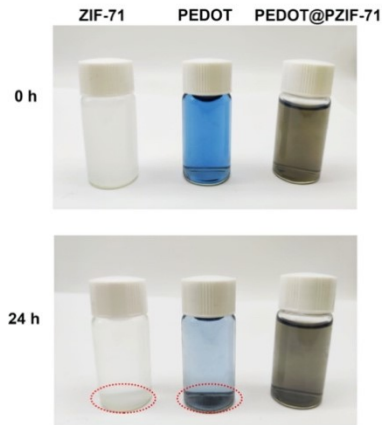


Fig. S2. The graphs of as-prepared ZIF-71, PEDOT, and PEDOT@PZIF-71 NPs were dispersed in the aqueous solution.

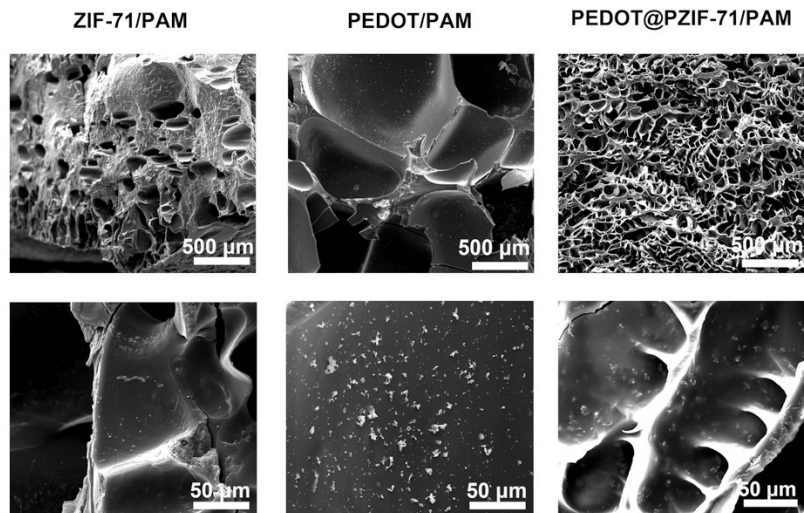


Fig. S3. Morphologies of ZIF-71/PAM, PEDOT/PAM and PEDOT@PZIF-71/PAM hydrogel

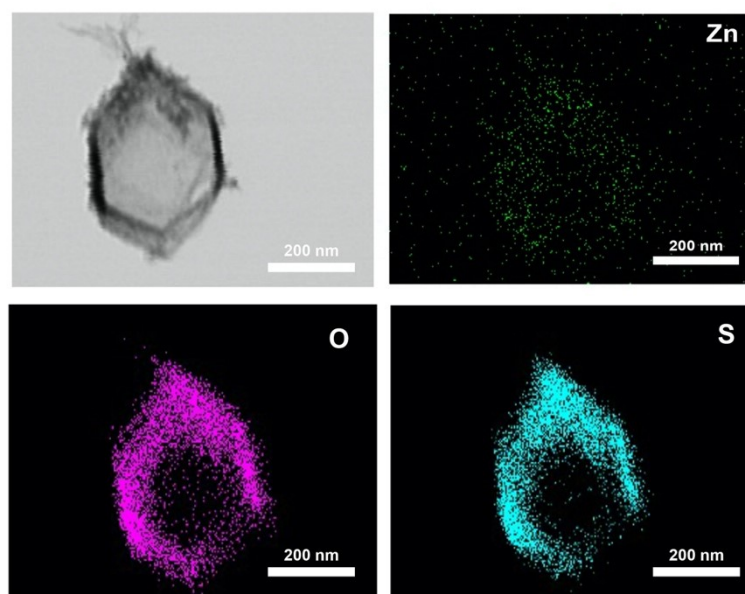


Fig. S4. High-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) image and the corresponding EDAX elemental mappings of PEDOT@PZIF-71

