

Supporting Information

Enhancing oxygen reduction activity of dinuclear copper complexes loaded on N-doped carbon support via low-temperature pyrolysis strategy

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Experimental

Chemicals and Materials.

All reaction reagents and chemicals were obtained and used without further purification. High-purity water ($\geq 18.25 \text{ M}\Omega \cdot \text{cm}$) and acetonitrile was used to prepare the solutions. Carbon black (Black Pearls 2000) was purchased from Cabot Corporation. 3,6-di-2-pyridine-1,2,4,5-tetraazine (DPTZ) was prepared according to the reported literature.S1

Characterizations

The FTIR spectra were recorded on a Shimadzu Fourier transform infrared spectrometer (IR Prestige-21). UV-vis diffuse reflectance spectra were recorded on a Shimadzu UV-vis spectrophotometer (UV-2600). Transmission electron microscopy (TEM) characterization was performed using Thermo Fisher Talos F200X (FETEM, 200 kV). High angle annular dark field (HAADF-STEM) images were recorded using a convergence semi angle of 11 mrad, and inner- and outer collection angles of 59 and 200 mrad, respectively. X-ray Diffraction (XRD) patterns were recorded on an X-ray powder diffractometer (D/max2550 V, Rigaku Japan). X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo ScientificTM K-Alpha^{TM+} spectrometer equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6 \text{ eV}$) operating at 100 W. All binding energies were corrected for reference to the C1s peak (284.8 eV) corresponding to the adventitious carbon. N₂ adsorption-desorption data were

recorded at liquid nitrogen temperature (77 K) on a Micromeritics ASAP 2460 apparatus. The Brunauer-Emmett-Teller (BET) method was used to calculate the catalyst surface areas. Raman spectra were recorded using a Renishaw 2000 instrument with a 532 nm excitation wavelength. The elemental contents of the catalysts were measured by ICP OES (Perkin Elmer Ltd., USA).

Materials Synthesis

Preparation of CNB

1.0 g of carbon black and 2.0 g of melamine were physically mixed by grinding, placed in a quartz tube, and pyrolyzed at 900 °C in nitrogen atmosphere for 60 min at a heating rate of 5 °C min⁻¹. After cooling to room temperature the samples was collected and donated at CNB.

Preparation of Cu-BPOZ@CNB

50 mg CNB and 236 mg DPTZ were mixed in 10 mL acetonitrile under sonication for 30 min to form solution A. In addition, 500 mg of CuSO₄·5H₂O was dissolved in 30 mL water to form solution B. Solution A was added into solution B rapidly in a flask. The above mixed solution was reacted with constant stirring at 55 °C for 12 h, during which process the DPTZ ligand hydrolyzed and converted into the BPOZ ligand with the assistance of Cu²⁺. After cooling, the resultant composite was collected by a centrifugation process and washed with acetonitrile and water, and dried under vacuum overnight at 60 °C. The as-prepared samples were donated at Cu-BPOZ@CNB.

Preparation of Cu-BPOZ@CNB-T

The composite of Cu-BPOZ@CNB was placed into a quartz tube, followed by pyrolysis under N₂ atmosphere at a designated temperature for 60 min at a heating rate of 5 °C min⁻¹. The as-prepared samples were donated at Cu-BPOZ@CNB-T, where T represents the carbonization temperature (300-450 °C).

Preparation of Cu-BPOZ@CNB-800

The composite of Cu-BPOZ@CNB was placed into a quartz tube, followed by pyrolysis under N₂ atmosphere at 800 °C for 60 min at a heating rate of 5 °C min⁻¹. After cooling to room temperature,

the pyrolyzed sample was etched by 1 M HCl solution at 80 °C for 10 h to remove the nanoparticles. Finally, the resultant composite was centrifuged and washed with water and ethanol, and dried under vacuum overnight at 60 °C. The as-prepared samples were donated at Cu-BPOZ@CNB-800.

Preparation of Cu-Phen@CNB-400

The composite was prepared in a similar procedure for preparing Cu-BPOZ@CNB-400 by replacing DPTZ with o-Phenanthroline.

Electrocatalytic Measurements

The preparation of catalyst ink was as follows: firstly, 5 mg of the as-obtained catalyst was added to a glass vial with 25 μL of a 5 wt% solution of Nafion (Aldrich) and 225 μL of isopropanol, and then ultrasonic dispersion for 30 min until a homogeneously dispersed suspension was formed. 10 μL of catalyst ink was dropped on the surface of the glassy carbon disk (diameter: 5 mm; geometric area: 0.196 cm^2), and dried under room temperature to form a dense catalyst film with a catalyst mass loading of 1.0 mg cm^{-2} .

