

## Supporting information

# Zn/N/S Co-Doped Hierarchical Porous Carbon as a High-Efficiency Oxygen Reduction Catalyst in Zn-Air Batteries

Mincong Liu,<sup>a</sup> Jing Zhang,<sup>b</sup> Guohua Ye,<sup>a</sup> Yan Peng<sup>a</sup> and Shiyu Guan<sup>\*a</sup>

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a. Department of Chemistry, College of Science, Shanghai University, 99 Shang-Da Road, Shanghai 200444, China; Email: [syguan@shu.edu.cn](mailto:syguan@shu.edu.cn)

b. College of Sciences&Institute for Sustainable Energy, Shanghai University, 99 Shang-Da Road, Shanghai 200444, China.

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### 1. Materials characterizations

X-ray diffraction (XRD) was obtained over the 2θ range from 10° to 90° on a Bruker D8 Advance XRD powder diffractometer. Raman spectrum were analyzed by the Horiba Evolution laser Raman spectrometer with an wavelength of 532 nm. Scanning electron microscopy (SEM) images were obtained on a ZEISS Gemini 300. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and the corresponding energy dispersive spectrometry (EDS) mapping images were obtained from a field emission Tecnai G2 F20 electron (Hillsboro, OR, USA) microscope. X-ray photoelectron spectroscopy (XPS) analyses were performed on Thermo Scientific K-Alpha spectrometer. N<sub>2</sub> sorption curves were collected by an ASAP 2460 instrument at 77 K and the Brunauer-Emmett-Teller (BET) multipoint adsorption theory were used to calculate the specific surface area.

### 2. Electrochemical measurements

ORR catalytic activity was evaluated by using CHI760E electrochemical workstation with a typical three-electrode cell in in O<sub>2</sub>-saturated 0.1 M KOH. An Ag/AgCl electrode and graphite rod served as the reference electrode and the counter electrode, respectively. 5 mg of the catalyst was mixed with Nafion solution (40 μL), DI water (480 μL) and ethanol (480 μL) to form a homogeneous catalytic ink. Nextly, the 10μL catalytic ink was dripped on a glassy carbon (GC) electrode (5 mm in diameter). Cyclic voltammetry (CV) curves were recorded in the potential from 0.2-0.8V with a sweep rate of 50mV s<sup>-1</sup>. A series of Linear sweep voltammetry (LSV) tests were measured at various rotating speed from 400 to 2500 rpm with a scan rate of 10 mV s<sup>-1</sup>. The electron transfer number (n) was calculated based on the Koutechy-Levich (K-L) equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_K} = \frac{1}{J_K} + \frac{1}{B\omega^{1/2}} \quad \#(1)$$

$B = 0.62nFC_0D_0^{2/3}\nu^{-1/6}$  # (2) where J is the measured current density, JK and JL are the kinetic and limiting current densities, ω is the angular velocity of the disk, n is the electron transfer number, F is the Faraday constant (96485 C·mol<sup>-1</sup>), C<sub>0</sub> is the bulk concentration of O<sub>2</sub> (1.2 × 10<sup>-6</sup> mol cm<sup>-3</sup>), D<sub>0</sub> is the diffusion coefficient of O<sub>2</sub> (1.9 × 10<sup>-5</sup>cm<sup>2</sup> s<sup>-1</sup>), and ν is the kinematic viscosity of the electrolyte (0.01 cm<sup>2</sup> s<sup>-1</sup>).

Rotating ring disk electrode (RRDE, Pine) measurements were performed at 5 mV s<sup>-1</sup> with Pt ring potential set to 1.23 V vs. RHE, and the H<sub>2</sub>O<sub>2</sub>/HO<sup>2-</sup> yield and electron transfer number (n) were determined based on the following two equations:

$$H_2O_2(\%) = 200 \times \frac{I_r/N}{I_d + I_r/N} \quad \#(3)$$

$$n = 4 \times \frac{I_d}{I_d + I_r/N} \quad \#(4)$$

where  $I_d$  is the disk current,  $I_r$  is the ring current, and  $N=0.4$  is the current collection efficiency of the Pt ring.