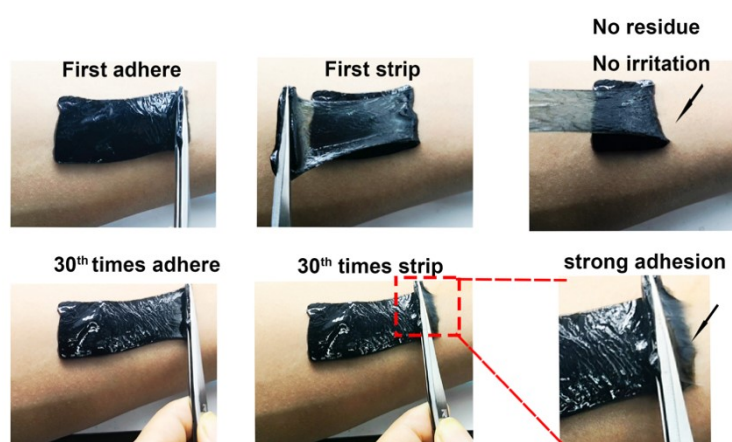


Fig. S5. The PEDOT@PZIF-71/PAM hydrogel was repeatedly adhered on the skin of the author. And no residue or irritation was found after peeling off.

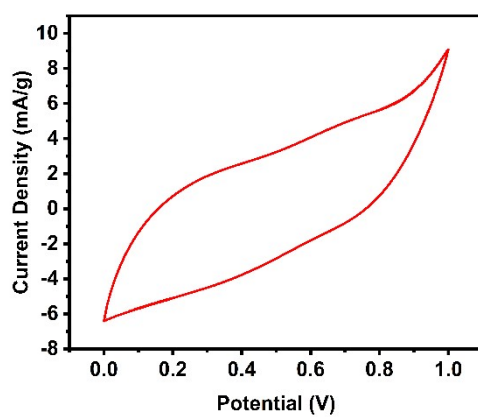


Fig. S6. Cyclic voltammetry curves of PEDOT@PZIF-71/PAM at a scan rate of 50 mV s⁻¹.

