Supporting Information:

Controllable Construction of 3D-Honeycomb-like porous carbon network as High-Performance Cathodes for Promoting Zn-Ion Storage

Qian Li^a[#], Tongde Wang^b[#], Tie Shu^c, Xiaoyi Pan^a, Yousheng Tao^{a*}

^a College of Materials Science and Engineering, Sichuan University, Chengdu,

610065, People's Republic of China

^b Shanghai Key Laboratory of Special Artificial Microstructure Materials and Technology, School of Physics Science and Engineering, Tongji University, Shanghai 200092, China.

^c Multi-scale Porous Materials Center, Institute of Advanced Interdisciplinary Studies, & School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, People's Republic of China

*Corresponding author. E-mails: taoys@scu.edu.cn (Yousheng Tao)

Qian Li and Tongde Wang contributed equally to this manuscript.

Experimental

S1. Material characterizations

The morphologies and structures of the as-prepared samples were characterized by SEM (INCA X-Max) and TEM (JEOL JEM 2100F). The Phase composition and surface chemistry states of samples were characterized by powder X-ray diffractometer (Bruker D8, Cu K α radiation (λ =0.15418 nm) between 5 and 90°) and XPS (Thermo ESCALAB 250XI with a monochromatic Al-K α radiation (1486.6 eV).). The Raman spectra were s performed using laser Raman spectrometer ((LabRAM HR, HORIBA, laser excitation: 532 nm). Moreover, the specific surface area, and pore size of the assynthesized materials were evaluated by N₂ adsorption/desorption measurement (ASAP 2460 Version 3.01) and Brunauere- Emmette-Teller method. The contact Angle of the film on the electrode surface was measured by a contact Angle measuring instrument (DSA25E).

S2. Electrochemical calculations

All Cyclic voltammetry (CV, 0.2-1.8V) and electrochemical impedance spectroscopy (EIS, 100kHz-10Hz) tests were carried out in CHI 660E electrochemical workstation (Shanghai ChenHua Instrument Co., Ltd.). The galvanostatic charge– discharge (GCD, 0.2-1.8V) and cycling performance were tested by Land cell tester system (Wuhan Land Electronics Co., Ltd. CT3002A-5V-2mA&10mA). The calculations on the specific capacitances, energy and power densities of the cells are provided in SI.

Coin-type ZICs were tested in the voltage range of 0.2-1.8 V. The specific

capacitance, energy and power densities of ZICs were calculated as described below.

Specific capacitances were calculated from GCD curves according to Eq. (1):

$$Cm = \frac{I \times \Delta t}{m} \tag{1}$$

where Cm (mAh g⁻¹) is the specific capacity of a single electrode based on the mass of active material in three-electrode system or based on the total mass of active materials in two-electrode system. I(A) is the constant charge/discharge current, and m (g) is the mass laoding.

Energy density (*E*, Wh kg⁻¹) and power density (*P*, W kg⁻¹) of PICs were calculated based on Eqs. (2) and (3):

$$E = Cm \times \Delta V \tag{2}$$

$$P = \frac{ECm \times \Delta V}{1000 \times \Delta t} \tag{3}$$

S3. Theoretical simulations details

The DFT calculation of this work were performed using Vienna Ab-initio Simulation Package (VASP version 6.4.1). The interaction between nuclei and valence electrons were described by Projector augmented wave (PAW) pseudopotential, while the exchange behavior and correlation between electrons were approximated by the generalized gradient of Perdew- Burke-Ernzerhof (PBE). Specifically speaking, the truncation energy was set to 520 eV in the calculation, while the convergence criteria for energy and mechanics were respectively delimited as 10E-6 eV and 0.01 eV A-1, ensuring that the energy error is less than 1mev/atom. DFT-D4 was used to correct the van der Waals force in the calculation, and the free energy was calculated based on the following formula:

 $\Delta G = \Delta E + \Delta Z P E - T \Delta S - e U$

Where, ΔE is the change in system energy before and after the reaction, ΔZPE represents the change in zero-point energy, and ΔS is the change in entropy for each reaction. During vibration analysis, all atoms are fixed (T = 298.15 K). U is the electrode potential and e is the transfer charge (U = 0 V).



