Supporting Information

Interface engineered *in situ* anchoring Co₉S₈ nanoparticles into multiple doped carbon matrix: highly efficient zinc-air battery

Materials

All chemicals were purchased and used without further purification. Zinc nitrate hexahydrate $(Zn(NO_3)_2 \cdot 6H_2O)$, Aladdin Industrial Corporation, 99.99%), cobalt nitrate hexahydrate $(Co(NO_3)_2 \cdot 6H_2O)$, Aladdin Chemistry Co., Ltd., 99%), 2-Methylimidazole $(C_4H_6N_2,Aladdin Industrial Corporation, 98%)$, iridium oxide $(IrO_2,Aladdin Industrial Corporation, 99.99%)$, Cobalt(II) sulfide, (CoS, 99.5%-Co Chemicals, Inc), methyl Alcohol (CH₃OH, Shanghai Titan Scientific Co., Ltd. AR, 98.5%), ethanol (C₂H₅OH, Sinopharm Chemical Reagent Co., Ltd. AR, 99.7%), Sulfur powder (-325 mesh, A Johnson Matthey Company, 99.5%). De-ionized water was obtained by reverse osmosis by ion-exchange and filtration (YA.ZD-5 Controlled type, Shanghai ShenAn Medical instrument Factory). 20 wt.% Pt/C electrocatalyst (HPT 020) for electrochemical measurements was purchased from Shanghai Hesen Bio.

Instrumentation

Powder X-ray diffraction (PXRD) analyses were conducted with a MiniFlex II diffractometer with Cu K α radiation (λ = 1.54056 Å), with a step size of 1. The surface area measurements were performed with N₂ adsorption/desorption isotherms at liquid nitrogen temperature (77 K) after dehydration under vacuum at 100 °C for 12h using ASAP 2010 analyzer. Raman spectra were collected on LabRAM HR instrument with a 532 nm excitation laser. X-ray photoelectron spectroscopic (XPS) was performed on ESCALAB 250xi instrument. The morphology and elemental mapping were performed using Tecnai G2F20.

Preparation of Catalysts

Synthesis of ZIF-8 Nanocrystals: In a typical synthesis, Zn(NO₃)₂·6H₂O (1.68 g) was

dissolved in 80 mL of methanol to form clear solution, and then pour into 1.4 mole per liter methanol solution (80 mL) with vigorous stirring for 24 h. The resultant white particles were separated by centrifugation at 6000 rpm and washed thoroughly with deionized water and methanol for several times and finally dried under vacuum at 60 °C for later reaction.

Synthesis of Zn, Co-Bimetallic ZIF(BZIF) Nanocrystals: Similar to the synthetic procedure of ZIF-8, typically, $Co(NO_3)_2 \cdot 6H_2O$ and $Zn(NO_3)_2 \cdot 6H_2O$ with certain molar ratio of Zn^{2+}/Co^{2+} was dissolved in 80 mL of methanol to form light red solution. Than the above solution was poured into 1.4 mole per liter methanol solution (80 mL) with vigorous stirring for 24 h at room temperature. The resulting purple precipitates were collected by centrifuging and washed thoroughly with deionized water and methanol in sequence for at least three times. Finally, the product was dried under vacuum at 60 °C for 120 min.

Preparation of NCM Carbon Material from ZIF-8 Nanocrystals: In atypical procedure, dried ZIF-8 (100 mg) was grinded to powder and then placed in a porcelain boat. Then, the boat was heated to 800 °C at a heating rate of 5 °C min⁻¹ and carbonized at 800 °C for 120 min under nitrogen gasatmosphere. After the temperature dropped to room temperature naturally under N₂ protection, the final black powder was collected and washed with HCL (50 mL de-ionized water containing 3 mL HCl) for 6 h. Finally, the mixture was centrifugated at 8000 rpm for 3 min and washed with de-ionized water for several times, and then dried under vacuum at 60 °C for the further measurement.