### 3. Zn-air battery test

The Zn-air batteries (ZABs) was assembled with a polished Zn plate as anode and a carbon paper coated with the catalyst ink as the cathode. 5 mg of catalyst and 5 mg of  $RuO_2$  were added to the solution, containing 40  $\mu$ L of Nafion, 480  $\mu$ L of DI water and 480  $\mu$ L ethanol to form the catalyst ink. The average catalyst loading was 0.52 mg  $cm^{-2}$ . The electrolyte is 6 M KOH with 0.1 M  $ZnCl_2$ .

### 4. Theoretical calculation

The first principle calculations are performed by Vienna Ab initio Simulation Package(VASP)<sup>1</sup> with the projector augmented wave (PAW) method<sup>2</sup>. The exchange-functional is treated using the Perdew-Burke-Ernzerhof (PBE)<sup>3</sup> functional, in combination with the DFT-D3 correction<sup>4</sup>. The cut-off energy of the plane-wave basis is set at 450 eV. For the optimization of both geometry and lattice size, the Brillouin zone integration is performed with  $2*2*1$  Monkorts-Pack<sup>5</sup> kpoint sampling. The self-consistent calculations apply a convergence energy threshold of 10<sup>-5</sup> eV. The equilibrium geometries and lattice constances are optimized with maximum stress on each atom within 0.02 eV/ $\text{\AA}$ .

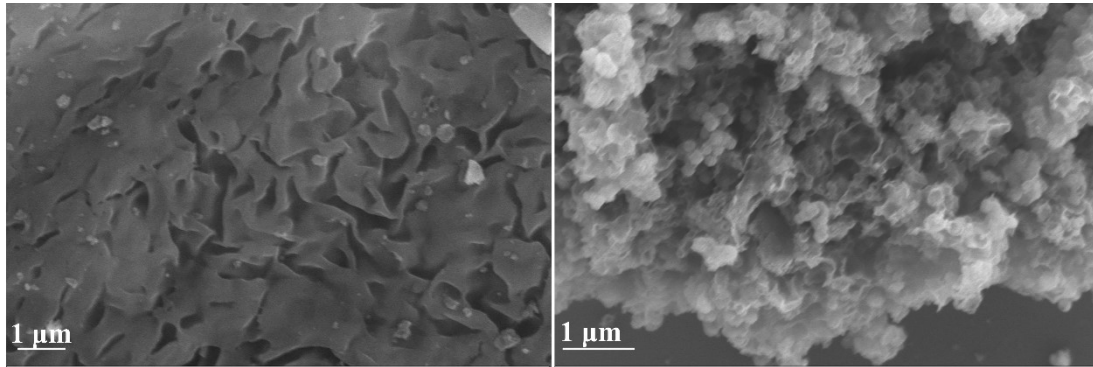


Figure S1. SEM images of Zn-N/S-C(Z) and Zn-N/S-C(S).