Figure S1. SEM images of (a, d) ZIF-8/SA-2, (b, e) ZIF-8/SA-1 and (c, f) ZIF-8/SA-0.5.



Figure S2. SEM images of (a-c) HPCN-1 and (d-f) HPCN-3



Figure S3. SEM images of NPCP.



Figure S5. The high-resolution C1_s spectrum of HPCN-1, HPCN-3 and NPCP

I able SI	Relative	concentra	ition of C	Labon I	oonaing	

Binding	nding Carbon Relative Concentration(%))
Energy (eV)	ergy (eV) bonding		HPCN-3	HPCN-2	HPCN-1
284.5	C=C	42.55	40.83	38.71	42.06
285.0	C-C	27.16	35.18	33.04	27.76
286.1	C-O/C-N	21.26	16.04	18.62	20.90
287.5	C=O	4.31	3.74	5.51	5.44
288.7	-COOH	4.72	4.21	4.12	3.84

Binding	Oxygen	Relative Concentration(%)				
Energy (eV)	bonding	NPCP	HPCN-3	HPCN-2	HPCN-1	
532.0	O-C/C-OH	46.4	46.46	53.41	48.36	
530.8	C=O	25.08	21.76	22.69	29.60	
533.3	O-C=O	28.46	31.79	23.90	22.04	

Table S2 Relative concentration of Oxygen bonding

Table S3 Relative concentration of Nitrogen bonding

Binding	Nitrogen	Relative Concentration(%)					
Energy (eV)	bonding	NPCP	HPCN-3	HPCN-2	HPCN-1		
398.2	Pyridinic-N	47.35	48.65	51.50	49.26		
399.8	Pyrrolic-N	35.85	25.66	23.25	36.46		
401.2	Graphitic-N	14.34	20.65	20.02	11.16		
402.8	Oxidized-N	2.46	5.13	5.23	3.13		



Figure S6. Pore size distribution HPCNs and NPCP:

Table S4 The simulated R_{s} and R_{ct} of NPCP, HPCN-3, HPCN-2 and HPCN-1 cathodes for ZICs.

Parameters	NPCP	HPCN-3	HPCN-2	HPCN-1
R _s (ohm)	2.2	1.6	1.2	1.4
R _{ct} (ohm)	188.7	130.9	108	168.3



Figure S7. Electrochemical performance of NPCP: (a) CV curves at different scan rates, (b-c) GCD curves at different current density and (d-i) capacitive contribution at different scan rates (the red region;1-20 mV·s⁻¹).



Figure S8. Electrochemical performance of HPCN-1: (a) CV curves at different scan rates, (b-c) GCD curves at different current density and (d-i) capacitive contribution at different scan rates (the red region;1-20 mV·s⁻¹).



Figure S9. Electrochemical performance of HPCN-2: (a) CV curves at different scan rates, (b-c) GCD curves at different current density and (d-i) capacitive contribution at different scan rates (the red region;1-20 mV·s⁻¹).



Figure S10. Electrochemical performance of HPCN-3: (a) CV curves at different scan rates, (b-c) GCD curves at different current density and (d-i) capacitive contribution at different scan rates (the red region;1-20 mV \cdot S⁻¹).