Preparation of NSCM Carbon Material from ZIF-8 Nanocrystals: In a typical procedure, sulfur powder (5 mg) and dried ZIF-8 were grinded to powder respectively and then placed in two porcelain boats. The porcelain boat with sulfur powder was put in the front end of the port of tubular furnace and the porcelain boat with ZIF-8 was put in the middle of tubular furnace. Then, the boat was heated at 800 °C under nitrogen gas for 120 min with the warming rate of 5 °C /min. After the temperature was down to room temperature under the nitrogen gas environment and acid treatment (similar to the synthesis process of NCM), the

obtained powder can be collected for the further measurements.

Preparation of CoS-NCM: In atypical procedure, Cobalt (II) sulfide (20 mg) and dried NCM (80 mg) were grinded to powder and then the black powder was dispersed in 20 mL ethanol by sonication for 1 h. After that, the mixture was centrifugated at 8000 rpm for 3 min and washed with de-ionized water for several times and then dried under cacuum at 60 °C for the further measurements.

Preparation of Co@NCM Carbon Material from Zn,Co-BZIF Nanocrystals: In atypical procedure, Zn,Co-BZIFs Nanocrystals (100 mg) was grinded to powder and then placed in the porcelain boat. Then, the boat was annealed under nitrogen gas flow at 800 °C in a tubular furnace for 120 min affording Co@NCM. After the temperature was down to room temperature naturally, black sample was collected and treated with HCL and water. (similar to the synthesis process of NCM).

Electrochemical measurements

Cyclic voltammetry (CV) measurements of ORR were carried out in N₂- or O₂saturated 0.1 M KOH solution with a scan rate of 10 mV s⁻¹. The catalyst loaded working electrode was cycled by cyclic voltammetry (CV), until stabilized current was obtained. The ORR performance was also tested by linear sweep voltammetry (LSV) at a scan rate of 10 mV s⁻¹ and various rotating speeds from 225 to 2500 rpm. For all ORR experiment, O₂ was bubbled and maintained in the headspace of the electroyte throughout the testing process. Electrochemical impedance spectroscopy (EIS) measurement was carried out from 1000 kHz to 100 mHz at the open-circuit voltage of -1.3 V. For OER experiments, the LSV curves were obtained at a scan rate of 10 mV s⁻¹ and in order to obtain a stable current, the LSV date were collected after multiple CV cycles. The electrochemical stability of the sample was performed by chronoamperometric at 0.6 V and 1.7 V.

Koutecky-Levich equation was used for determining the electron transfer number (n):

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{B\omega^{1/2}} + \frac{1}{J_K} (1)$$
$$B = 0.2nFC_0 (D_0)^{2/3} v^{-1/6} (2)$$

where J, J_L and J_K are the measured current density, kinetic- and diffusion limiting current density, respectively; ω is the electrode rotation speed, F is the Faraday constant (96485 C·mol⁻¹), C₀ is the bulk concentration of O₂ (1.2 × 10⁻⁶ mol·cm⁻³ in 0.1 M KOH), D₀ is the diffusion coefficient of O₂ (1.9 × 10⁻⁵ cm²·s⁻¹ in 0.1 M KOH), v is the kinematic viscosity of the electrolyte (0.01 cm²·s⁻¹ in 0.1 M KOH). When expressing the rotation speed in rpm, the constant 0.2 is applied.

Calculation of specific capacity and energy density.

All the Zn-air batteries were tested under ambient atmosphere at 25 °C. The charge and diacharge polarization curve measurements were performed by LSV (5 mV·s⁻¹) with CHI 760E electrochemical working station. Both the current density and power density were normalized to the effective surface area of air electrode. The energy density and the specific capacity were calculated from discharge polarization curve measurements and the galvanostatic discharge measurements.

The specific capacity (mAh·g⁻¹) of the device was calculated according the equation below:

 $\frac{\text{current} \times \text{service hours}}{\text{weight of consumed zinc}} (3)$

The energy density (Wh kg⁻¹) was calculated according the equation below:

 $\frac{\text{current} \times \text{service hours} \times \text{average discharge voltage}}{\text{weight of consumed zinc}} (4)$

The galvanostatic discharge-charge cycling curves (10 mA cm⁻² at 10 min per cycle) were performed by LAND (100 mA) testing system.



