## **Supporting Information**

## Crystalline Tetra-aniline with Chloride Interactions towards a Biocompatible Supercapacitor

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## **EXPERIMENTAL SECTION**

**Preparation of c-TANI.** Tetra-aniline (TANi) was synthesized according to a modified previously reported method.<sup>1, 2</sup> In brief, 1.84 g (10 mM) of N-phenyl-1,4-phenylenediamine (aniline dimer) (Sigma-Aldrich, USA, ACS reagent, >98%) was vigorously stirred (800 r/min) in 1.0 M (50 mL) hydrochloric acid (HCl, Enox, China, Analytical Reagent, 36%~38%) for 30 min in an ice bath. A stoichiometric amount of ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, Greagent, China, Analytical Reagent,  $\geq$  99%) was dissolved in HCl (1.0 M, 50 mL) and quickly poured into the N-phenyl-1,4-phenylenediamine solution. Subsequently, additional HCl (1.0 M, 50 mL) was added into the mixed solution with vigorous stirring (800 r/min) for 2 h. The suspension was then centrifuged and washed repeatedly more than 10 times with HCl (0.1 M) and acetone (Yonghua, China, Analytical Reagent,  $\geq$ 99.5%) to remove any iron ions and unreacted aniline dimer. Afterwards, the product was de-doped using 100 mL 2.0 M ammonium hydroxide (NH<sub>3</sub>·H<sub>2</sub>O, Yonghua, China, Analytical Reagent, 25%~28%) for 2 h. The resulting precipitate was washed repeatedly with DI water until the pH reached neutral.

The c-TANi nanosheets were fabricated by a classical solution preparation method.<sup>1, 3</sup> Typically, 200 mg of as-prepared TANi powder was dispersed into a mixed solution composed of 100 mL of absolute ethanol (Adamas-beta, China, Analytical Reagent, 99.5%) and 400 mL of 1.0 M sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, Enox, China, Analytical Reagent, 95%~98%). The mixture was ultrasonicated (KQ-500DE, Shumei, 500 W) for 5 min followed by being left undisturbed for 4 days at room temperature. Finally, the product was washed in a dialysis bag using deionized water several times until the resultant dialysis water reached a neutral pH.

**Preparation of leucoemeraldine TANi.** The leucoemeraldine oxidation state of TANi was achieved by using phenylhydrazine as a reducing agent according to a reported route.<sup>38</sup> Typically, 100 mg of de-doped TANi after purification with ethanol was dispersed into 100 mL of ethanol. After adding 0.4 mL of phenylhydrazine (Adamasbeta, China, Guarantee Reagent, 99%), the mixture was stirred for 4 h. Then the precipitate was separated by centrifugation and washed with deionized water and

ethanol each 3 times to remove any residual phenylhydrazine. Finally, the product was collected by vacuum drying overnight at room temperature.

**Preparation of PANi.** Aniline was purchased from Adamas-beta (China, Analytical Reagent, >99%) and used without any further purification. PANi was prepared by a typical method as previously reported.<sup>4</sup> Typically, 32 mmol aniline and 8 mmol ammonium peroxydisulfate ((NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, APS, Sigma-Aldrich, USA, ACS reagent,  $\geq$  98%) were dissolved in 1.0 M HCl (100 mL). Next the solution was mixed promptly with vigorous stirring for 2 h at 0 °C. Then the green product was purified by centrifugation using deionized water and ethanol until reaching a neutral pH value.

**Preparation of self-healing c-TANi-polyethylene glycol (PEG-2000) film electrode.** The self-healing c-TANi-PEG film was prepared by a modified reported route.<sup>5</sup> In short, 368  $\mu$ L c-TANi aqueous suspension (12 mg mL<sup>-1</sup>) and 32  $\mu$ L 1g mL<sup>-1</sup> polyethylene glycol 2000 (PEG-2000, weight-average molecular weight, 1900 to 2200, Sinopharm, China,  $\geq$ 98%) was mixed with vigorous stirring for 60 min. Then the mixed solution was drop-cast onto glass slides and baked on a digital hot plate (Wiggens, WH240-HT) with temperature programming at 40 °C for 2 h and 60 °C for 2 h. Afterwards, a continuous film was obtained and detached from the glass slides with a blade. The film loading mass per area was ~2-3 mg cm<sup>-2</sup>.