Table	S5 The	Performance	comparison	of This	work wit	h reported	ZIHCs
1 4010		I ci ioi intance	comparison	01 11115		n reported	

Cathode	Electrolyte	Capacity	Span life	Energy/power density	Potential window	Ref
Zn-MET-800	2 M ZnSO ₄	121.4 mAh • g ⁻¹ @ 0.5A • g ⁻¹ 110.2 mAh • g ⁻¹ @ 1A • g ⁻¹ 98.7 mAh • g ⁻¹ @ 2A • g ⁻¹ 1 81.6 mAh • g ⁻¹ @ 5A • g ⁻¹	30,000cycles @ 90.4%	128.5 Wh kg ⁻¹ @ 70 W • kg ⁻¹	0.1-1.7V	1
PZC-A750	1M Zn(CF ₃ SO ₃) ₂	119 mAh • g ⁻¹ @ 0.5A • g ⁻¹ 108 mAh • g ⁻¹ @ 1A • g ⁻¹ 102 mAh • g ⁻¹ @ 3A • g ⁻¹ 99.6 mAh • g ⁻¹ @ 5A • g ⁻¹	10,000cycles @ 100%	107.3 Wh kg ⁻¹ @ 214.9W • kg ⁻¹	0.2-1.8V	2
HPCS-900	2 M ZnSO ₄	104.9mAh • g ⁻¹ @	30,000cycles @ 95.2%	90.17 Wh kg ⁻¹ @ 81.2 W • kg ⁻¹	0.1-1.7V	3

		0.1A • g ⁻¹				
		90.7 mAh • g ⁻¹ @				
		0.2A • g ⁻¹				
		82.3 mAh • g ⁻¹ @				
		0.5A • g ⁻¹				
		75.6 mAh • g ⁻¹ @ 1A • g ⁻				
		1				
		64.8mAh • g ⁻¹ @ 2A • g ⁻¹				
		55.8 mAh • g ⁻¹ @ 5A • g ⁻ 1				
		48.5 mAh • g ⁻¹ @				
		10A • g ⁻¹				
C-800	3 M ZnSO ₄	121.7 mAh • g ⁻¹ @	10,000cycles @ 98.7%	119.7 Wh kg ⁻¹ @ 400.8	0.2-1.8V	4
		0.05A • g ⁻¹		W • kg ⁻¹		
		80 mAh • g ⁻¹ @ 0.5A • g ⁻ 1				
		55 mAh • g ⁻¹ @ 5A • g ⁻¹				
		41.4 mAh • g ⁻¹ @				
		20A • g ⁻¹				
SOCNs	3M Zn(CF ₃ SO ₃) ₂	151 mAh • g ⁻¹ @		103.1 Wh kg ⁻¹ @ 51.6 W • kg ⁻¹	0.2-1.8V	5
		0.1A • g ⁻¹				
		121.4 mAh • g ⁻¹ @				
		0.2A • g ⁻¹				
		105.6 mAh • g ⁻¹ @				
		0.5A • g ⁻¹				
		101.2 mAh • g ⁻¹ @				
		1A • g ⁻¹				
		92 mAh • g ⁻¹ @ 2A • g ⁻¹				
		84 mAh • g ⁻¹ @ 5A • g ⁻¹				
		81 mAh • g ⁻¹ @ 10A • g ⁻¹				
N/S-PCD	2 M ZnSO ₄	133.4 mAh • g ⁻¹ @	10,000cycles @ 97.1%	106.7 Wh kg ⁻¹ @ 160 W • kg ⁻¹	0.2-1.8V	6
		0.2A • g ⁻¹				
		128.9 mAh • g ⁻¹ @				
		0.5A • g ⁻¹				
		123.7 mAh • g ⁻¹ @				
		1A • g ⁻¹				
		117.8 mAh • g ⁻¹ @				
		2A • g ⁻¹				
		107.5 mAh • g ⁻¹ @				
		5A • g ⁻¹				
		98.2 mAh • g ⁻¹ @				