Figure S1. (a) The synthetic process for ZIF-8 and 2-methylimidazole in methanol solution at room temperature; (b) The synthetic process for bimetallic Zn,Co-BZIF by simply mixing of Zn^{2+} and Co^{2+} in certain Zn^{2+}/Co^{2+} molar rations with 2-methylimidazole in methanol solution at room temperature.



Figure S2. Powder PXRD patterns of simulated ZIF-8, as-synthesized ZIF-8, and Zn,Co-BZIF.



Figure S3. The SEM images of Zn,Co-BZIFs. Scale bar: 1 μm (a), 500 nm (b).



Figure S4. N_2 sorption isotherms for ZIF-8 and Zn,Co-BZIF at 77K. Filled and open symbols represent adsorption and desorption branches, respectively.



Figure S5. TG analysis of ZIF-8 (a) and Zn,Co-BZIF (b). (c) Programmed temperature applied for the synthesis of the catalysts.



Figure S6. TEM images and corresponding particle sizes distribution of the Co_9S_8 @NSCM nanoparticles.



Figure S7. XPS survey spectrum analyses of samples.



Figure S8. (a) N_2 sorption isotherms of $Co_9S_8@NSCM$, Co@NCM, NSCM and NCM at 77 K. (b) Pore size distributions for all carbon material based on the density functional theory (DFT) method.



Figure S9. Fourier-transformed magnitudes of Co K-edge EXAFS spectra in *R* space for Co foil (a) and CoS-NCM (b) sample. Measured and calculated spectra are matched very well, and the best-fit parameters are shown in **Table S3.**



Figure S10. CV curves of (a) NCM, (b) NSCM, (c) Co@NCM and CoS-NCM in N_2 -saturated (black line) and O_2 -saturated (red line) 0.1 M KOH



Figure S11. LSVs curves of (a) NCM, (b) NSCM, (c) Co@NCM (d) CoS-NCM, (e) Pt/C and (f) Co₉S₈@NSCM for ORR in O₂-saturated 0.1 M KOH at different rotating speeds.



Figure S12. LSV curves of Co_9S_8 @NSCM and Pt/C for ORR in O_2 -saturated 0.1 M KOH at a rotation rate of 1600 rpm (a) and the corresponding to Tafel plots (b).



Figure S13. K-L plots at various potentials of (a) NCM, (b) NSCM, (c) Co@NCM, (d) CoS@NCM, (e) Pt/C, (f) Co₉S₈@NSCM.



Figure S14. Chronoamperometric response at a constant potential of 0.6 V versus the Ag/AgCl electrode of Co_9S_8 @NSCM (black line) and Pt/C (red line) in O₂-saturated 0.1 M KOH solution with a rotation rate of 1600 rpm.



Figure S15. Chronoamperometric response at a constant potential of 1.7 V versus the Ag/AgCl electrode of $Co_9S_8@NSCM$ (red line) and IrO_2 (black line) in 0.1 M KOH solution.



Figure S16. Digital photograph of the primary or rechargeable ZnAB. The air-cathode was prepared by carbon cloth with polytetrafluoroethylene (PTFE) on one side followed by the loading of our catalysts and a gas diffusion layer on the other side. The catalyst ink was prepared as described in electrochemical experiments. A polished zinc plate (0.3 mm thickness) was used as anode. Such a fabricated cathode is separated by electrolyte with a zinc metal anode. The primary and rechargeable ZnABs has the same configuration except for adding the 0.2 M zinc acetate into 6 M KOH electrolyte.