The rotating ring disc electrode (RRDE) was used to investigate the electrochemical performance of catalysts on a CHI 760D electrochemical workstation using a standard three-electrode system in electrolyte solution with a graphite rod (diameter: 4.0 mm) as the counter electrode and an Hg/HgO electrode as the reference electrode. The cyclic voltammetry (CV) and RRDE tests were conducted in an O_2 -saturated 0.1 M KOH solution at a scanning rate of 10 mV s^{-1} at room temperature. The stability test of catalysts for ORR was conducted at 0.55 V (vs. RHE) in O_2 -saturated 0.1 M KOH at 900 rpm by using a chronoamperometric method. The Accelerate Durability Testing (ADT) was performed at 0.6-1.0 V (vs. RHE) in O_2 -saturated 0.1 M KOH at 0 rpm. The ORR polarization curves were deducted the current in Ar-saturated 0.1 M KOH solution from those in O_2 -saturated 0.1 M KOH solution.

The disc current (I_d) and ring current (I_r) obtained by the RRDE electrode can be used to calculate the H_2O_2 yield and the number of transferred electrons (n) by the following equations:

$$\text{H}_2\text{O}_2(\%) = \frac{200 \times I_r}{I_r + N + I_d}$$
$$n = \frac{4 \times N \times I_d}{I_r + N + I_d}$$

where N is the collection coefficient, and the value is 0.26.

Zn-air battery test

The catalyst ink was loaded on carbon fiber paper (1.0 cm²) and conducted as the negative electrode. Meanwhile, the zinc plate was used as the positive electrode and the mixed solution of 6 M KOH and 0.2 M Zn(Ac)₂ was used as the electrolyte.

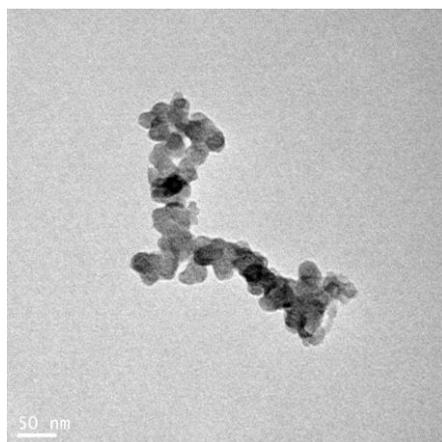


Fig S1. TEM image of Cu-BPOZ@CNB-400.

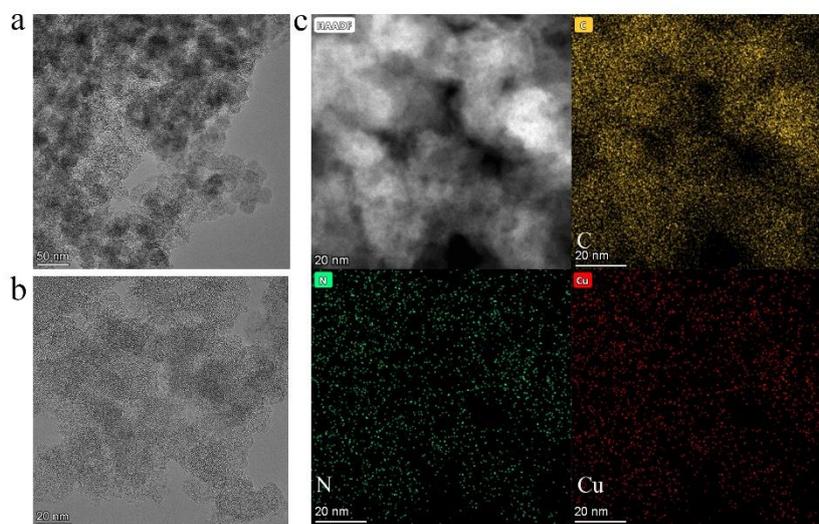


Fig S2. (a-b) HR-TEM images, (c) HAADF-STEM and corresponding elemental mapping images of C, N, and Cu elements in Cu-BPOZ@CNB-800.