		10A • g ⁻¹ 90.7 mAh • g ⁻¹ @ 15A • g ⁻¹ 84.4 mAh • g ⁻¹ @ 20A • g ⁻¹			
LDC	1 M ZnSO4	127.7 mAh • g ⁻¹ @ 0.5A • g ⁻¹ 42.8 mAh • g ⁻¹ @ 20A • g ⁻¹		97.6 Wh kg ⁻¹ @ 400 W • kg ⁻¹	0.2-1.8V
DCPs-800	2 M ZnSO ₄	140mAh • g ⁻¹ @ 0.2A • g ⁻¹ 121.2 mAh • g ⁻¹ @ 0.4A • g ⁻¹ 103.5mAh • g ⁻¹ @ 0.8A • g ⁻¹ 98.8 mAh • g ⁻¹ @ 1.6A • g ⁻¹ 90.1mAh • g ⁻¹ @ 3.2A • g ⁻¹ 86.2 mAh • g ⁻¹ @6.4A • g ⁻¹	16,000cycles @ 99.5%	111.1 Wh kg ⁻¹ @ 150 W • kg ⁻¹	0.2-1.8V
SA-3	2 M ZnSO ₄	$100 \text{ mAh} \cdot \text{g}^{-1} @$ 0.1A \cdot \text{g}^{-1} 92 mAh \cdot \text{g}^{-1} @ 0.2A \cdot \text{g} 1 84 mAh \cdot \text{g}^{-1} @ 0.5A \cdot \text{g} 1 80 mAh \cdot \text{g}^{-1} @ 0.8A \cdot \text{g} 1 77 mAh \cdot \text{g}^{-1} @ 1A \cdot \text{g}^{-1} 72 mAh \cdot \text{g}^{-1} @ 2A \cdot \text{g}^{-1} 70 mAh \cdot \text{g}^{-1} @ 5A \cdot \text{g}^{-1} 49 mAh \cdot \text{g}^{-1} @ 10A \cdot \text{g}^{-1}	50,000cycles @ 93%	100 Wh kg ⁻¹ @ 120 W • kg ⁻¹	0.2-1.8V
This work	2 M ZnSO ₄	128 mAh • g ⁻¹ @ 0.1A • g ⁻¹ 121 mAh • g ⁻¹ @ 0.2A • g ⁻¹ 118 mAh • g ⁻¹ @	50,000cycles @ 97.8%	128.5 Wh kg ⁻¹ @ 130 W • kg ⁻¹	0.2-1.8V

 $\begin{array}{c} 0.5 A \cdot g^{-1} \\ 115 \text{ mAh} \cdot g^{-1} @ \\ 0.8 A \cdot g^{-1} \\ 108 \text{ mAh} \cdot g^{-1} @ 1 A \cdot g^{-1} \\ 101 \text{ mAh} \cdot g^{-1} @ 2 A \cdot g^{-1} \\ 96 \text{ mAh} \cdot g^{-1} @ 5 A \cdot g^{-1} \end{array}$



Figure S11. Ex situ SEM images at different states for cathode.



Figure S12. Ex situ SEM images at different states for cathode.



Figure S13. Ex situ XPS (b)Zn 2p, (c) S 2p,

Table S6 Relative concentration of Cabon bonding

Binding	Carbon	Relat	tive Concentrati	ion(%)
Energy (eV)	bonding	1.8 V	0.2V	1.0 V
284.6	C=C/C-C	35.57	27.23	26.13
285.7	C-O/C-N	21.54	31.91	29.94
286.3	C=O	27.13	20.29	24.26
288.3	C-O-Zn	5.46	9.45	7.82
290.6	C-F	10.30	11.12	11.46

Table S7 Relative concentration of Oxygen bonding

Binding	Oxygen	Relati	tion(%)	
Energy (eV)	bonding	1.8 V	0.2V	1.0 V
533.1	C-O	63.82	71.76	61.28
534.2	O-C=O	13.99	18.09	14.11
532.0	C=O	22.19	10.15	14.60

Table S8 Relative concentration of Nitrogen bonding

Binding	Nitrogen	Relat	ive Concentra	tion(%)
Energy (eV)	bonding	1.8 V	0.2 V	1.0V
398.3	Pyridinic-N	27.92	19.58	24.03
400.0	Pyrrolic-N	48.36	43.23	37.08
401.8	Graphitic-N	19.85	22.61	32.63
403.6	Oxidized-N	3.87	14.59	6.26