Figure S17. (a) Galvanostatic discharge curves of the primary ZnAB with $Co_9S_8@NSCM$ catalyst at different current densities, which was normalized to the area of air-cathode. The galvanostatic discharge voltage plateaus decreased with increasing current density. (b) The galvanostatic discharge curves of the primary zincair batteries at the current density of 10 mA·cm⁻². When normalized to the mass of consumed Zn, the specific capacity of ZnAB with the $Co_9S_8@NSCM$ cathode was 810 mAh·g⁻¹, which is higher than CoS-NCM (420 mAh·g⁻¹) and even better than that of Pt/C (740 mAh·g⁻¹).



Figure S18. Specific capacities of the primary ZnABs normalized to the mass of consumed Zn at the current density of 10 mA·cm⁻² (a) and 30 mA·cm⁻² (b). At the discharge current densities of 20 and 30 mA·cm⁻², the Specific capacities of primary ZnAB with $Co_9S_8@NSCM$ as ORR catalyst were 676 and 612 mAh·g⁻¹, respectively, which is better than that of Pt/C (655 and 591 mAh·g⁻¹) when normalized to the weight of consumed zinc electrode. These values are higher than those of ZnAB with CoS-NCM as the cathode (420, 406, 384 mAh·g⁻¹, at the discharge rate of 10, 20, 30 mA·cm⁻²), which should be attributed to weak interface interaction between Co-S active species and carbons matrix in the CoS-NCM air-cathode.



Figure S19. Mechanically recharged ZnAB with Co_9S_8 @NSCM catalyst at a current density of 10 mA·cm⁻². The Zn and electrolyte were mechanically replaced at the point where the color of the curve changes (the numbers represent the first, second, third and fourth charge cycles). Electrolyte for ZnAB was 6.0 M KOH. Catalyst loading was 0.5 mg·cm⁻².



Figure S20. Galvanostatic discharge-charge cycling curves at 10 mA·cm⁻² of rechargeable ZnABs with CoS-NCM (black line) and Co₉S₈@NSCM (red line). The rechargeable ZnAB with Co₉S₈@NSCM air-cathode shows the initial discharge and charge voltage are about 1.19 V and 2.00 V, and the voltage gap is only about 0.81 V. Whereas CoS-NCM-baesd rechargeable ZnAB demonstrated a great change in the voltages are observed after 400 cycles charge and discharge cycles.



Figure S21. Nyquist plots (a) and the charge transfer resistance values (b) of all samples.



Figure S22. Structure models of the Co_9S_8 @NSCM with different interface distances and corresponding electron densities distribution.



Figure S23. Free-energy diagram of intermediates during ORR and OER for $Co_9S_8@NSCM$ and Co@NCM.

Sample	C (at.%)	N (at.%)	S (at.%)	Co (at.%)	O (at.%)
NCM	96.4	3.6	-	-	2.3
NSCM	93.2	3.2	1.32	-	2.28
Co@NCM	92.9	2.9	-	1.0	3.2
Co ₉ S ₈ @NSCM	90.5	2.2	2.05	0.97	4.28

Table S1. Elemental analysis of NCM, NSCM, Co@NCM and Co₉S₈@NSCM.

Sample	$S_{BET}(m^2 \cdot g^{-1})$	S _{Langmuir} (m ² ·g ⁻¹)	V _{pore} (cm ³ ·g ⁻¹)	Pore size (nm)
NCM	393.9346	583.7862	0.45	4.6
NSCM	360.2287	532.3298	0.12	4.1
Co@NCM	635.5359	999.7807	0.36	2.29
Co ₉ S ₈ @NSCM	636.6647	929.4767	0.34	2.14

Table S2.Surface areas, pore volumes and pore size of NCM, NSCM, Co@NCM,Co9S8@NSCM.