**Preparation of self-healing ferric ion cross-linking sodium polyacrylate (Fe<sup>3+</sup>-PANa) electrolyte.** The self-healing ferric ion cross-linking sodium polyacrylate (Fe<sup>3+</sup>-PANa) electrolyte was fabricated according to a reported method.<sup>6</sup> Typically, 0.14 g of FeCl<sub>3</sub>·6H<sub>2</sub>O was added into a 14.1 mL acrylic acid (Energy Chemical, China, Analytical Reagent, 90%) monomer solution with stirring for 60 min. The mixed solution was neutralized using a concentrated sodium hydroxide solution (NaOH, Aladdin, China, ACS, >97%), which was added into the solution by (13 mL, 25 mol L<sup>-</sup> <sup>1</sup>) using a syringe pump for 6 h with an ice bath. Subsequently, APS was added into the above solution and continuously stirred for 30 min. Then the solution was degassed to remove the dissolved oxygen and transferred to a custom-mold (5 cm × 5 cm). Afterwards, the solution was polymerized at 40 °C for 30 min and dried at 80 °C for 2 h. Finally, the as-prepared electrolyte was soaked in a normal saline (0.9 wt% NaCl) solution.

**Preparation of normal saline, PBS and artificial sweat electrolytes.** The normal saline was prepared by dissolving 2.25 g sodium chloride (NaCl, Aladdin, China, Analytical Reagent, 99.8%) in 247.7 mL deionized water (153.8 mmol L<sup>-1</sup>). The artificial sweat solution was obtained by dissolving 1.25 g of NaCl (85.5 mmol L<sup>-1</sup>), 0.25 g of urea (16.7 mmol L<sup>-1</sup>, Aladdin, China, Analytical Reagent,  $\geq$ 99.5%) and 0.285 g (12.7 mmol L<sup>-1</sup>) of lactic acid (Sinopharm, China, Analytical Reagent, 85%) in 250 mL of deionized water. The PBS was prepared by mixing 0.06 g of dipotassium phosphate (KH<sub>2</sub>PO<sub>4</sub>, 1.76 mmol L<sup>-1</sup>, Macklin, Analytical Reagent, China, >99.5%), 0.36 g of disodium hydrogen phosphate (Na<sub>2</sub>HPO<sub>4</sub>, 10.1 mmol L<sup>-1</sup>, Macklin, Guarantee Reagent, China, >99%), 2 g of NaCl (136.8 mmol L<sup>-1</sup>) and 0.05 g of potassium chloride (KCl, 2.68 mmol L<sup>-1</sup>, Sinopharm, China, Guarantee Reagent,  $\geq$ 99.8%) in deionized water with NH<sub>3</sub>·H<sub>2</sub>O to adjust the pH to 7.14.

Cytotoxicity analysis. Cell viability was tested on L929 cells (mouse fibroblast cells). L929 cells were cultured in Dulbecco's modified eagle medium (DMEM, Shanghai Basalmedia Technologies) supplemented with penicillin/streptomycin (Shanghai Basalmedia Technologies), and 0.25% trypsin/ethylene diamine tetraacetic acid (EDTA) solution (Shanghai Basalmedia Technologies). Cells were seeded on Dulbecco's modified eagle medium (DMEM) with aniline dimer and c-TANi. The DMEM culture with and without cells were used as a positive and blank control, respectively. 200 µL of staining solution for each condition was transferred into ELISA (enzyme-linked immunosorbent assay, Synergy2 SLFPTAD, USA, BioTek Instruments, Inc.) for spectrophotometric microscopy (U-LH100HGAPO, Japan, Olympus corporation). The cell viability was analyzed using a commercial assay according to the manufacturer's protocol (Cell Counting Kit-8 (CCK8), Beyotime Biotechnology). The absorbance of the solutions was measured spectrophotometrically at 450 nm. The relative growth rate (RGR) was used to quantify the cytotoxicity of the cells according to the manufacturer's instructions until day-3. Finally, the cells were imaged using an inverted fluorescence microscope. RGR was calculated using the following equation:

$$RGR = \frac{Average \ OD_{experiment} - Average \ OD_{blank}}{Average \ OD_{positive \ control} - Average \ OD_{blank}}$$

where  $OD_{experiment}$  is the absorbance of the cell seeded on the supercapacitor component with DMEM with CCK8. The  $OD_{positive \ control}$  is the absorbance of the cells cultured in DMEM with CCK-8. The  $OD_{blank}$  is the absorbance of DMEM and CCK-8.

