

Supplementary Information

Nitrogen-doped hollow carbon nanoboxes in zwitterionic polymer hydrogel electrolyte for superior quasi-solid-state zinc-ion hybrid supercapacitors

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1. Experimental section

1.1. Materials. Pyrrole (Py) was purchased from Aladdin Bio-Chem Technology Co. Ltd. (Shanghai, China) and used after distillation. Cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and 2-methylimidazole were supplied by Aladdin Bio-Chem Technology Co. Ltd. (Shanghai, China). Cetyltrimethylammonium bromide (CTAB) was received from Shanghai Shanpu Chemical Co. Ltd. (Shanghai, China). Zinc trifluoromethanesulfonate ($\text{Zn}(\text{CF}_3\text{SO}_3)_2$) was bought from Beijing J&K Scientific Co. Ltd (Beijing, China). [2-(Methacryloyloxy)ethyl]diethyl-(3-sulopropyl) (SBMA, 97%) and acrylic acid (AA, 99%) were purchased from Aladdin Bio-Chem Technology Co. Ltd. (Shanghai, China). N, N'-methylenebisacrylamide (MBAA, 98%) were received from Baishi Chemical Co. Ltd. (Shanghai, China). Hydrochloric acid (37%) was obtained from Zhengzhou Xinyang Yellow River Chemical No. 1 Factory (Zhengzhou, China).

1.2. Preparation of the PZ precursor. The ZIF-67 was prepared by the metal coordination reaction according to the previous report with minor modification.¹ In a typical run, 1.816 g 2-methylimidazole was dissolved to 28 mL deionized (DI) water with stirring at RT. Then, 0.116 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 5.0 mg CTAB were thoroughly dissolved in 5 mL DI water under stirring at RT and was poured into the above aqueous solution to obtain a homogeneous ZIF-67 suspension under stirring for 20 min. Following, the above suspension was placed in the ice-water bath, stirred for 10 min, and then 0.5 mL Py monomer was added. After stirring for 1 h, APS aqueous solution (the molar ratio of Py to APS was 1:1, 15 mL DI water) was added and stirred in an ice-water bath for another 4 h. Finally, the dark precipitate was centrifugally washed with ethanol and DI water and dried at 60 °C to produce polypyrrole/ZIF-67 (PPy/ZIF-67, PZ). For comparison, the similar method was used to prepare pure PPy without the addition of CTAB, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 2-methylimidazole.

1.3. Preparation of the APZC sample. Typically, the prepared ZP was annealed at 350 °C

for 1.5 h under an Ar/H₂ (5%) flow with a heating rate of 2 °C min⁻¹. Being cooled into RT, the obtained black powder was washed with 1.0 M HCl solution and DI water, and dried at 60 °C to prepare a pre-carbonized material (PZC). After that, the PZC sample was dispersed in a KOH aqueous solution under stirring for 2 h (the mass ratio of PZC to KOH was set as 1:2), dried at 90 °C, and activated at 750 °C for 2 h using a 5 °C min⁻¹ rate in an Ar/H₂ (5%) atmosphere. Finally, the black solid was washed thoroughly with 1.0 M HCl and DI water, and dried at 60 °C to obtain the activated porous carbon (APZC). Likewise, PPy-derived carbon material (PC) was also prepared for comparison.

1.4. Preparation of the P(SBMA-co-AA)/Zn(CF₃SO₃)₂ hydrogel electrolyte. A thermal polymerization approach was employed for the synthesis of the P(SBMA-co-AA) hydrogel. In detail, 1 g SBMA monomer and 2 mL AA monomer were added to 8 mL DI water under stirring at room temperature (RT). After stirring for 10 min, 40 mg APS as the initiator and 16 mg MBAA as the crosslinker were added to the above solution under stirring for about 30 min to form a homogeneous solution. The prepared solution was poured into a glass mold and the polymerization reaction occurred at 60 °C and lasted 3 h to synthesize a polymer hydrogel of P(SBMA-co-AA). Finally, the P(SBMA-co-AA)/Zn(CF₃SO₃)₂ hydrogel electrolyte was obtained via the immersion of the P(SBMA-co-AA) hydrogel in a 1.0 M Zn(CF₃SO₃)₂ aqueous solution for 6 h. Similarly, polyacrylic acid/Zn(CF₃SO₃)₂ (PAA/Zn(CF₃SO₃)₂) and poly[2-(methacryloyloxy)ethyl]diethyl-(3-sulopropyl)/Zn(CF₃SO₃)₂ (PSBMA/Zn(CF₃SO₃)₂) were prepared for comparison.