Table S3. Co K-edge EXAFS Curve Fitting Parameters							
Sample	Shell	Ν	$R(\text{\AA})$	σ^2 (Å ²)	$\Delta E_0 (\mathrm{eV})$	<i>R</i> , %	
Co foil ^b	Co-Co	12	2.49	0.007	0.4	0.01	
Co ₉ S ₈ @NSCM ^c	Co-C	2.4	2.07	0.010	-3.9		
	Co-S	4.0	2.35	0.017	1.4	0.1	
	Co-Co	2.5	2.46	0.013	1.4		
CoS-NCM ^d	Co-S	6	2.28	0.014	2.2	0.05	
	Co-Co	2	2.47	0.013	2.2		

^a*N*, coordination number; *R*, distance between absorber and backscatter atoms; σ^2 , Debye–Waller factor to account for both thermal and structural disorders; ΔE_0 , inner potential correction; *R* factor (%) indicates the goodness of the fit. Error bounds (accuracies) that characterize the structural parameters obtained by EXAFS spectroscopy are indicated in parenthesis. S_0^2 was fixed to 0.93 as determined from Ni standard fitting. Bold numbers indicate fixed coordination number (*N*) according to the crystal structure. The structural parameters for CoS-NCM and bulk Co are in good agreement with previous results in the literature. ^bFitting range: $3.9 \le k$ (/Å) ≤ 13.9 and $1.4 \le R$ (Å) ≤ 2.7 . ^cFitting range: $1.9 \le k$ (/Å) ≤ 13.3 and $1.0 \le R$ (Å) ≤ 2.8 . ^dFitting range: $3.2 \le k$ (/Å) ≤ 13.5 and $1.0 \le R$ (Å) ≤ 2.4 .

Materials	Surface area (m ² ·g ⁻¹)	Electrolyte	Loading mg/cm ²	ORR onset potential	ORR half-wave potential	Ref.
Co ₉ S ₈ @NSCM	636.6647	0.1 M KOH	0.15 mg/cm ²	0.97 V vs. RHE	0.81V vs.	This work
Co ₄ N/CNW/CC derived from ZIF-67.	226	1.0 M KOH	0.2 mg/cm ²		0.80 V vs. RHE	J. Am. Chem Soc., 2016 , 32, 138.
Nanoporous Carbon Fiber Films	756	0.1 M KOH	0.1 mg/cm ²	0.97 V vs. RHE		<i>Adv. Mater.</i> 2016 , 28, 3000.
N-doped carbon nanotube	513	0.1 M KOH	0.2 mg/cm ²	0.97 V vs. RHE	0.87V vs. RHE	Nat. Commun. 2016 , 1, 1.
N and S dual-doped porous carbons immobilizing cobalt sulfide NPs	1791	0.1 M KOH	0.4 mg/cm ²	-0.05 V	-0.17 V vs. Ag/AgCl	<i>Adv. Mater.</i> 2016 , 28, 6391
Co ₃ O ₄ nanocrystals on graphene		0.1 M KOH	0.17 mg/cm ²	0.88V vs. RHE	0.83V vs. RHE	Nat. Mater. 2011, 10, 780.
Co ₉ S ₈ /N-doped graphene		0.1 M KOH	0.2 mg/cm ²	0.941V vs. RHE		Energy Environ. Sci., 2016 , 9, 1320
Co, N-doped porous carbons	1225	0.1 M KOH	0.1 mg/cm ²	0.89V vs. RHE	0.82V vs. RHE	Adv. Mater. 2015, 27, 5010.
Co ₃ (PO ₄) ₂ C-N- HA/rGO	30.1	0.1 M KOH	0.25 mg/cm ²	0.962 V vs. RHE	0.837 V vs. RHE	Energy Environ. Sci., 2016, 9, 2563.
Co@Co ₃ O ₄ encapsulated in carbon nanotube	111	0.1 M KOH	0.21 mg/cm ²		0.8 V vs. RHE	Angew. Chem. Int. Ed. 2016, 55, 4087.
Sulfur and Nitrogen co-doped mesoporous graphene		0.1 М КОН		-0.06 V		Angew. Chem. Int. Ed. 2012 , 51, 11496.
Cobalt-manganese oxide supported on N- doped carbon nanotubes		1.0 M KOH	0.21 mg/cm ²	0.96V vs. RHE	0.84V vs. RHE	Nano Energy. 2016 , 20, 315.
FeCo alloy	42	0.1 М КОН	0.8 mg/cm ²	0.94V vs. RHE	0.80 V vs. RHE	<i>Electrochimica Acta</i> 2016 , <i>220</i> , 354.
N, P and Fe-tridoped nanoporous carbon	1038.9	0.1 M KOH	0.2 mg/cm ²	0.957V vs. RHE	0.852V vs. RHE	J. Mater. Chem. A, 2016, 4, 8602.
Iron-nitrogen -doped carbon nanotube	504	0.1 M HClO ₄		0.89V vs. RHE	0.76 V vs. RHE	<i>Adv. Funct. Mater.</i> 2016 , <i>26</i> , 738.
NiFe@NC _X	350	0.1 M KOH	0.4 mg/cm ²	1.03V vs. RHE	0.86 V vs. RHE	ACS Catal., 2016 , <i>6</i> , 6335.
N, P and Fe-tridoped nanoporous carbon	265.8	0.1 M KOH	0.2 mg/cm ²	0.957V vs. RHE	0.852 V vs. RHE	J. Mater. Chem. A, 2016, 4, 8602.