Physicochemical characterization. The molecular mass was confirmed using a matrix assisted laser desorption ionization-time of flight mass spectrometer (MALDI-TOF, Bruker Autoflex Speed MALDI TOF MS system, Bruker Daltonics). The crystal structure was determined using powder X-ray diffraction (Bruker D8 Advance Diffractometer) with Cu-K $\alpha$  radiation ( $\lambda = 1.5406$  Å) at a scan rate of 1° min<sup>-1</sup> and a spherical aberration corrected high-resolution transmission electron microscope (CS-Corrected Electron Microscope FEI Titan 80-300 kV). To avoid the electron beam effect on the sample, an electron dose rate of up to 2 e<sup>-</sup> pixel<sup>-1</sup> s<sup>-1</sup> was applied restrictively. Each image needs to take 40 frames and each frame takes 0.2 s exposure, the total exposure time is therefore 8 s and the total electron dose is about 16  $e^{-1}$  pixel<sup>-</sup> <sup>1</sup>. The morphology was acquired using a scanning electron microscopy (Hitachi SU8010). Other characterization methods for molecular structure used were Raman spectroscopy with a 632.8 nm laser (Horiba, HR Evolution), FT-IR spectroscopy (Bruker Tensor 27) with potassium bromide pellets, UV-vis absorption spectra with ethanol or acetonitrile as the solvent (Shimadzu, UV2600 spectrophotometer) and XPS spectra (Thermo Fisher, Escalab 250Xi spectrophotometer) with a monochromatic Al K $\alpha$  X-ray source. The stress strain measurements of the self-healing Fe<sup>3+</sup>-PANa were recorded on a Mark-10 ESM 305 testing station at a constant strain rate of 5 mm min-<sup>1</sup>. The sample size was  $\sim 8 \text{ mm} \times 0.5 \text{ mm}$  with a 10 mm gauge length.

The inherent conductivity was measured using *I-V* curves on a 2400 SourceMeter instrument (Keithley). A freestanding pellet with thickness of ~40  $\mu$ m (Figure S3) was fabricated by a pressing method. Two pieces of Cu conductive tape were used as the conductive leads. The conductivity ( $\sigma$ ) was calculated using Equation (1):

$$\sigma = \frac{l}{R \times A} \tag{1}$$

where *l* is the length between the conductive wires, *A* is the cross sectional area of the film, and *R* is the resistance, which can be calculated by the *I-V* curve.

*Ex situ* characterization. *Ex situ* electrochemical characterization was carried out using the 2<sup>nd</sup> GCD curve at a constant current of 1 A g<sup>-1</sup> to a settled potential of -0.2, 0.3, 0.6 V in the charging process and 0.2, -0.2 V in the discharging process with a delay time of 300 s. The electrodes were prepared by filtration of a c-TANi nanosheet dispersion in deionized water without adding any conductive additives or binder. The *ex situ* measurement samples were obtained from the electrodes after reaching the preset potentials and then washed by ultrapure water (50 mL) 6 times and vacuum dried overnight at room temperature before further characterization. The *ex situ* XPS, XRD, FTIR and MALDI-TOF MS were measured using a consistent approach to the physicochemical characterization procedures. The UV-vis spectra of the electrode degraded after 2000 GCD cycles was obtained by pretreatment using an acetonitrile extraction.

**Electrochemical performance evaluation.** The three-electrode CV measurements were carried out across a potential range from  $-0.2\sim0.6$  V *vs.* Ag/AgCl and the two-electrode CV measurements were carried out across a potential range from  $0\sim0.8$  V. All the electrochemical measurements were performed on an electrochemical workstation (Princeton PMC2000). Electrochemical impedance spectroscopy (EIS) was measured at a frequency sweep from 100 kHz to 0.01 Hz with a voltage amplitude of 10 mV.

Assembly of the three-electrode measurement system. The three-electrode measurement system was assembled by using a three-necked Swagelok cell. The electrodes were fabricated by vacuum filtration of a c-TANi and super P dispersion with a mass ratio of 3:1 in deionized water. The loading mass of a single electrode was about  $0.8 \sim 1.2 \text{ mg cm}^{-2}$ . The three-electrode electrochemical measurements were performed using an Ag/AgCl reference electrode and activated carbon as a counter electrode.