1.5. Materials characterization. General characterizations regarding the morphology, structure, and composition of various samples were conducted by scanning electron microscopy (SEM, SU-8010), transmission electron microscopy (TEM, JEM-2100F), Fourier transform infrared (FTIR) spectroscopy (Brüker VERTEX70), X-ray diffraction spectroscopy with Cu K α radiation ($\lambda = 0.154$ nm) (XRD, Brüker D8 Advance), Raman spectroscopy with

excitation wavelength of 532 nm (Brüker Senterr), and X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250Xi). N₂ adsorption-desorption tests (3H-2000PM1/2) was performed to obtain the the specific surface area and pore size distribution results of the samples. An optical microscope (XSP-003) was used to in situ observe Zn plating/stripping in Zn//Zn symmetrical cells. The cells under different charge and discharge voltages were disassembled and its cathode and anode were rinsed with DI water for ex situ characterization. Similarly, the cathode and anode in the cycled cell was also treated for SEM analysis.

1.6. Mechanical properties. The hydrogel samples were prepared by injecting the hydrogel into a silicone mould (length: 50 mm, width: 10 mm, thickness: 1 mm). Mechanical properties of the P(SBMA-co-AA)/Zn(CF₃SO₃)₂ hydrogel electrolyte were measured by using a universal testing machine (ZQ-990LB) with a 50 N load cell at an extension rate of 20 mm min⁻¹. The cyclic compressive test was conducted on a cylindrical sample (20 mm in height, 10 mm in diameter) for loading-unloading cycles at a compressive rate of 2 mm min⁻¹ and a strain of 60% with intervals between 5 consecutive cycles.

1.7. Electrochemical performance. Before electrochemical tests, CR2032 coin cells were first assembled with the carbon cathode, Zn anode, Waterman filter paper separator, and 1.0 M Zn(CF₃SO₃)₂ aqueous electrolyte. Meanwhile, the soft-packaged ZHSC device was fabricated, where P(SBMA-co-AA)/Zn(CF₃SO₃)₂ as the hydrogel electrolyte/separator was sandwiched between the carbon cathode and Zn anode. All the cathodes used were prepared by pressing a uniform sheet containing 80 wt% carbon sample (as the active material), 10 wt% acetylene black (as the conductive agent), and 10 wt% polytetrafluoroethylene (PTFE, as the binder) on the graphite paper (as the current collector), and the loading of the active material on the cathode was fixed at approximately 2.0 mg cm⁻². Zn anode was made by punching the cleaned zinc foil (thickness of 80 μm) into small discs with a diameter of 12

mm. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were performed on a CHI660D electrochemical workstation, and the galvanostatic charge-discharge (GCD) was conducted on a M340A Land battery tester. The CV and GCD were measured at various scan rates and current densities in a voltage window of 0.2–1.8 V, respectively, and the EIS was recorded from 10^5 to 10^{-2} Hz. The specific capacity (C , mAh g^{-1}) and energy density (E , Wh kg^{-1}) were read directly from the Land Battery Test System. The power density (P , W kg^{-1}) based on the mass of active materials in cathode using the Equation (S1):

$$P = \frac{3600E}{t} \quad (S1)$$

where t (s) represents the discharging time.