Materials	Surface area (m ² ·g ⁻¹)	Electrolyte	loading	OER onset potential	OER potential @ 10mA cm ⁻²	Ref.
Co ₉ S ₈ @NSCM	636.6647	0.1 M KOH	0.15 mg/cm ²	1.34 V vs. Ag/AgCl	1.60 V vs. Ag/AgCl	This work
Co ₄ N/CNW/CC derived from ZIF-67	226	1.0 M KOH	0.2 mg/cm ²		1.54 V vs. RHE	J. Am. Chem Soc., 2016 , 32 138
Nanoporous Carbon Fiber Films	756	0.1 M KOH	0.1 mg/cm ²	1.43 V vs. RHE	1.84 V vs. RHE	<i>Adv. Mater.</i> 2016 , 28, 3000
Interacting carbon nitride and titanium carbide nanosheets	205	0.1 M KOH	flexible films	1.44 V vs. RHE	1.65 V vs. RHE	Angew. Chem. Int. Ed. 2016 , 55, 1138
N-doped carbon nanotube frameworks	513	0.1 М КОН	0.2 mg/cm ²	1.47 V vs. RHE	1.60 V vs. RHE	Nat. Energy. 2015 , 1,15006
Mn _x O _y /N-doped carbon		0.1 M KOH	0.21 mg/cm ²	1.55 V vs. RHE	1.68 V vs. RHE	Angew. Chem. Int. Ed. 2014 , 53, 8508
Co@Co ₃ O ₄ encapsulated in carbon nanotube	76	0.1 М КОН	0.21 mg/cm ²		1.64 V vs. RHE	Angew. Chem. Int. Ed. 2016 , 55, 1
Carbon-Encapsulated Co ₃ O ₄ @CoO@Co Nanocomposites	69	1.0 М КОН	Ni foam	1.58 V vs. RHE		<i>Electrochimica Acta</i> 220 (2016) 322
Cobalt-manganese oxide supported on N- doped carbon nanotubes		1.0 М КОН	0.21 mg/cm ²		0.34 V	Nano Energy. 2016 , 20, 315
FeCo alloy	42	1.0 М КОН	0.8/0.4 mg/cm ²	1.45 V vs. RHE	1.49 V vs. RHE	<i>Electrochimica Acta</i> 2016 , 220, 354
ZnCo ₂ O ₄ quantum dots anchored on nitrogen-doped carbon nanotubes	159	0.1 M KOH	0.2 mg/cm ²	1.56 V vs. RHE	1.65 V vs. RHE	Adv. Mater. 2016 , 28. 3777
NiFe@NC _x	350	0.1 M KOH	0.4 mg/cm ²	1.22 V vs. RHE	1.55 vs. RHE	ACS Catal., 2016 , 6 (10), 6335
Heteroatom-doped and edge graphene material	1100	0.1 M KOH	0.25 mg/cm ²	1.2 V vs. RHE	1.67 V vs. RHE	Adv. Mater. 2016, 28, 6845

Table S5. Summary of representative OER catalysts in varied electrolyte.