Reference

Jia, D. D.; Shen, Z. L.; Zhou, W.; Li, Y.; He, J.; Jiang, L.; Wei, Y. C.;
 He, X. J., Ultrahigh N-doped carbon with hierarchical porous structure derived from metal-organic framework for high-performance zinc ion hybrid capacitors. *Chem. Eng. J.* 2024, *485*, 12 https://doi.org/10.1016/j.cej.2024.149820

2. Zhu, X. Q.; Guo, F. J.; Yang, Q.; Mi, H. Y.; Yang, C. C.; Qiu, J. S., Boosting zinc-ion storage capability by engineering hierarchically porous nitrogen-doped carbon nanocage framework. *J Power Sources* **2021**, *506*, 10 https://doi.org/10.1016/j.jpowsour.2021.230224

3. Shang, K. Z.; Liu, Y. J.; Cai, P. W.; Li, K. K.; Wen, Z. H., N, P, and S codoped 3D porous carbon-architectured cathode for high-performance Zn-ion hybrid capacitors. *J Mater Chem A* **2022**, *10* (12), 6489-6498 https://doi.org/10.1039/d2ta00202g

4. Wei, F.; Tian, H. D.; Chen, P. M.; Lv, Y. H.; Huang, J. R., Construction of porous carbon nanosheets by dual-template strategy for zinc ion hybrid capacitor. *Appl Surf Sci* **2023**, *613*, 9 <u>https://doi.org/10.1016/j.apsusc.2022.156021</u>

5. Zhu, C. L.; Long, R.; Zhu, L. Y.; Zou, W. Y.; Zhang, Y. F.; Gao, Z. Y.; Shi, J.; Tian, W. Q.; Wu, J. Y.; Wang, H. L., Sulfate template induced S/O doped carbon nanosheets enabling rich physi/chemi-sorption sites for high-performance zinc ion hybrid capacitors. *J Colloid Interf Sci* **2023**, *652*, 590-598 https://doi.org/10.1016/j.jcis.2023.08.110 Yang, Y.; Chen, D. L.; Wang, H. Y.; Ye, P. C.; Ping, Z. T.; Ning, J. Q.;
 Zhong, Y. J.; Hu, Y., Two-step nitrogen and sulfur doping in porous carbon dodecahedra for Zn-ion hybrid supercapacitors with long term stability. *Chem. Eng. J.* 2022, 431, 9 <u>https://doi.org/10.1016/j.cej.2021.133250</u>

7. Lu, Y. Y.; Li, Z. W.; Bai, Z. Y.; Mi, H. Y.; Ji, C. C.; Pang, H.; Yu, C.;
Qiu, J. S., High energy-power Zn-ion hybrid supercapacitors enabled by layered B/N
co-doped carbon cathode. *Nano Energy* 2019, 66, 9
<u>https://doi.org/10.1016/j.nanoen.2019.104132</u>

8. Liu, L. T.; Sun, Z. Y.; Lu, Y. P.; Zhang, J. P.; Li, Y. M.; Zhang, G. X.; Chen, X. H.; Omanovic, S.; Sun, S. H.; Song, H. H., d-Calcium pantothenate-derived porous carbon: carbonization mechanism and application in aqueous Zn-ion hybrid capacitors. *J Mater Chem A* **2023**, *11* (26), 14311-14319 <u>https://doi.org/10.1039/d3ta02498a</u>

9. Pan, X. Y.; Li, Q.; Wang, T. D.; Shu, T.; Tao, Y. S., Controllable synthesis of electric double-layer capacitance and pseudocapacitance coupled porous carbon cathode material for zinc-ion hybrid capacitors. *Nanoscale* **2024**, *16* (7), 3701-3713 <u>https://doi.org/10.1039/d3nr06258a</u>