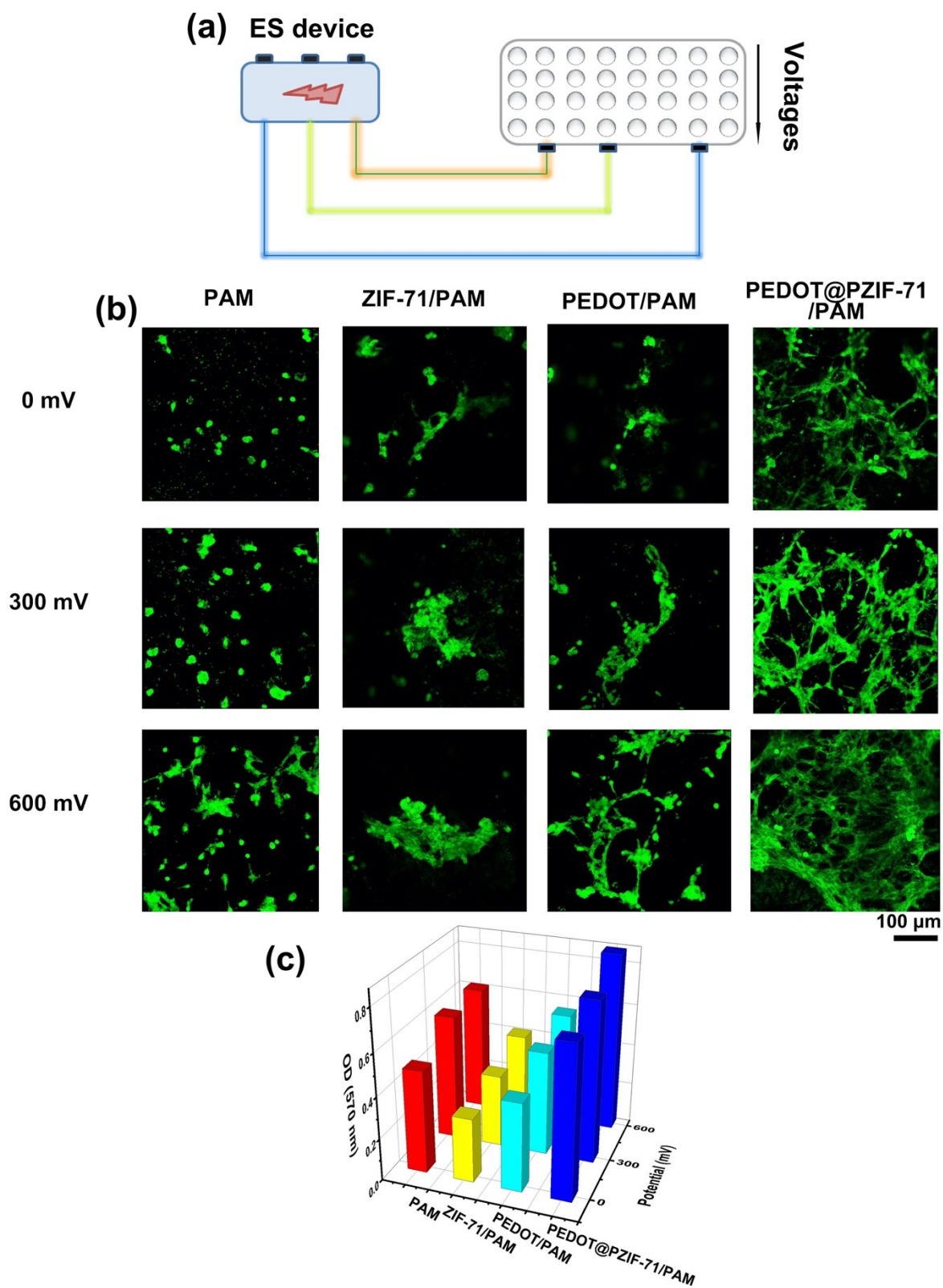


Fig. S7. Hydrogel electrical stimulation response cells. (a) Schematic diagram of hydrogels, (c) The added value of C2C12 on different conductive hydrogels under MTT electrical stimulation (7 days). Scale = 100 μm .