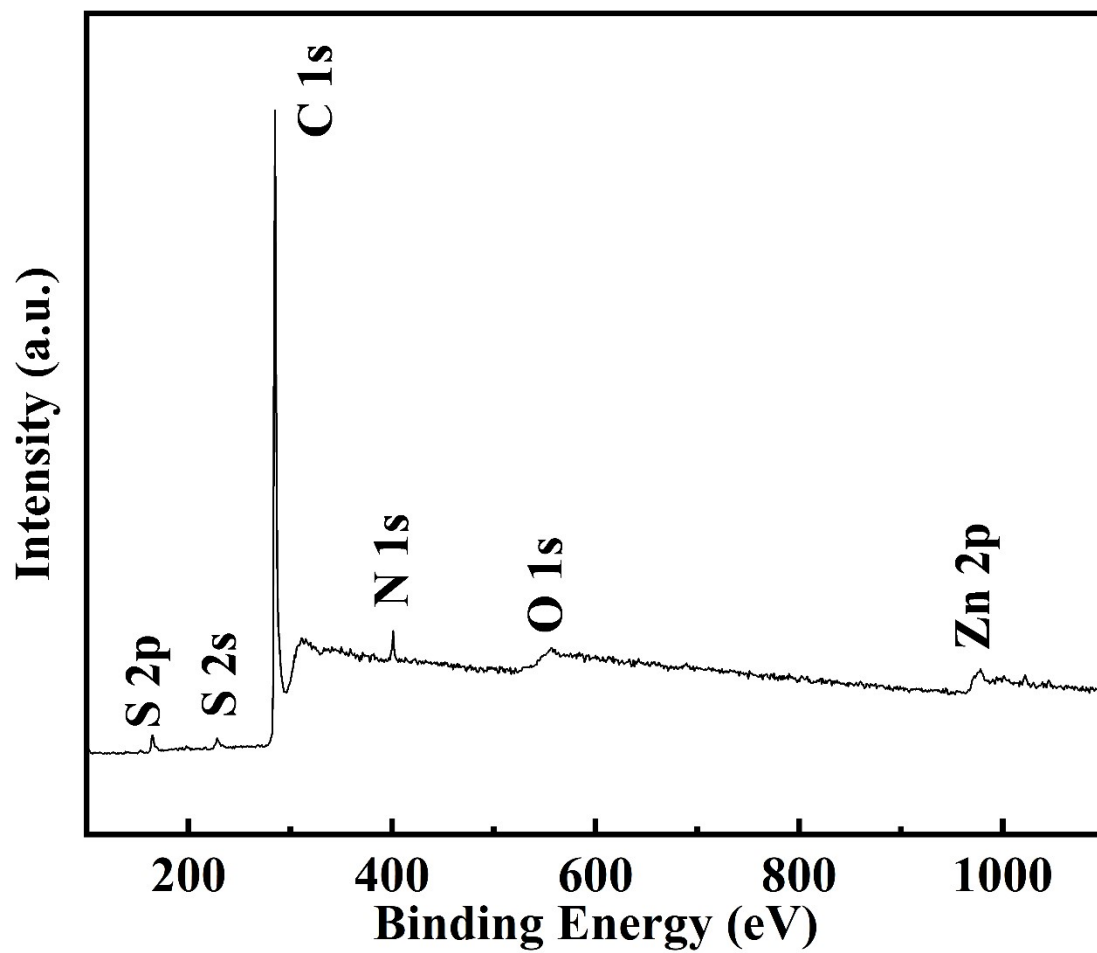


Figure S2. XPS spectra of Zn-N/S-C(S, Z).

