

---

## Supporting Information

### **Synergistic action of highly-active porous carbon-based bifunctional electrocatalysts and neutral electrolyte: endowing Zinc-air batteries with ultra-long cycle stability**

Juanjuan Zhao<sup>a</sup>, Xiaohang Ma<sup>\*a</sup>, Lingyun Liu<sup>a</sup>, Weiguang Fang<sup>a</sup>, Zhenfa Zi<sup>a\*</sup>, Mingzai Wu<sup>b,c\*</sup>

a.School of Physics and Materials Engineering, Hefei Normal University, Hefei, 230601, PR China. E-mail: a. E-mail: zjj@hfnu.edu.cn; mxh@mail.ustc.edu.cn; zfzi@issp.ac.cn.

b.School of Physics and Materials Science, Anhui University, Hefei, 230601, China. E-mail: wumz@ahu.edu.cn.

c.Key Laboratory of photoelectric conversion energy materials and devices of Anhui Province, Key Laboratory of hybrid material structure and function regulation, Ministry of Education, Anhui University, Hefei, 230601, China.

#### **Experimental Section**

##### **Synthesis of compound 2 ( $\{[Co(ADC)(bpp)]\}_n$ )**

According to the synthesis method in the literature<sup>1</sup>:

The 22.4 mg of H<sub>2</sub>ADC (0.10 mmol, H<sub>2</sub>ADC = 1,3-Amantadane dimethyl acid) and 18 mg of bpp (0.10 mmol, bpp = 1,3-two- (4-pyridyl) propane) was dissolved in 5 mL of methanol as solution A. Subsequently, the 28.8 mg of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.1 mmol) was dissolved in 5 mL of deionized water as solution B. Solution B was then dispersed into solution A. Subsequently, the pH of the mixed solution was adjusted to 7.5 with 0.5 M NaOH solution. After resting for 48 h at room temperature, the purple precipitate was the synthesized marked as compound 2.

##### **Synthesis of the SiO<sub>2</sub>-nanosphere**

The SiO<sub>2</sub> nanospheres with an average particle size of 200 nm were synthesized by Stober: first, a mixture of 65 mL of anhydrous ethanol and 4.5 mL of ethyl orthosilicate was added to 25 mL of deionized water under stirring conditions. Next, 9 ml of ammonia water was poured into the above mixture under stirring conditions. The final mixed solution obtained above was stirred for 5 hours, and then the resulting milky solution was centrifuged and washed several times with deionized water and ethanol. Finally, the resulting white product was the SiO<sub>2</sub> nanosphere by drying in a 60°C oven.

##### **SiO<sub>2</sub>@ Compound 2 synthesis**

Disperse 2 g SiO<sub>2</sub> nanosphere into solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as solution A. Subsequently, 22.4 mg H<sub>2</sub>ADC and 18.0 mg bpp were dissolved in 5 mL of methanol as solution B. Then solution B was added to solution A, adjusted pH with 0.5 M NaOH to 7.5, and rested for 48 h at room temperature until the purple powder was the target product.

---

### **Synthesis of N/SdCF-OIM / Co<sub>9</sub>S<sub>8</sub>**

Take the SiO<sub>2</sub>@ compound 2 precursor above 200 mg and put it into the quartz boat, and put 50 mg of sublimated sulfur into the quartz boat. The sublimation sulfur was put into the upstream area of the tube furnace, then SiO<sub>2</sub>@ compound 2 was put into the downstream area of the tube furnace. Subsequently, the tube furnace was heated up to 700 °C with the rate of 5°C/min and heated at 700 °C for 2h in N<sub>2</sub> atmosphere to obtain black powder. Finally, the black powder was soaked in 3 M KOH solution for 48 h, and then the solution was centrifuged and washed with deionized water for 6 times. Then the target product was acquired through the final drying marked as N/SdCF-OIM/Co<sub>9</sub>S<sub>8</sub>.

### **Synthesis of N/SdCF-Co<sub>9</sub>S<sub>8</sub>**

Compound 2 (100 mg) was prepared directly placed into a quartz boat with 0.5 mg of sublimated sulfur at the upstream, then under N<sub>2</sub> atmosphere at a heating rate of 5°C/min, calcined at 700°C for 2h to obtain black powder marked as N/SdCF-Co<sub>9</sub>S<sub>8</sub>.

