Supporting Information

A safe and robust dual-network hydrogel electrolyte coupled with multi-heteroatom doped carbon nanosheet for flexible quasi-solid-state zinc ion hybrid supercapacitor

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1. Experimental section

1.1 Materials.

All chemicals were used as received without further purification. $Zn(CF_3SO_3)$, κ-carrageenan, and 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone were purchased from Aladdin Industrial Corporation. Citric acid was purchased from Shanpu chemical Co. Ltd. (Shanghai, China). Thiourea was obtained from Damao Chemical Regent Factory (Tianjin, China). Sodium chloride was obtained from Xinbote chemical Co. Ltd. (Tianjin, China). Potassium hydroxide was procured from Beilian Chemical Co. Ltd. Acrylamide was supplied by Hongyan Chemical Regent Factory (Tianjin, China). Potassium chloride and N,N′-methylenebisacrylamide were bought from Baishi chemical Co. Ltd (Shanghai, China).

1.2 Synthesis of N and S co-doped carbon nanosheet (ACNS)

All chemicals were analytical grade without further purification. Specifically, certain amount of NaCl, citric acid, and thiourea were dissolved in 80 mL deionized water to form a transparent aqueous solution. After evaporating the solvent at 80 °C, a uniformly blended mixture of precursor@NaCl sample was obtained. Subsequently, the precursor@NaCl was calcined at 600 °C with a ramp rate of 5 °C min^{-1} for 2 h under a N_2 atmosphere. After cooling down to room temperature, the NaCl template was removed by deionized water, and the CNS product was obtained after dried. Finally, the CNS sample was activated with the addition of potassium hydroxide aqueous solution, followed by drying and calcining at 650 °C with a heating rate of 5 °C min^{-1} under a N_2 atmosphere for 2 h. After washing with 1 mol L^{-1} HCl solution and deionized water, the N and S co-doped carbon nanosheet (denoted as ACNS) was obtained.

1.3 Synthesis of κ-CG/PAAm and κ-CG/PAAm/Zn(CF_3SO_3)$_2$ hydrogel

The double crosslinked hydrogel was synthesized via the formation of physically and chemically cross-linked networks. Acrylamide monomer (3.84 g), N,N′-methylenebisacrylamide (1.15 mg), UV-initiator (0.115 g), and KCl (0.028 g) were successively added into 20 mL deionized water and stirred for 30 min to from a homogeneous and transparent solution. Then κ-CG (0.48 g) was slowly added to the solution and stirred vigorously at 60 °C for 1 h. Next, the resulting solution was transferred into a glass mold followed by cooling the solution at 4 °C for 30 min to form the physically cross-linked κ-CG first network. Subsequently, a photopolymerization process was triggered under the UV irradiation (wavelength of 365 nm and intensity of 8 W) for 1 h to form the κ-CG/PAAm double crosslinked hydrogel. Finally, the resultant hydrogel was immersed in 1 M Zn(CF_3SO_3)$_2$ aqueous solution at room temperature overnight to form the hydrogel electrolyte.

1.4 Material characterizations

The field emission scanning electron microscopy (FESEM, SU-8010), transmission electron microscopy (TEM, FEI Tecnai G2 F30), high-resolution transmission electron microscope (HRTEM), and the corresponding selected area electron diffraction technology (SEAD, FEI Tecnai G2 F30) were employed to reveal the microstructure of the prepared samples. The crystalline structure of the prepared sample was examined by X-ray powder diffraction (XRD, Brüker D8) measurement with Cu Kα radiation. Raman spectra were performed from Micro-Raman spectrometer (Brüker Senterra spectrometer). Nitrogen adsorption/desorption isotherms were conducted at 77 K using a microporous analyzer equipment (3H-2000PM1/2). Fourier transform infrared spectra (FTIR) were obtained by a VERTEX 70 spectrometer in the range of 550–4000 cm^{-1}. X-ray photoelectron spectroscopy spectra (XPS) were recorded from ESCALAB 250Xi instrument to reveal the chemical valence states of the samples.

1.5 Assembly of aqueous and quasi-solid-state ZHSC devices

The ACNS cathode consists of 80 wt% active materials, 10 wt% acetylene black, and 10 wt% of polytetrafluoroethylene (PTFE) in a mixture paste of ethanol and DI water. Then the obtained slurry was dried and rolled into a round sheet and further dried in an oven at 60 °C for 8 h. Finally, this round sheet was pressed on a flexible graphite paper. It should point out that the mass loading of active materials is about 1.6 mg cm^{-2}. Aqueous Zn//ACNS ZHSC was assembled by ACNS cathode, Zn foil (thickness: 80 μm) anode, a Whatman GF/D (Glass Microfiber Filters) separator in 1 M aqueous $Zn(CF_3SO_3)_2$ electrolyte with CR2032 coin-type battery shell. The quasi-solid-state device was assembled by ACNS cathode, Zn foil anode, and κ-CG/PAAm/$Zn(CF_3SO_3)_2$ hydrogel electrolyte. The quasi-solid-state device was further packaged by polyimide tape in order to prevent the decrease of water content of the hydrogel.