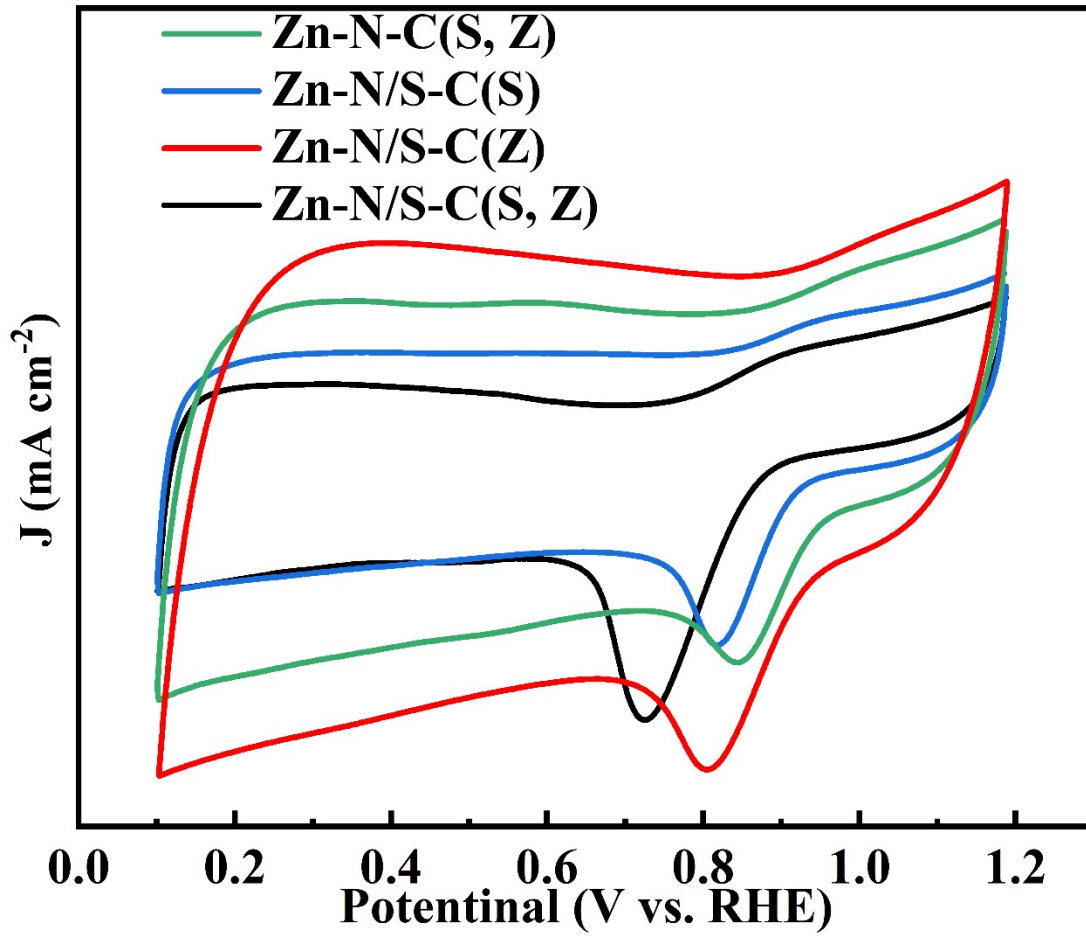


Figure S3. CV curves for Zn-N/S-C(S), Zn-N/S-C(Z), Zn-N/S-C(S, Z) and Zn-N-C(S, Z) at a scan rate of 50 mV s<sup>-1</sup>.

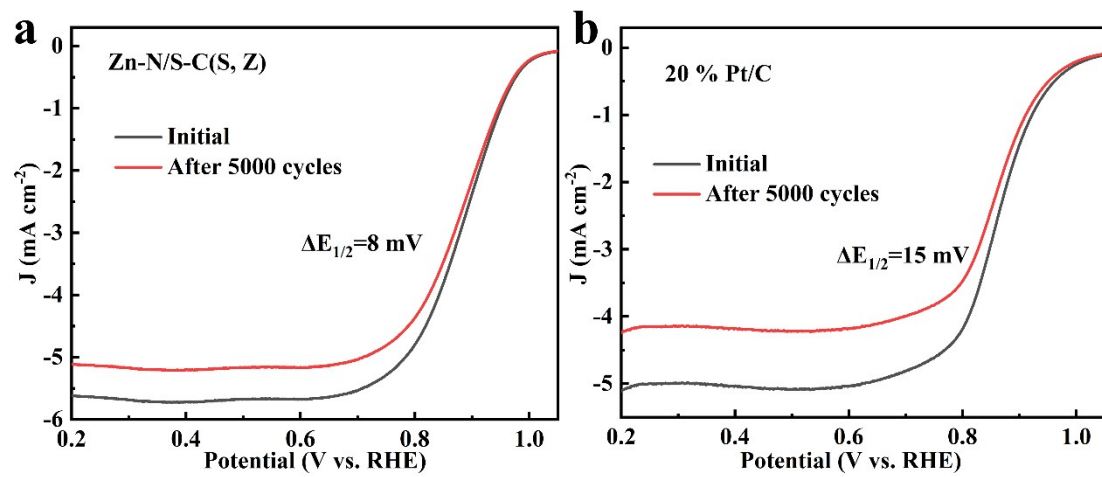


Figure S4. RDE curves recorded in 0.1 M KOH before and after 5,000 cycles for Zn-N/S-C(S, Z) (a) and 20 wt% Pt/C (b).