### **Fabrication and test of liquid rechargeable Zn-air batteries (ZABs)**

The liquid ZAB was assembled with Zn-plate served as the anode and carbon cloth coated bifunctional electrocatalyst (1 cm<sup>2</sup>) served as the air electrode, the mixed solution of 6 M KOH and 0.2 M Zn (CH<sub>2</sub>COO)<sub>2</sub> and the 2.5 M NH<sub>4</sub>Cl and 0.5 M ZnCl<sub>2</sub> mixed solution as electrolyte respectively. Typically, 10 mg of electrocatalyst was fully dispersed in a solvent consisting of 700 μL DI water, 240 μL isopropanol, and 60 μL Nafion solution by sonication for 2 h. Then, 100 μL electrocatalyst ink was dripped on 1 cm<sup>2</sup> carbon cloth to achieve a electrocatalyst loading amount of 1 mg cm<sup>-2</sup>. ZABs tests were measured with electrochemical workstation (CHI 760E) and LAND battery testing system (LAND-CT2001A, China). Both the discharge/charge current and corresponding power densities were standardized to the active area of air cathode electrode.

### **Materials and characterization**

All reagents and solvents were commercially available and were used without further purification. In addition, the microstructure and phase composition of the as-obtained samples were characterized by Field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan), Transmission electron microscopy (TEM, JEM-2100, JEOL, Japan), X-ray powder diffraction (XRD Bruker D8-ADVANCE) with an 18 kW advanced X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda=1.54056$  Å). XPS was conducted with a Mg K $\alpha$  achromatic X-ray source.

### **Electrochemical characterizations**

The catalyst ink was prepared by dispersing catalyst (10 mg) and 50 μL Nafion (DuPont) into

700  $\mu\text{L}$  DI water and 250  $\mu\text{L}$  isopropanol by sonication. The electrochemical activities (CV, ORR and OER) of the catalysts were tested in a standard three electrodes system on the electrochemical workstation (CHI 760E) in 0.1 M saturated KOH electrolyte and 0.1 M  $\text{NH}_4\text{Cl}$  at room temperature respectively. The working electrode was a glassy carbon rotating disk electrode (diameter 5 mm) which drop casted with the catalyst ink to a loading amount of 0.2  $\text{mg cm}^{-2}$ . The counter electrode was a platinum electrode, and a saturated calomel electrode (SCE) as a reference electrode. All potentials here are converted to a reversible hydrogen electrode (RHE) scale,  $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E_{\theta_{\text{Ag/AgCl}}}$ . In 0.1 M saturated KOH electrolyte, the catalytic performance toward the ORR was measured from -0.8 to 0.2 V (vs. Ag/AgCl), and the catalytic activity for OER was evaluated from 0 to 1.0 V (vs. Ag/AgCl). In comparison, commercial 20 wt% Pt/C catalyst ink (for ORR) and the  $\text{RuO}_2$  catalyst ink (for OER) were prepared using the same procedure. The cyclic voltammetry (CV) measurements were performed at 20  $\text{mV s}^{-1}$  from -0.8 to 0 V (vs. Ag/AgCl) in  $\text{O}_2$ -saturated and  $\text{N}_2$ -saturated electrolyte, respectively. In order to test the electrochemical performances of the catalysts for ORR, the linear sweep voltammetry (LSV) curves were performed at a scanning rate of 5  $\text{mV s}^{-1}$  from -0.8 V to 0.2 V (vs. Ag/AgCl) at different rotation rates (400~2500 rpm) in  $\text{O}_2$ -saturated electrolyte.

The electron transfer number ( $n$ ) per  $\text{O}_2$  molecule in the ORR was determined by the slopes of the linear fit lines on the basis of the following K-L equation:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B \times \omega^{1/2}} \quad (1)$$

$$B = 0.2 \times n \times F \times C_{\text{O}_2} \times D_{\text{O}_2}^{2/3} \times \nu^{-1/6} \quad (2)$$

where  $j$  is the measured current density,  $j_k$  is the kinetic current density,  $\omega$  is the electrode rotation rate,  $F$  is the Faradic constant ( $96,485 \text{ C mol}^{-1}$ ),  $C_{\text{O}_2}$  is the saturated oxygen concentration in 0.1 M KOH aqueous solution ( $1.2 \times 10^{-6} \text{ mol cm}^{-3}$ ),  $D_{\text{O}_2}$  is the oxygen diffusion coefficient ( $1.73 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ),  $\nu$  is the kinematic viscosity of the solution ( $0.01 \text{ cm}^2 \text{ s}^{-1}$ ) and  $n$  is the electron transfer number in the ORR.