Assembly of c-TANi symmetrical supercapacitor. The c-TANi symmetrical supercapacitor was assembled by using a two-electrode Swagelok cell. The electrode

materials were composed of c-TANi, polytetrafluoroethylene (PTFE, Sigma-Aldrich, USA, Guarantee Reagent, 60% dispersion in H<sub>2</sub>O) and super P with a mass ratio of 75:20:5. These materials were dispersed in deionized water with vigorous stirring for 12 h to make a homogeneous dispersion. Then the dispersion was evaporated at 30 °C until the slurry became tacky. Subsequently, the sizing agent was extruded uniformly into a self-standing film followed by cutting into an area of about 0.6 cm<sup>2</sup>. The loading mass of a single electrode was ~3-5 mg cm<sup>-2</sup>. The glass fiber membrane was utilized as a separator and immersed in 2.0 M NaCl or another physiological electrolyte (normal saline, PBS or artificial sweat).

The capacitance was calculated based on the discharge area of the CV curve based on the following equation:

$$C = \frac{1}{\nu \times \Delta V} \int_{V_0}^{V_0 + \Delta V} I(V) \, dV \tag{2}$$

where *C* is the capacitance (F) according to the discharge curve, *v* is the scan rate (V s<sup>-1</sup>), I(V) is the response current,  $V_0$  is the lower potential limit (V) and  $\Delta V$  is the potential range (V). For the three-electrode configuration, the specific capacitance was calculated using the following equation:

$$C_m = \frac{c}{m} \tag{3}$$

where  $C_m$  is the mass specific capacitance (F g<sup>-1</sup>), and *m* is the mass loading of the active materials of the electrode (g).

In the two-electrode system, the area specific capacitance was calculated using the following equation:

$$C_S = \frac{1}{A \times v \times \Delta V} \int_{V_0}^{V_0 + \Delta V} I(V) \, dV \tag{4}$$

where  $C_s$  is the area specific capacitance (F cm<sup>-2</sup>) and A is the surface area (cm<sup>2</sup>) of the electrode.

The area energy density  $(E_s)$  and power density  $(P_s)$  were calculated according to Equation (5) and Equation (6), respectively:

$$E_s = \frac{C_s \times \Delta V^2}{7200} \tag{5}$$

$$P_s = \frac{E_s \times 3600}{\Delta t} \tag{6}$$

where  $\Delta V$  (V) is the voltage range upon discharge in the negative CV curve,  $\Delta t$  is the discharge time (s),  $E_s$  is the areal energy density (mWh cm<sup>-2</sup>), and  $P_s$  is the areal power density (mW cm<sup>-2</sup>).

Self-healing supercapacitor fabrication. Self-healing symmetrical supercapacitors were constructed using the as-prepared c-TANi-PEG film as both the self-healing cathode and anode. The electrodes were cut into  $1 \times 1.5$  cm<sup>2</sup> pieces with loading masses of 3~4 mg. Ferric ion cross-linked sodium polyacrylate acted as the self-healing electrolyte with a thickness of ~500 µm. Carbon cloth was utilized as the current collector. Conductive copper tape was used as tabs to transmit current to the external load. The full self-healing device was packed in polyimide (PI) tape with a size of  $3 \times 2$  cm<sup>2</sup>.

**Characterization of the supercapacitor flexibility and self-healing ability.** The flexibility characterization was conducted using a Mark-10 dynamometer with bending angle of 45°, 90°, 135° and 180° at a curvature radius of 0.4 cm. Before the self-healing measurements, each electrode was cut in half using a razor blade. Afterwards, the damaged electrode was immediately exposed to infrared radiation for 60 min in order to heal. The dissected gel electrolytes were wet with a small amount of water and healed at room temperature without any external stimuli for 60 min. The self-healing characterization of the fully self-healable supercapacitor was conducted after repeated cutting and healing under the same conditions.

**Powering an LED lamp experiment.** A high loading mass of 25~30 mg with  $1.5 \times 1$  cm<sup>2</sup> c-TANi-PEG of the self-healing electrode and Fe<sup>3+</sup>-PANa/0.9 wt% NaCl electrolyte was applied to assemble the biocompatible supercapacitor. Then three biocompatible supercapacitors connected in series were charged to 2.4 V with a current at 2.0 mA and then charged at a constant voltage for 600 seconds.