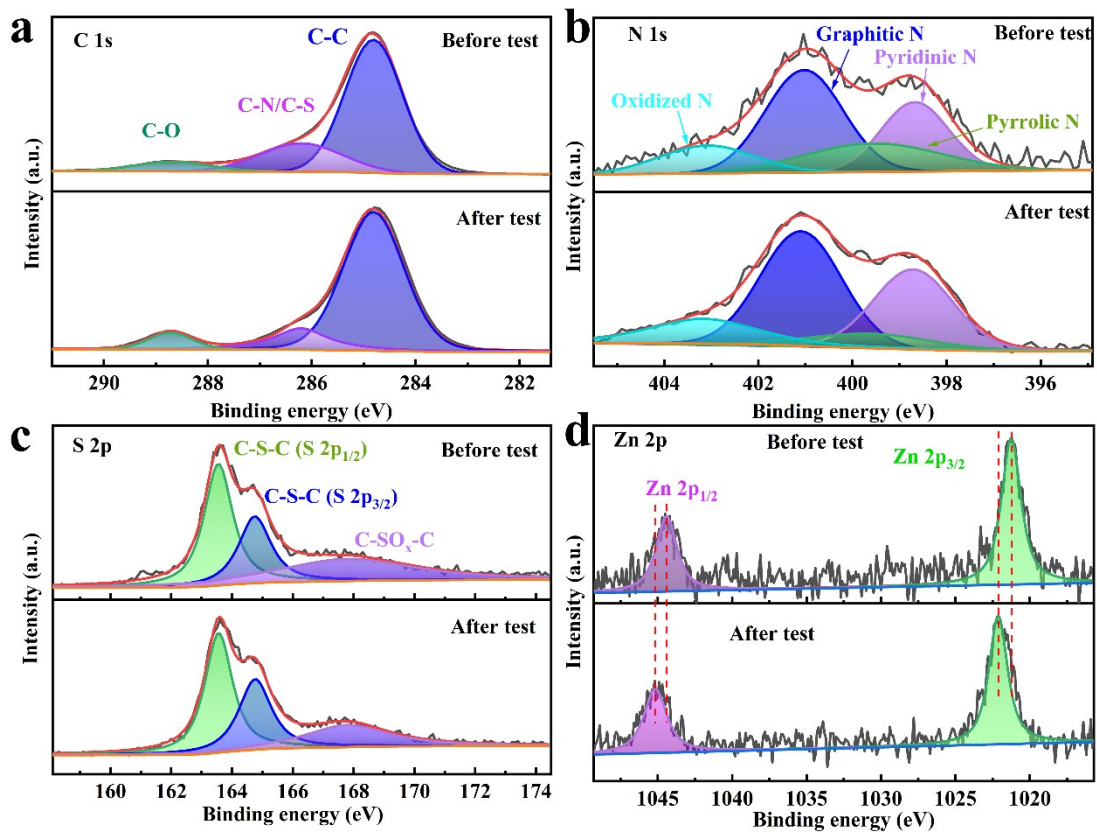


Figure S5. XPS high-resolution spectrum of Zn-N/S-C(S, Z) after stability test. (a) C 1s, (b) N 1s, (c) S 2p and (d) Zn 2p.