2. Results and discussion

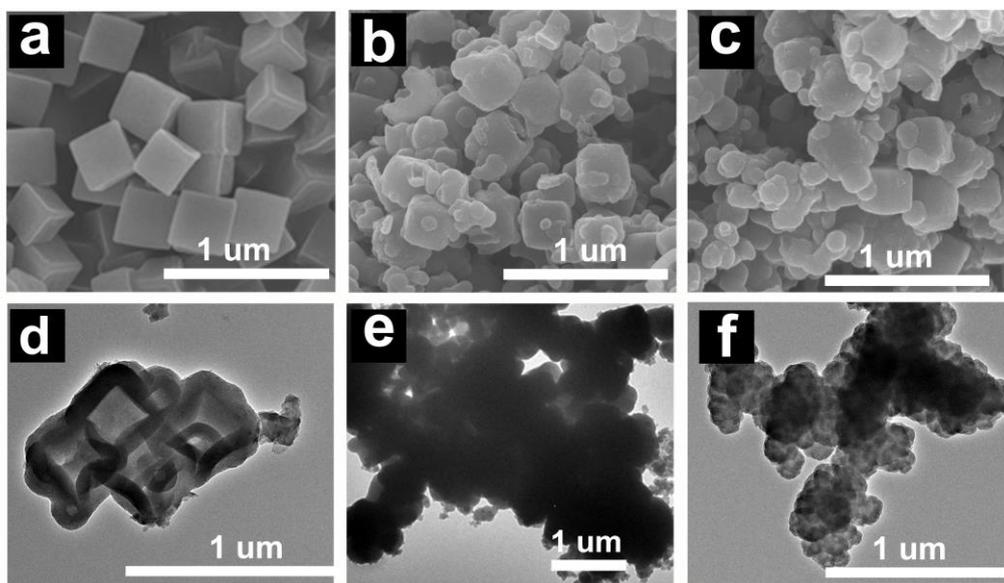


Fig. S1 SEM images of (a) ZIF-67, (b) PZ, and (c) PZC. TEM images of (d) PZC, (e) PZ, and (f) PC.

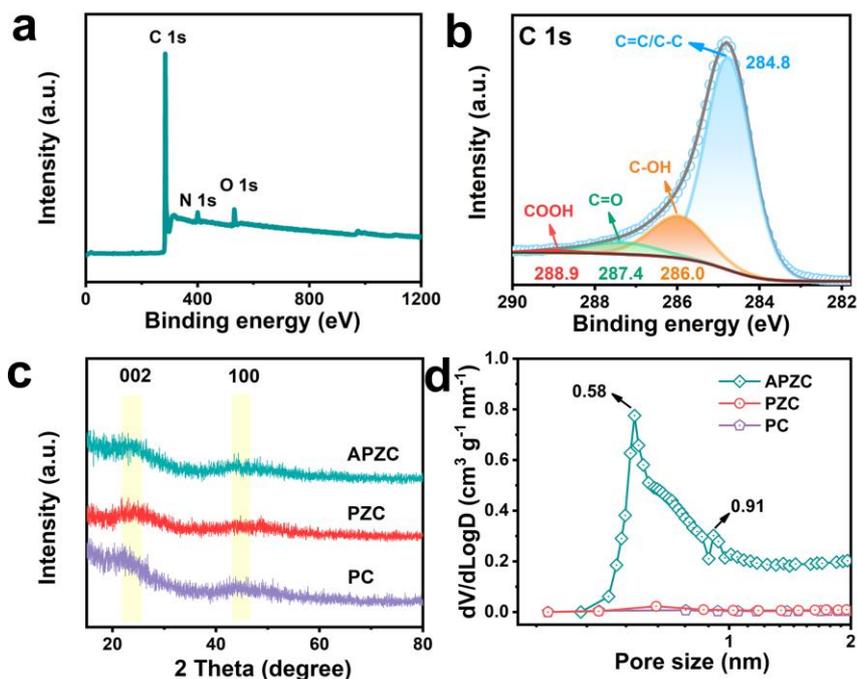


Fig. S2. (a) The wide-scan XPS spectrum and (b) C 1s XPS spectra of APZC. (c) XRD patterns and (d) micropore size distribution plots of APZC, PZC, and PC.

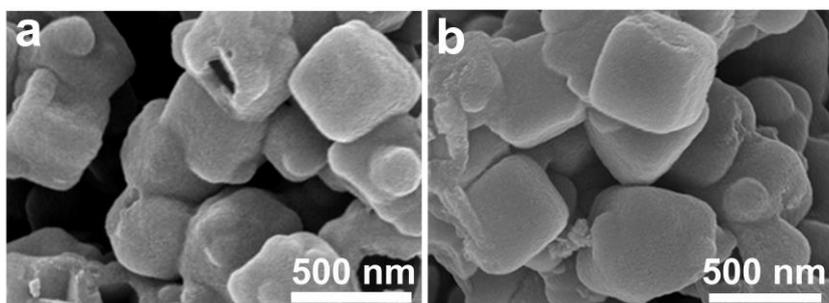


Fig. S3 SEM images of the APZC cathode (a) before and (b) after 20000 cycles in the aqueous ZHSC.