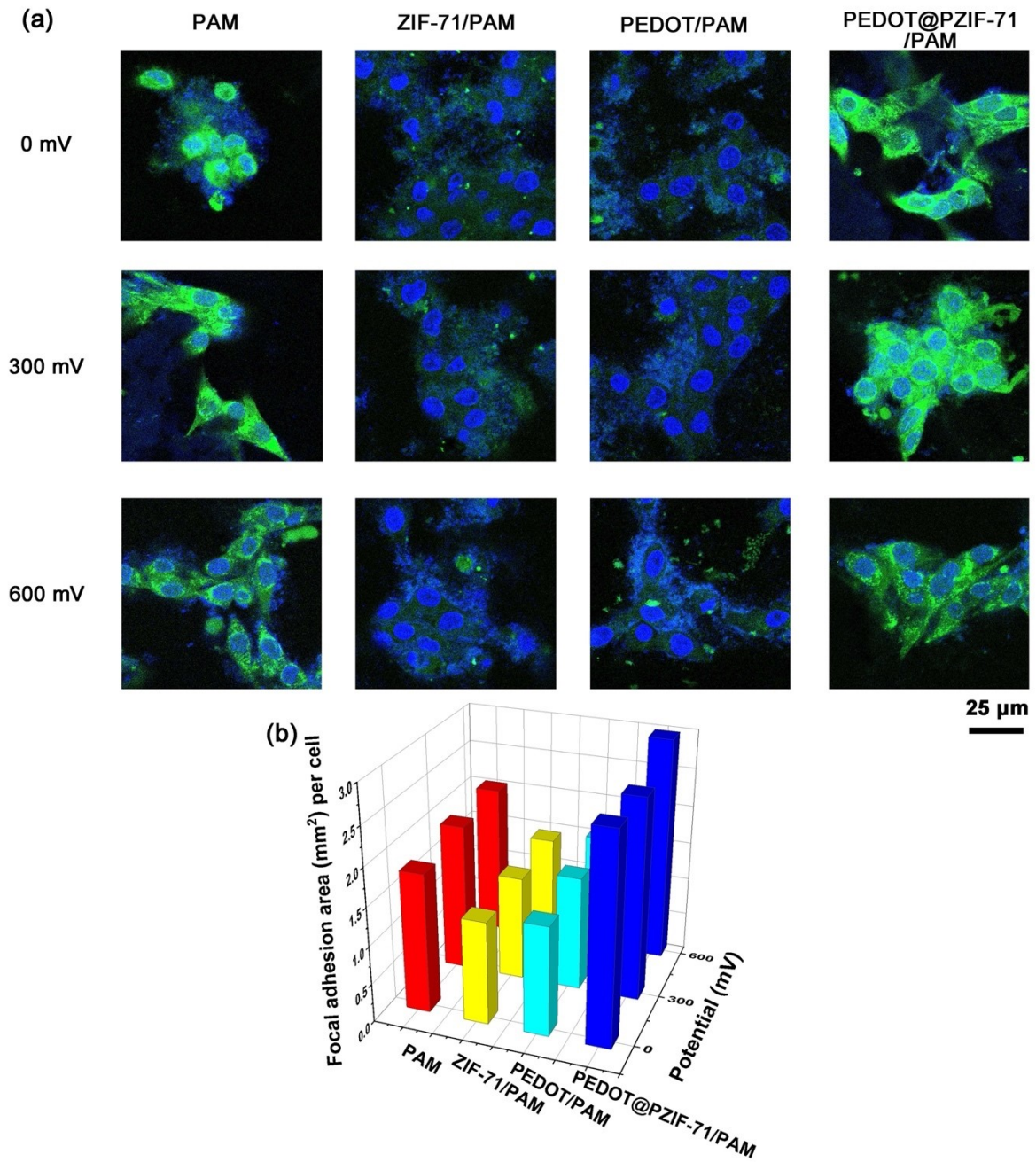


Fig. S8. Formation of C2C12 adhesion spots under electrical stimulation. (a) Pictures of C2C12 myoblast adhesion spots under different voltage conditions (0mV, 300mV, 600mV) on PAM, PEDOT/PAM, ZIF-71/PAM and PEDOT@PZIF-71/PAM, (b) C2C12 adhesion area of each cell, Scale = 25 μ m.

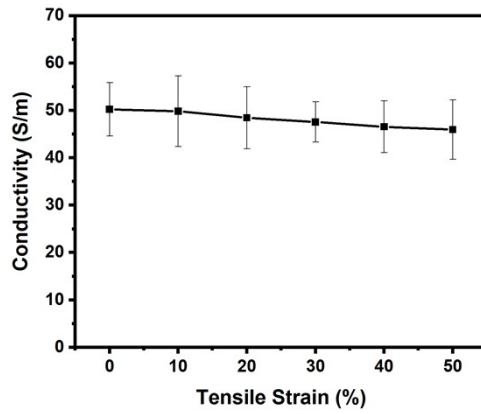


Fig. S9. Conductivity of PEDOT@PZIF-71/PAM hydrogels at different strain.

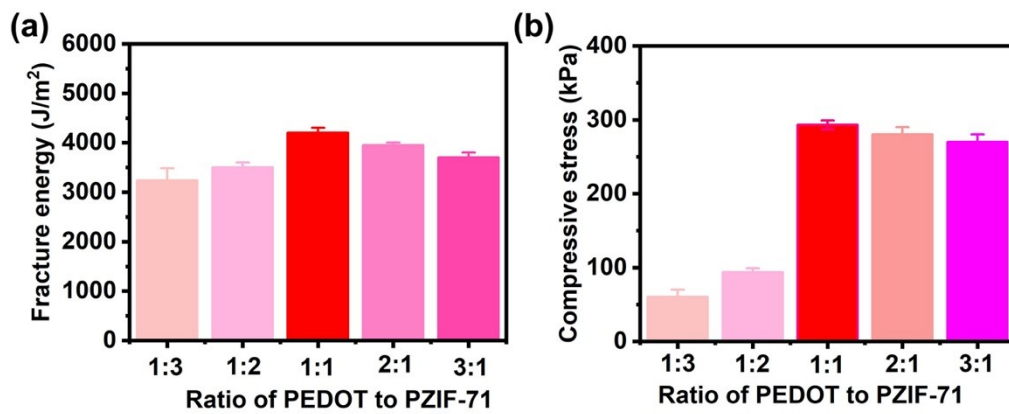


Fig. S10. (a) Fracture energy and (b) compressive stress of the hydrogel with different PEDOT to PZIF-71 ratios