**Figure S1**. Characterization of c-TANi and PANi. (A) SEM image of as-prepared c-TANi nanosheets. (B) SAED pattern of c-TANi with a lattice spacing of 4.6 Å. (C) SEM image of the PANi nanowires. (D) Normalized UV-vis spectra of PANi, a de-doped powder of TANi and c-TANi nanosheets dispersed in ethanol. (E) FT-IR pattern of doped c-TANi, PANi, and de-doped powder of TANi prior to self-assembly. (F) A 3D packing model of c-TANi chains showing the corresponding lattice spacings and chain stacking along the *b*- and *c*-axes.



**Figure S2**. HRTEM characterization of the crystal structure of c-TANi nanosheets. (A, D, G) HRTEM images of c-TANi from the top-view (A), side-view (D) and front view (G) directions, as demonstrated in Figure S1F. (B, C) Profile curves extracted from the HRTEM image (A). 0.34 nm lattice spacing corresponds to the  $\pi$ - $\pi$ \* stacking along the *b*-direction (B) and 1.32 nm corresponds to the mono c-TANi chain length along the *a*-direction (C). (E, F) Profile curves extracted from the HRTEM image (D). 0.27 nm

corresponds to the c-TANi chain width along the *c*-direction (E) and 1.34 nm approximately stands for the c-TANi chain length along the *a*-direction (F). (H) Profile curves extracted from the HRTEM image (G). 0.46 nm matches closely to the distance indicated from the peak at 19.3° in the XRD pattern.



**Figure S3**. Cross-section SEM images of (A) c-TANi and (B) PANi to obtain the thickness to evaluate conductivity from *I-V* curves.



**Figure S4**. The GCD curves and the specific capacitances comparison for c-TANi and PANi tested in 2.0 M NaCl using a three-electrode configuration. The GCD curves of (A) c-TANi and (B) PANi. (C) The corresponding specific capacitances at different current density of c-TANi and PANi.



**Figure S5.** CV curves, EIS spectra and calculated capacitive contribution summary. (A) CV curves at various scan rates from 2 mV s<sup>-1</sup> to 20 mV s<sup>-1</sup> for c-TANi tested in 2.0 M NaCl electrolyte using a three-electrode configuration. (B) Capacitive contributions to the total charge storage at 5 mV s<sup>-1</sup> for c-TANi. (C) EIS spectra of the c-TANi and PANi electrodes. Inset: corresponding equivalent circuit and magnified high-frequency region. (D) CV curves at various scan rates from 2 mV s<sup>-1</sup> to 20 mV s<sup>-1</sup> for PANi. (E) Capacitive contributions to the total charge storage at 5 mV s<sup>-1</sup> for PANi. (F) Capacitive and diffusion-controlled contribution ratios for PANi.



Figure S6. Ex situ characterization of c-TANi. (A) Ex situ XPS survey spectrum and (B) Na 2s XPS spectrum of c-TANi. (C) Ex situ MALDI-TOF MS patterns of c-TANi.
(D) The XRD comparisons of the leucoemeraldine, emeraldine base and emeraldine salt forms using chemical redox reactions. (E) Ex situ FT-IR spectra of a c-TANi electrode.



**Figure S7.** CV curves of c-TANi and PANi obtained at various scan rates. c-TANi in (A) normal saline (0.9 wt% NaCl), (B) artificial sweat and (C) PBS electrolyte. PANi in (D) 0.9 wt% NaCl, (E) artificial sweat and (F) PBS electrolyte.



**Figure S8**. CV and EIS spectra of c-TANi and PANi measured in 0.9 wt% NaCl (normal saline) electrolyte using a three-electrode system. (A) CV curves of c-TANi and PANi at a scan rate of 5 mV s<sup>-1</sup>. (B) The enlarged electrochemical impedance spectroscopy (EIS) plot of c-TANi and PANi electrode in 0.9 wt% NaCl.



**Figure S9.** GCD curves and capacitance comparison of a c-TANi electrode tested at various current densities. (A) Normal saline (0.9 wt% NaCl), (B) artificial sweat and (C) PBS electrolyte, respectively. (D) The corresponding specific capacitances of the c-TANi electrode in 0.9 wt% NaCl, artificial sweat and PBS electrolyte at different current densities according to the discharging time of GCD curves.