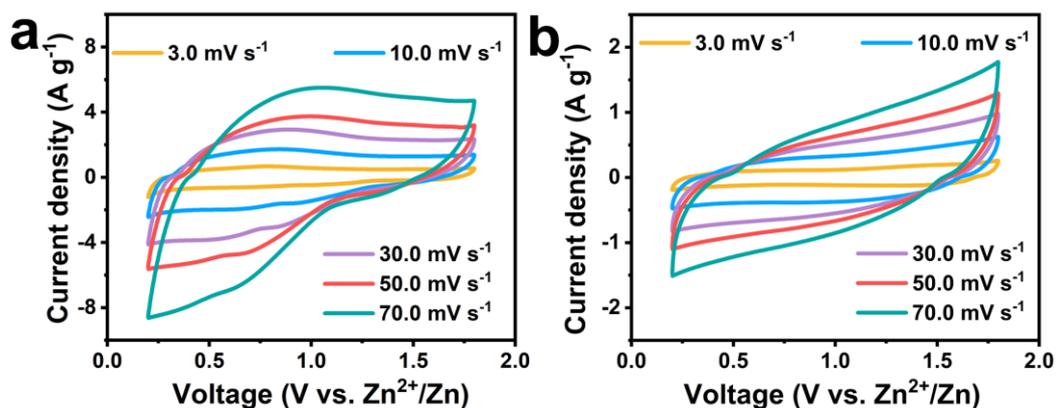


Fig. S4 CV curves at different scan rates for (a) Zn//PZC and (b) Zn//PC ZHSCs.

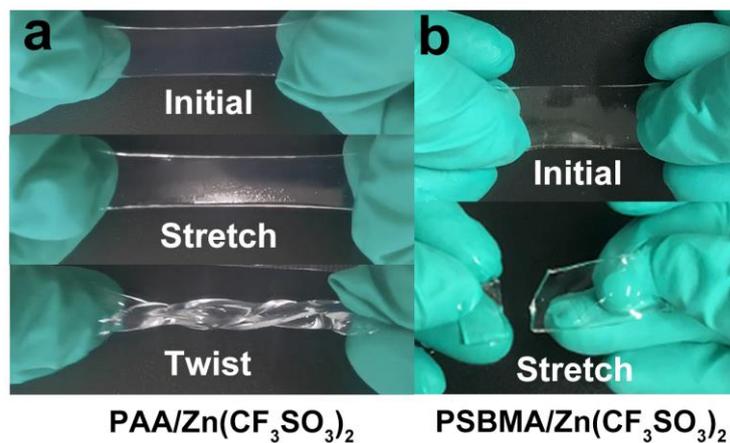


Fig. S5 Photographs illustrating the mechanical properties of (a) $\text{PAA/Zn(CF}_3\text{SO}_3)_2$ and (b) $\text{PSBMA/Zn(CF}_3\text{SO}_3)_2$ hydrogel electrolytes.