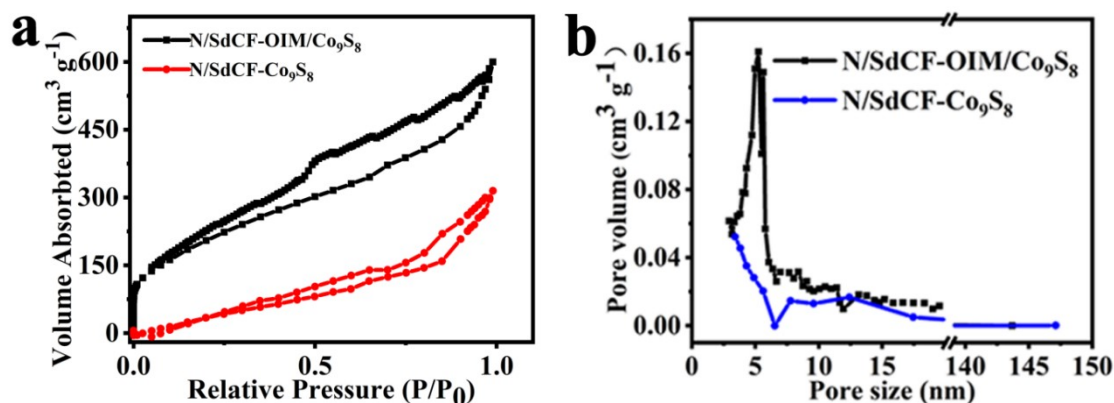


Figure S1 (a)  $\text{N}_2$  adsorption-desorption isotherms and (b) BJH pore-size distribution of the N/SdCF-OIM/ $\text{Co}_9\text{S}_8$  and N/SdCF- $\text{Co}_9\text{S}_8$ .

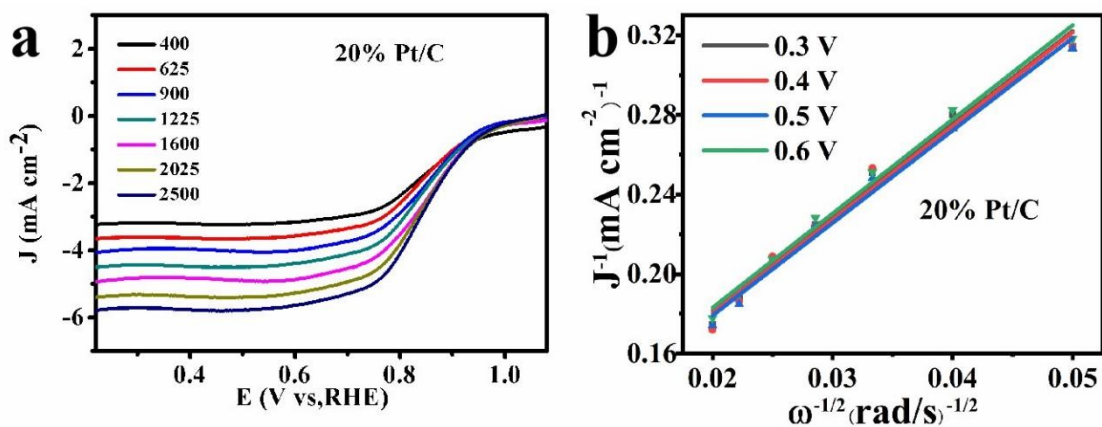


Figure S2 LSV curves of the Pt/C catalysts at different rotating speeds and the corresponding fitted curves.

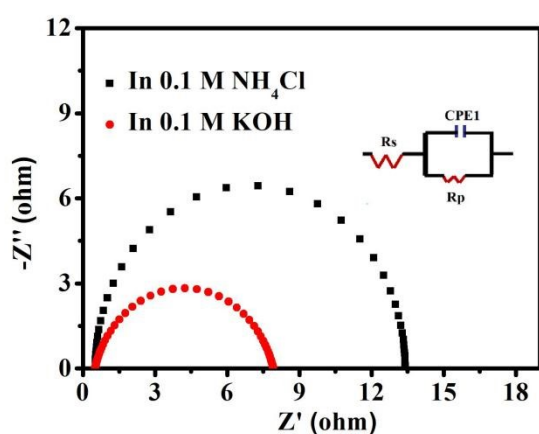


Figure S3 The electrochemical impedance spectra (EIS) of the N/SdCF-OIM/Co<sub>9</sub>S<sub>8</sub> catalysts obtained in 0.1 M KOH and 0.1 M NH<sub>4</sub>Cl by corresponding equivalent circuit.

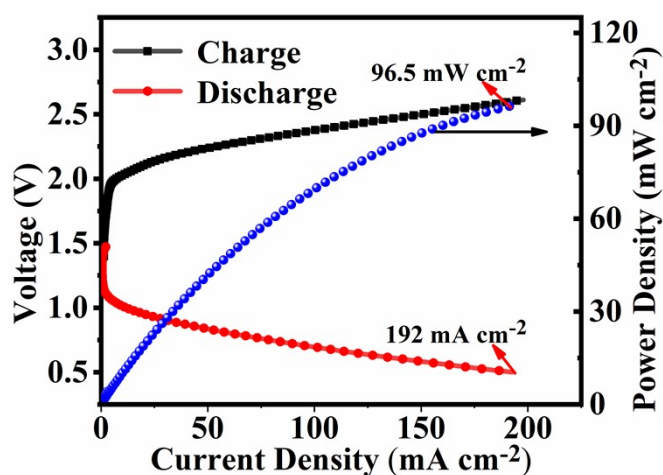


Figure S4 Charge-discharge polarization curves and the power density curves of the liquid ZABs in 2.5 M NH<sub>4</sub>Cl and 0.5 M ZnCl<sub>2</sub> mixed solution.