1.6 Electrochemical measurements

Galvanostatic charge/discharge (GCD) and cycling stability tests were conducted on a Land Battery Test System. The current densities were ranged from 0.25 to 20 A g^{-1}. Cyclic voltammetry (CV) tests were measured on an electrochemical workstation (CHI660D, shanghai Chenhua) between 0.2 to 1.8 V under different scan rates changed from 1 to 50 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) was carried out in the frequency ranged from 1 mHz to 100 kHz at an open circuit potential with an amplitude of 5 mV. 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 were calculated from the following Equations:

$$P = \frac{3600E}{t} \quad (1)$$

where E (Wh kg^{-1}) represents the energy density, t (s) is the discharging time.[1]

Table S1 The corresponding abbreviations of the full names used in this paper.

Full name	Abbreviation
Zinc ion hybrid supercapacitor	ZHSC
κ-carrageenan	κ-CG
Polyacrylamide	PAAm
κ-carrageenan/polyacrylamide hydrogel	κ-CG/PAAm
κ-carrageenan/polyacrylamide/$Zn(CF_3SO_3)_2$ hydrogel electrolyte	κ-CG/PAAm/$Zn(CF_3SO_3)_2$
Nitrogen and sulphur co-doped carbon nanosheets before activation	CNS
Activated nitrogen and sulphur co-doped carbon nanosheets	ACNS
Aqueous zinc ion hybrid supercapacitor based on ACNS cathode and Zn foil anode	Zn//ACNS ZHSC
Quasi-solid-state zinc ion hybrid supercapacitor based on ACNS cathode, Zn foil anode, and κ-CG/PAAm/$Zn(CF_3SO_3)_2$ hydrogel electrolyte	Zn//κ-CG/PAAm/$Zn(CF_3SO_3)_2$//ACNS ZHSC
Light-emitting diode	LED
Ultraviolet	UV
N,N′-methylenebisacrylamide	MBAA

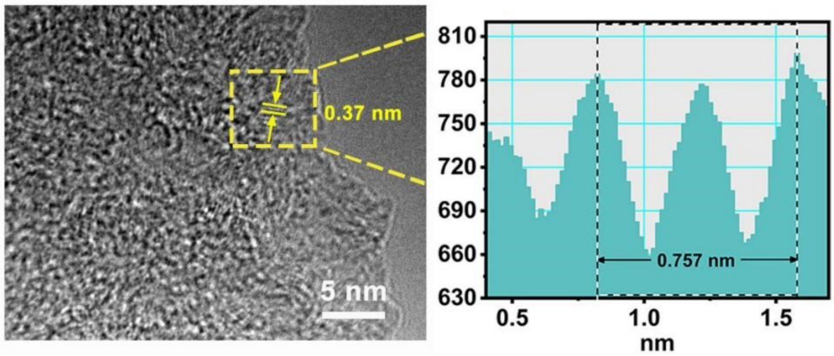

Fig. S1 HRTEM image of ACNS with the corresponding intensity profile for the line scan across the lattice fringes.

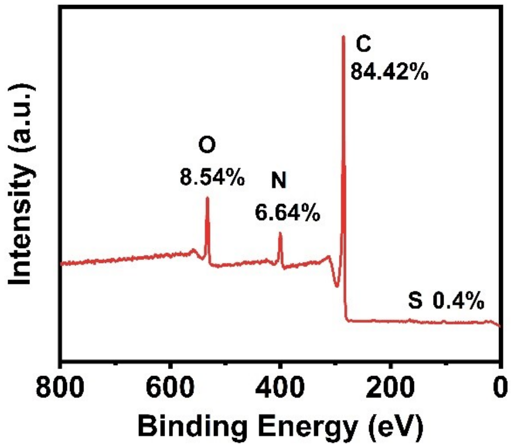

Fig. S2 XPS survey spectrum of ACNS.

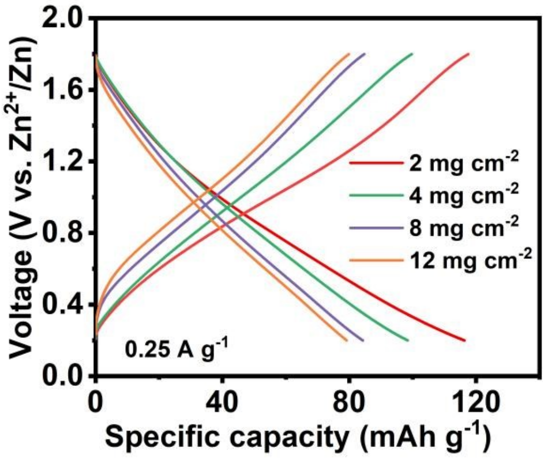

Fig. S3 GCD curves of the ACNS under various mass loadings.