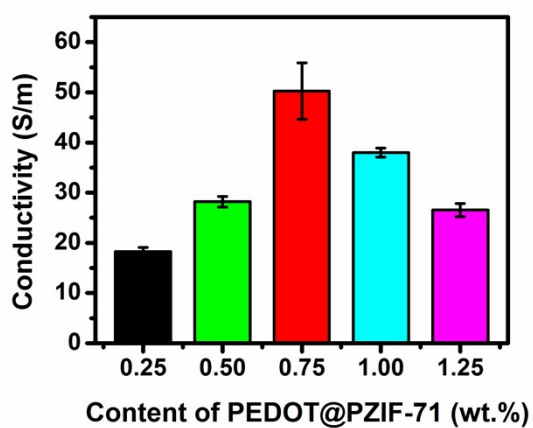


Fig. S11. Conductivity of various hydrogel with different content of PEDOT@PZIF-71

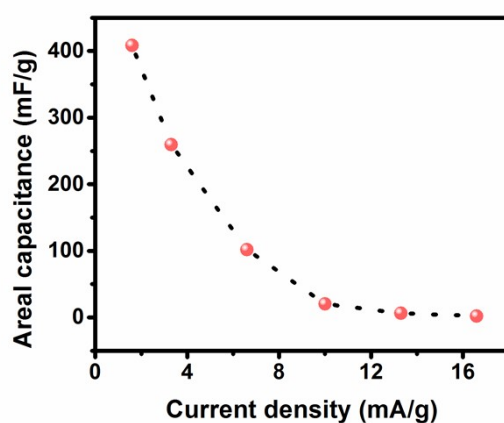


Fig. S12. Areal capacitance of PEDOT@PZIF-7/PAM under different recharge current density.

Table S4 Comparison between the performance of PEDOT@PZIF-71/PAM hydrogel and those reported in the literature

Hydrogels	Conductivity (S/m)	Adhesive strength (kPa)	Electrochemical performance	Reference
PEDOT@PZIF-71/PAM hydrogel	50.2	37	408.4 mF g ⁻¹ at a current density of 1.6 mA g ⁻¹	This study
CEC/PF/CNT hydrogels	8.45×10 ⁻³	8.5	---	8
DAL/rGO/SA/PAM Hydrogels	0.056	13.99	---	9
TiO ₂ -CD-loaded PVA/chitosan lignosulfonate	1.096×10 ⁻³	---	---	10
sodium (LS)-doped PAA hydrogels	0.45	30.5	---	11
PEDOT:Laponite-PAAM hydrogels	26	15	---	12
TB-doped PPy hydrogels	3.3	---	649 F g ⁻¹ at the current density 1 A g ⁻¹ .	13
polyvinyl alcohol/polyaniline hydrogel	20.5	---	260 F g ⁻¹ and 650 mF cm ⁻²	14
polyacrylamide-polyvinylpyrrolidone (PAAM-PVP) DN	2.0	---	308.9 F g ⁻¹ at a current density of 0.21 A g ⁻¹	15
PEDOT:PSS hydrogels with 6 wt% DMSO	5000	---	113 mF cm ⁻² at 2 mA cm ⁻²	16
polypyrrole hydrogels	230	---	560 F g ⁻¹ and an areal capacitance of 695 mF cm ⁻² at 0.75 A g ⁻¹	17
Pure PEDOT:PSS hydrogel	2000	---	---	18
RT-PEDOT:PSS	100	---	---	19

hydrogel				
PEDOT:PSS-PAM	0.06	0.6	---	20
hydrogel				
CMC-				
DA/PEDOT:PSS	41.6	65.1	---	21
hydrogel				

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