Table S1. Comparative summary of the performance of liquid ZABs employing currently reported bifunctional electrocatalysts with our work in alkaline electrolyte (6 M KOH+0.2 M Zn<sup>2+</sup>) with our work.

Electrocatal	OCP	Power density	Specific capacity	Cycling performanc	Test conditions of	Ref.
--------------	-----	---------------	-------------------	--------------------	--------------------	------

		(mW cm <sup>-2</sup> )	(mAh g <sup>-1</sup> )	e		
N/SdCF- OIM/Co <sub>9</sub> S <sub>8</sub>	1.425	181	803	510 cycles (170 h)	At a current density of 10 mA cm <sup>-2</sup> (20 min per cycle)	This work
Co <sub>9</sub> S <sub>8</sub> - NSHPCNF	1.44	113	823.5	200 cycles (66 h)	At a current density of 10 mA cm <sup>-2</sup> (20 min per cycle)	1
Fe-N-C/rGO	1.52	107	736	600 cycles (400 h)	At a current density of 5 mA cm <sup>-2</sup> (20 min per cycle)	2
Mn-SAS/CN	N.A	100	780	25 h	At a current density of 10 mA cm <sup>-2</sup> (20 min per cycle)	3
T-CoNCNTs // NiFe-LDH	1.39	245	N. A	100 cycles	At a current density of 10 mA cm <sup>-2</sup> (N.A)	4
Co <sub>5.47</sub> N/Co <sub>3</sub> F e <sub>7</sub> /NC	1.5	264	N. A	180 h	At a current density of 10 mA cm <sup>-2</sup> (N.A)	5
CNCNN electrode	N. A	N. A	N. A	600 cycles	At a current density of 20 mA cm <sup>-2</sup> (5 min per cycle)	6
CoSx/Co-NC	1.4	103	770	450 cycles (90 h)	At a current density of 5 mA cm <sup>-2</sup> (12 min per cycle)	7
Co@N-C	1.46	105	768	360 cycles (120 h)	At a current density of 2 mA cm <sup>-2</sup> (20 min per cycle)	8
Co <sub>4</sub> N and Co-N-C	1.4	174	774	408 cycles (136 h)	At a current density of 10 mA cm <sup>-2</sup> (20 min per cycle)	9

## References

1. W. Peng, Y. Wang, X. Yang, L. Mao, J. Jin, S. Yang, K. Fu and G. Li, *Appl. Catal. B Environ.*, 2020, 268, 118437.
2. L. Li, Y. J. Chen, H. R. Xing, N. Li, J. W. Xia, X. Y. Qian, H. Xu, W. Z. Li, F. X. Yin, G. Y. He and H. Q. Chen, *Nano Res.*, 2022, 15, 8056–8064.
3. X. Han, T. Zhang, W. Chen, B. Dong, G. Meng, L. Zheng, C. Yang, X. Sun, Z. Zhuang, D. Wang, A. Han and J. Liu, *Adv. Energy Mater.*, 2021, 11, 2002753.

- 
4. W. Xu, Z. Lu, T. Zhang, Y. Zhong, Y. Wu, G. Zhang, J. Liu, H. Wang and X. Sun, *Energy Storage Mater.*, 2019, 17, 358-365.
  5. L. Li, J. Chen, S. Wang, Y. Huang and D. Cao, *Appl. Surf. Sci.*, 2022, 582, 152375.
  6. Y. Chen, M. Zhou, J. Wu, X. Xiao and L. Xu, *J. Mater. Sci. Technol.*, 2024, 178, 155–161.
  7. Q. Lu, J. Yu, X. Zou, K. Liao, P. Tan, W. Zhou, M. Ni and Z. Shao, *Adv. Funct. Mater.*, 2019, 29, 1904481.
  8. S. S. Shinde, C. H. Lee, J. Y. Jung, N. K. Wagh, S. H. Kim, D. H. Kim, C. Lin, S. U. Lee and J. H. Lee, *Energy Environ. Sci.*, 2019, 12, 727-738.
  9. Y. N. Chen, Y. Guo, H. Cui, Z. Xie, X. Zhang, J. Wei and Z. Zhou, *J. Mater. Chem. A*, 2018, 6, 9716-9722.