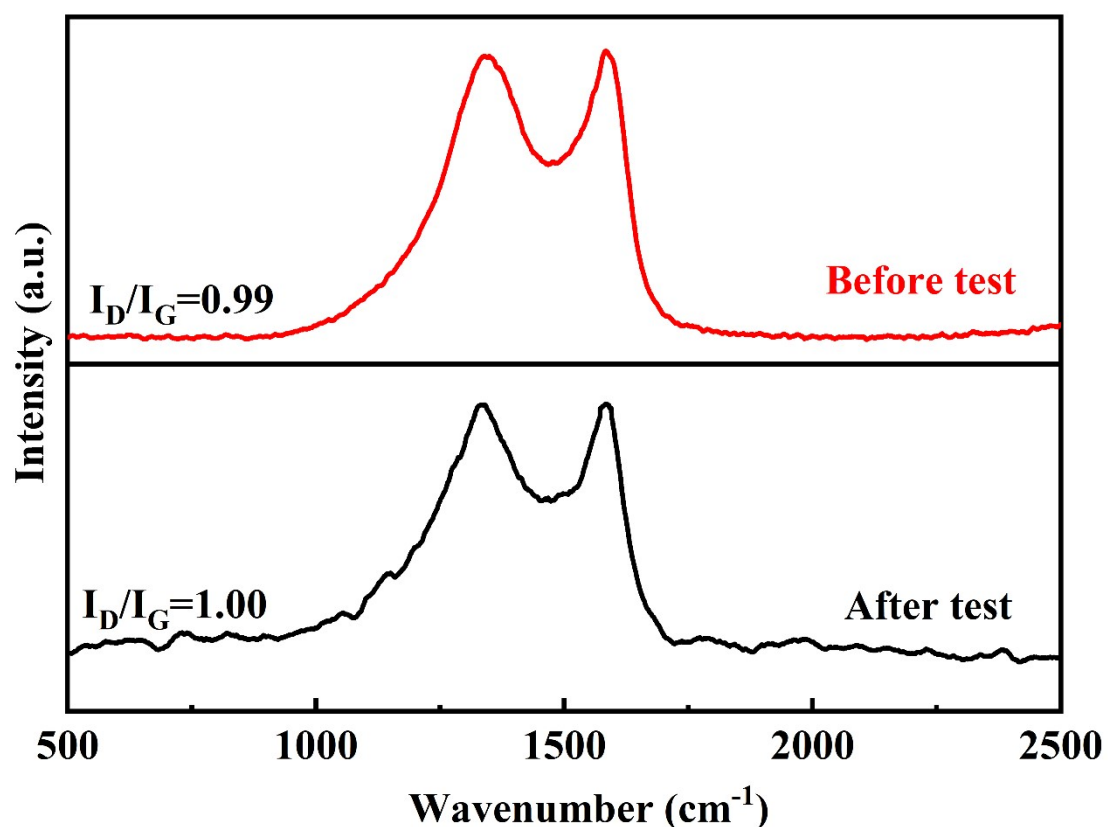


Figure S6. Raman spectrum of Zn-N/S-C(S, Z) after stability test.

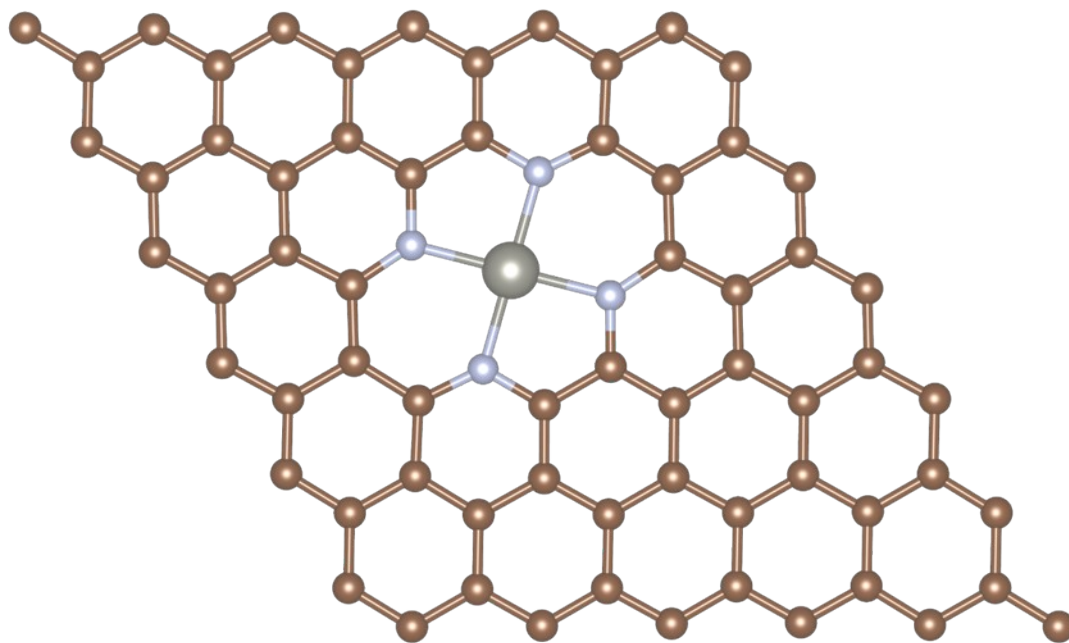


Figure S7. Optimized geometry of Zn-N/S-C(S, Z).