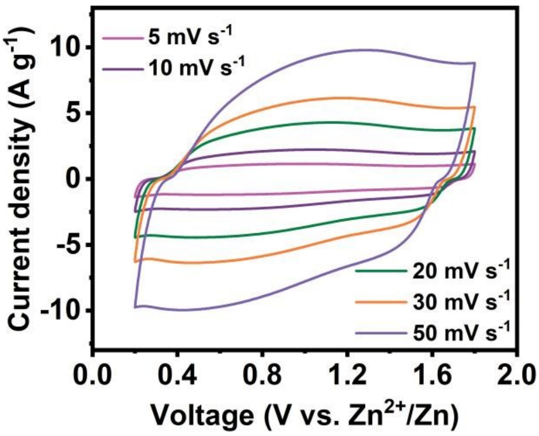

Fig. S4 CV curves of the quasi-solid-state Zn//κ-CG/PAAm/Zn(CF_3SO_3)$_2$//ACNS ZHSC at different scan rates.

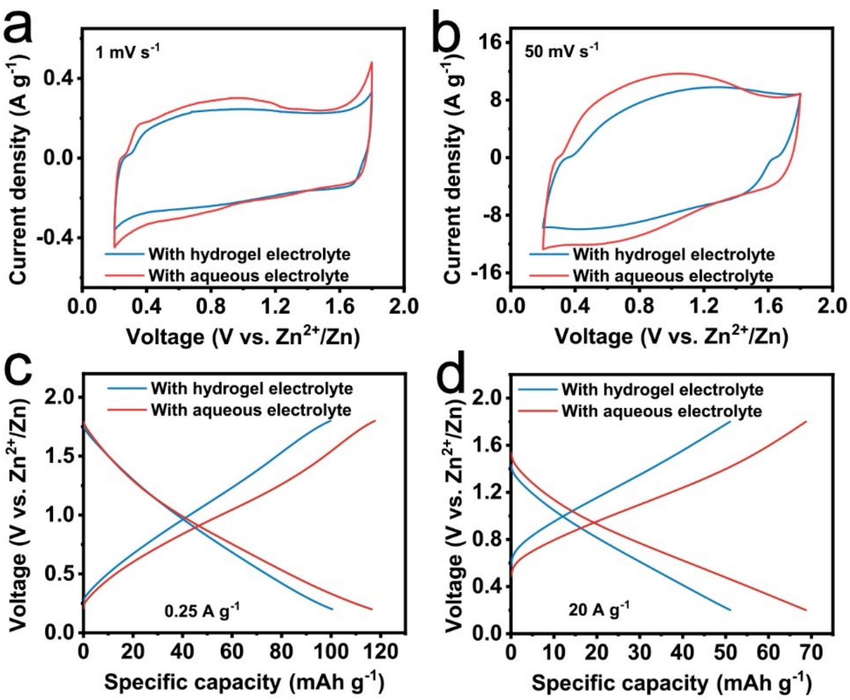

Fig. S5 CV curves of ZHSCs with different electrolytes at (a) 1 mV s^{-1} and (b) 50 mV s^{-1}. GCD curves of ZHSCs with different electrolytes at (c) 0.25 A g^{-1} and (d) 20 A g^{-1}.

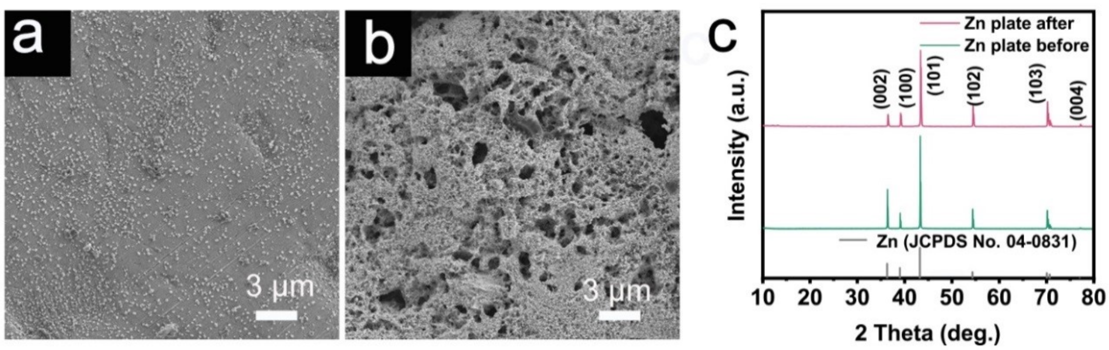

Fig. S6 SEM images of Zn anode (a) before and (b) after cycling. (c) XRD patterns of Zn anode before and after cycling.

Notes and references

1 J. Huang, L.Wang, Z. Peng, M. Peng, L. Li, X. Tang, Y. Xu, L. Tan, K. Yuan and Y. Chen, J. Mater. Chem. A, 2021, **9**, 8435-8443.