**Figure S10**. GCD curves and EIS spectra of c-TANi and PANi measured in artificial sweat and PBS electrolyte using a three-electrode system. (A) Cycling stability summary of c-TANi and PANi electrodes, in which c-TANi electrode exhibited outstanding cycling stability of 94.1% and 82.5%, respectively. (B) The enlarged EIS plots of the c-TANi and PANi electrodes.



**Figure S11**. SEM image comparison of PANi and c-TANi electrodes after 2000 cycles at a current density of 10 A g<sup>-1</sup> in normal saline (0.9 wt% NaCl). (A), (B) PANi and (C), (D) c-TANi electrodes.



**Figure S12.** FT-IR and UV-vis spectra of PANi and c-TANi electrodes obtained before and after 2000 cycles at 10 A  $g^{-1}$  in normal saline (0.9 wt% NaCl) electrolyte. FT-IR spectra of (A) PANi and (B) c-TANi. UV-vis spectra of (C) PANi and (D) c-TANi.



**Figure S13.** Electrochemical characterization of a c-TANi based symmetric supercapacitor in normal saline (0.9 wt% NaCl). (A) CV curves of a c-TANi symmetric supercapacitor in a two-electrode configuration. (B) Rate performance corresponding to the CV curves. (C) GCD curves. (D) EIS pattern. (E) Cycling stability at a current density of 10 A  $g^{-1}$  for 4000 cycles.



**Figure S14**. Representative fluorescence microscopy images of live assay of L929 cells cultured on the surface of aniline dimer and c-TANi electrodes for 24, 48 and 72 hours.



**Figure S15**. The L929 cell relative growth rate comparing the raw material of the dimer and c-TANi electrodes. The cell proliferation on the c-TANi electrode from the Cell Counting Kit-8 assay exceeds 100%, which indicates 0 level cytotoxicity according to the United States Pharmacopial (USP) biological reactivity test standard. In comparison, aniline dimer presents significantly higher cytotoxicity, while the relative growth rate (RGR) continues to decrease and falls to only 6.7% after 72 h.



**Figure S16.** Self-healing capability characterization of a c-TANi-PEG electrode. (A) Optical images of a self-healable c-TANi-PEG electrode under various conditions: (I) bending, (II) after being cut and (III) in a healed state. (B) Strain-stress curves of a pure PEG and c-TANi-PEG film. (C) FT-IR spectrum of c-TANi, PEG and a hybrid self-healable c-TANi-PEG electrode. (D) The *I-V* curves and (E) electronic conductivity summary of the self-healing c-TANi-PEG film after each cutting/healing cycle. Inset figure in (C) corresponds to the calculated film thickness.



**Figure S17.** Electrochemical performance of a self-healable c-TANi-PEG electrode in normal saline (0.9 wt% NaCl) electrolyte. (A) GCD curves after different cutting/healing cycles at  $1 \text{ A cm}^{-2}$  and (B) corresponding specific areal capacitance.



**Figure S18.** Self-healing capability characterization of an  $Fe^{3+}$ -PANa gel electrolyte. (A) Optical image of an  $Fe^{3+}$ -PANa gel electrolyte (1.05 mm thickness and 13 mm diameter) just cut (left) and after healing (right) lifting up a 50 g weight; the red rectangle range indicates the cutting/healing position. (B) Strain-stress curves of the  $Fe^{3+}$ -PANa gel electrolyte before cutting and after the 1<sup>st</sup> self-healing, indicating the great healing capability of the hybrid gel electrolyte. (C) Self-healing efficiency summary of 5 cutting/healing cycles based on the ionic conductivity of the Fe<sup>3+</sup>-PANa gel electrolyte in normal saline (0.9 wt% NaCl) solution.



**Figure S19.** Self-healing characterization of the assembled supercapacitor with a c-TANi-PEG electrode and an  $Fe^{3+}$ -PANa gel electrolyte in normal saline (0.9 wt% NaCl). (A) CV curves obtained at a scan rate of 10 mV s<sup>-1</sup> and (B) EIS spectra of the self-healing supercapacitor measured before/after every healing cycle.



**Figure S20.** Flexibility characterization of the self-healing supercapacitor after the 1<sup>st</sup> healing cycle. (A) CV curves at a scan rate of 10 mV s<sup>-1</sup> and (B) EIS pattern of the healed supercapacitor with bending angles from 0° to 180°.