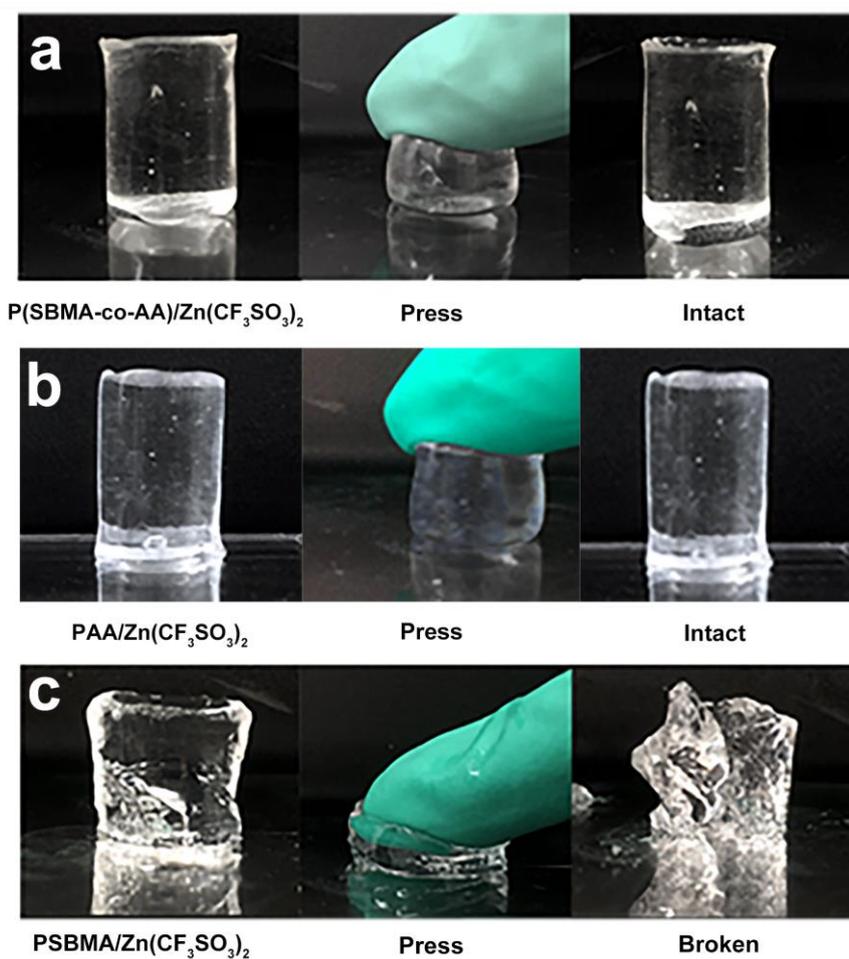


Fig. S6 Photographs of (a) $\text{P(SBMA-co-AA)/Zn(CF}_3\text{SO}_3)_2$, (b) $\text{PAA/Zn(CF}_3\text{SO}_3)_2$, and (c) $\text{PSBMA/Zn(CF}_3\text{SO}_3)_2$ hydrogel electrolytes before and after compression.

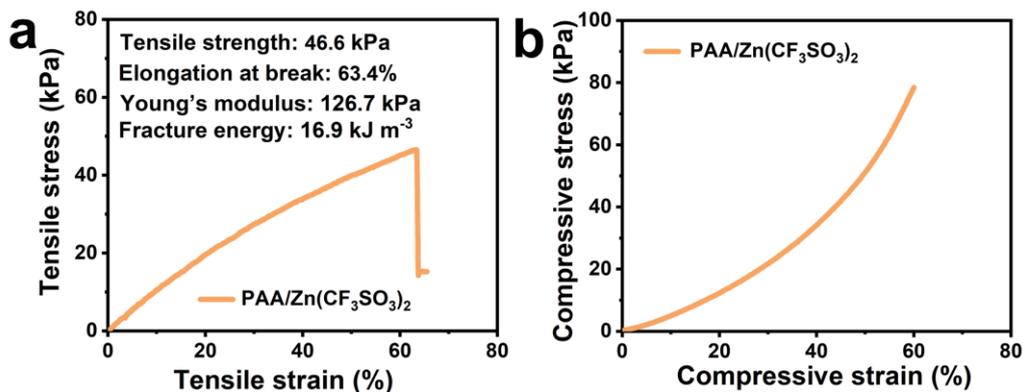


Fig. S7 (a) Tensile stress-strain curve and (b) compressive stress-strain curve of the PAA/Zn(CF₃SO₃)₂ hydrogel electrolyte.

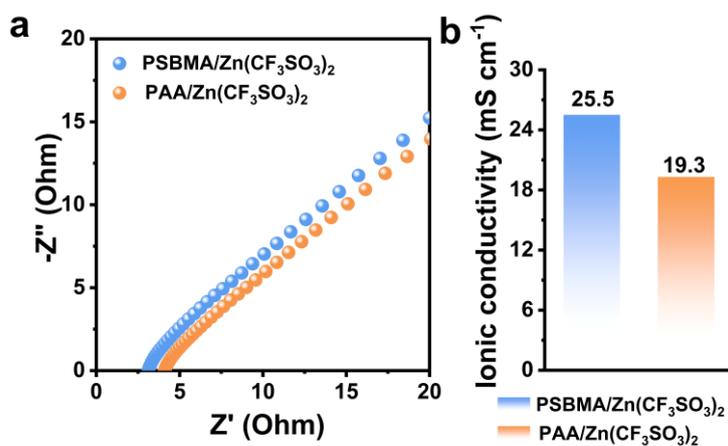


Fig. S8 (a) EIS spectra and (b) corresponding ionic conductivities of PSBMA/Zn(CF₃SO₃)₂ and PAA/Zn(CF₃SO₃)₂ hydrogel electrolytes.

References

1. Y. Jiang, K. Dong, X. Yan, C. Chen, P. Ni, C. Yang and Y. Lu, *Sustain. Energy Fuels*, 2020, **4**, 3370–3377.