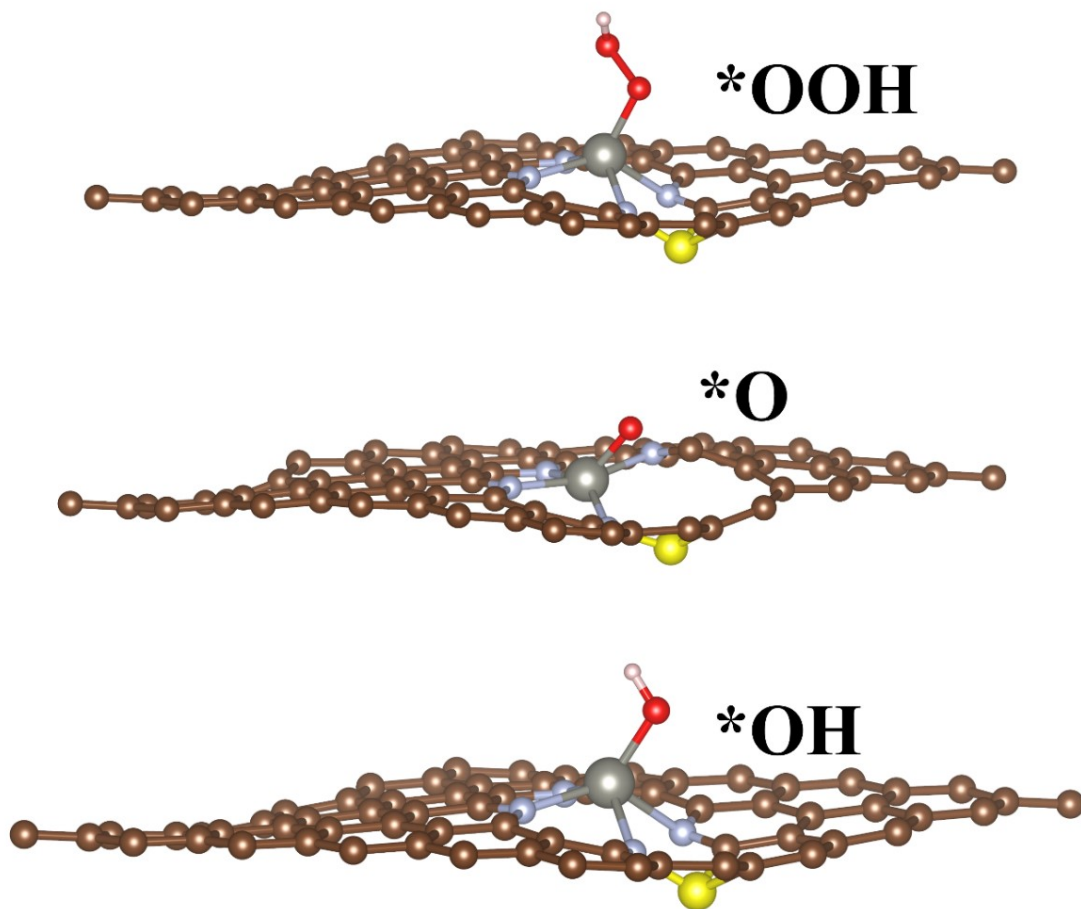


Figure S8. The adsorption configurations of ORR intermediates on the Zn-Nx site.

Table S1. ORR activity comparison for typical non-precious catalysts.

Sample	$E_{1/2}$ (V) in 0.1 M KOH	Ref.
Zn-N/S-C(S, Z)	0.89	This work
SA-Fe-HPC	0.89	6
Fe-N-C	0.90	7
Ni-B/NC	0.87	8
NiCo DASS/NC	0.88	9
OLC/Co-NC	0.855	10
MnNC + NaCl	0.88	11

Table S2. The comparison of power density of ZABs driven by Zn-N/S-C(S, Z)+RuO<sub>2</sub> or other reported catalysts.

Sample	Open-circuit potential (V)	Power density (mW cm <sup>-2</sup> )	Ref.
Zn-N/S-C(S, Z)	1.47	290.8	This work
CoFe/N-GCT	1.43	203	12
Fe-SA/N-HCS	1.49	191	13
CoSA/NCs	1.47	255	14
FeCoNC/SL	1.438	224.8	15
FePc-NHCS-500	1.524	230	16
Fe-N,O/G	1.55	164.7	17

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