**Figure S21.** Photograph records the biocompatible supercapacitor powered a LED at different discharge times.

Samples	Cl (%)	Na (%)	C (%)	N (%)
Ι	0.4	0.03	85.39	14.18
П	0.71	0.04	85.09	14.16
III	1.15	0.02	84.72	14.11
IV	0.97	0.05	84.90	14.08
V	0.36	0.03	85.44	14.17

Table S1. XPS elemental summary of the c-TANi electrode

Samples	$R_{s}(\Omega)$	$R_{ct}(\Omega)$	W-R (Ω)
c-TANi	0.161	4.028	2.943
PANi	0.86075	12.06	36.68

**Table S2.** Simulated equivalent circuit parameters from EIS spectra of c-TANi andPANi in normal saline (0.9 wt% NaCl)

Energy Storage System (Cathode//Electrolyte//Anode)	Capacity	Capacity Retention	Energy Density	Refs.
NMO//1 M NaSO4//NTPO@C	42 mAh $g^{-1}$ (0.2 A $g^{-1}$ )	54.8% (1000 cycle)	$30 \text{ Wh } \text{kg}^{-1}$ $4678 \text{ W } \text{kg}^{-1}$	7
PEDOT:PSS/ferritin/MWCNTs//PBS//PEDO T:PSS/ferritin/MWCNTs	$32.9 \text{ mF cm}^{-2}$ (100 mV s <sup>-1</sup> )	~100% (1000 cycle)	$0.82~\mu Wh~cm^{-2}$	8
PANI/CNT/PAH/Dgel//NIH <sub>3</sub> T <sub>3</sub> cell medium//PANI/CNT/PAH/Dgel	66.7 F $g^{-1}$ (1 A $g^{-1}$ )	94% (1000 cycle)	NA	9
Ag@PANi-PEC//PBS//Ag@PANI-PEC	140 F $g^{-1}$ (2.5 A $g^{-1}$ )	68% (1000 cycle)	NA	10
MnO2-MWCNT//body fluids//AC	$36 \text{ F g}^{-1}$ (5 mA cm <sup>-2</sup> )	99% (1000 cycle)	NA	11
PEDOT:PSS//sweat//PEDOT:PSS	8.94 F g <sup>-1</sup> 10 mF cm <sup>-2</sup> (1 mV s <sup>-1</sup> )	75% (4000 cycle)	0.80 Wh kg <sup>-1</sup> 0.4 mW cm <sup>-2</sup> 1.63 μWh cm <sup>-2</sup>	12
MoO <sub>3</sub> //0.35 M NaCl//MoO <sub>3</sub>	$1.6 \text{ mF cm}^{-2}$ (0.15 mA cm <sup>-2</sup> )	~100% (3000 cycles)	$0.14 \ \mu Wh \ cm^{-2}$ $1.0 \ mW \ cm^{-2}$	13
MoO <sub>x</sub> //sodium alginate//MoO <sub>x</sub>	$1.6 \text{ mF cm}^{-2}$ (0.15 mA cm <sup>-2</sup> )	86.7% (2000 cycles)	$15.64 \ \mu Wh \ cm^{-2}$ 2.53 mW cm <sup>-2</sup>	14
CNT//PBS//CNT	20.8 F g <sup>-1</sup> 10.4 F cm <sup>-3</sup> $(0.5 \text{ A cm}^{-3})$	98.3% (10000 cycle)	NA	15
PPy/PEDOT hydrogel//0.25 M Mg(NO <sub>3</sub> ) <sub>2</sub> //Mg	$32 \text{ mAh cm}^{-2}$ (200 µA cm <sup>-2</sup> )	NA	$22 \text{ mWh cm}^{-2}$	16
PANi/CNT//1 M NaCl//PANi/CNT	NA	<60% (2000 cycle)	$26 \ \mu Wh \ cm^{-2}$	17
c-TANi//0.9 wt% NaCl//c-TANi	413.7 mF cm <sup>-2</sup> 145.9 F g <sup>-1</sup> (5 mV s <sup>-1</sup> )	94.5% (4000 cycle)	80.3 μWh cm <sup>-2</sup> 20.4 mW cm <sup>-2</sup>	This work

 Table S3. Electrochemical performance summary for energy storage devices in physiological electrolytes

Healing cycles	Rs	R <sub>ct</sub>
0	5.015	38.15
1	7.044	45.88
2	10.13	47.61
3	11.14	49.16

**Table S4.** Simulated equivalent circuit parameters from EIS spectra of the self-healingsupercapacitor in normal saline (0.9 wt% NaCl)

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