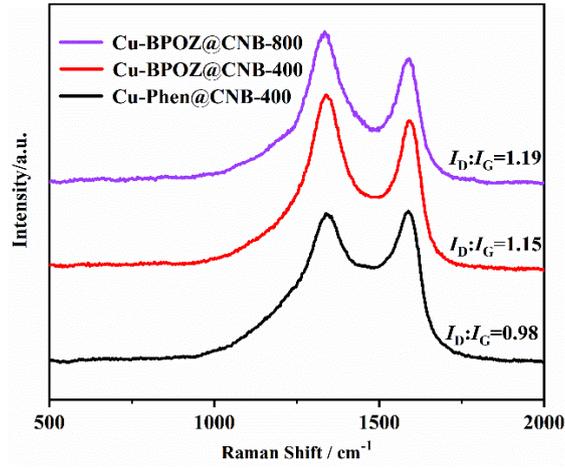


Fig S3. Raman spectra of Cu-BPOZ@CNB-800, Cu-BPOZ@CNB-400 and Cu-Phen@CNB-400

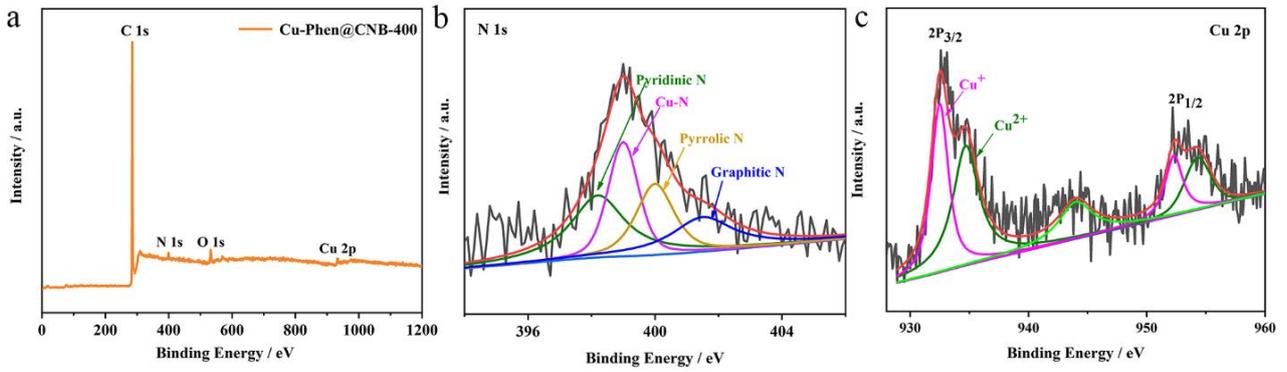


Fig S4. (a) XPS survey , (b) high-resolution N 1s, and (c) Cu 2p spectra of Cu-Phen@CNB-400.

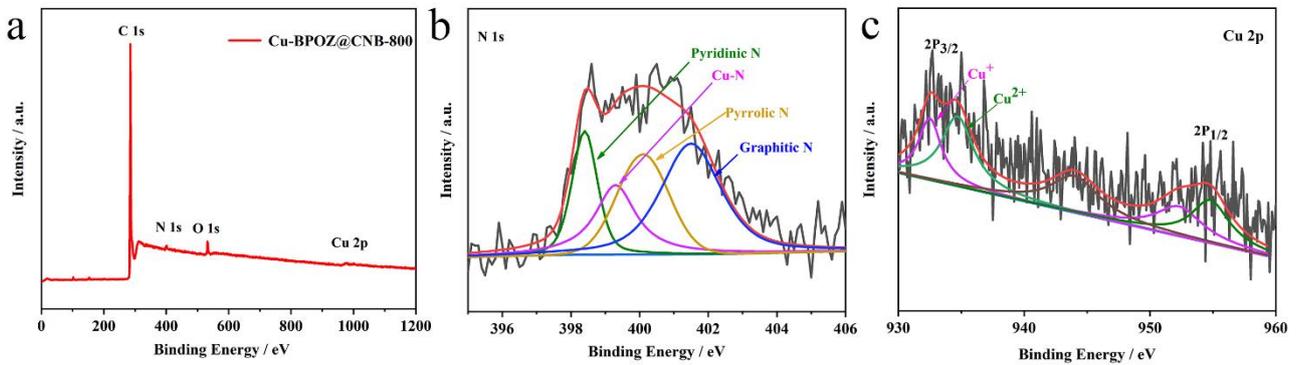


Fig S5. (a) XPS survey , (b) high-resolution N 1s, and (c) Cu 2p spectra of Cu-BPOZ@CNB-800.

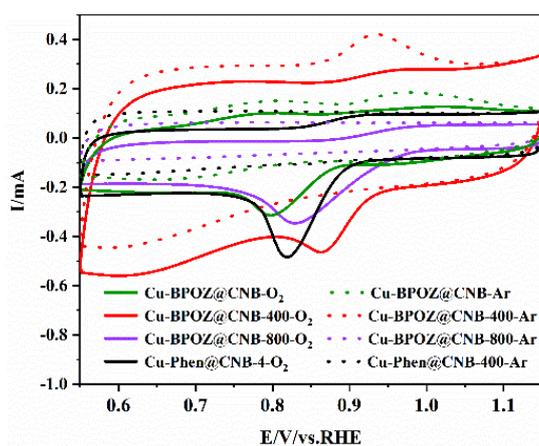


Fig S6. CV curves of Cu-BPOZ@CNB, Cu-BPOZ@CNB-400, Cu-BPOZ@CNB-800, and Cu-Phen@CNB-400 in an O₂- and Ar-saturated 0.1 M KOH solution.

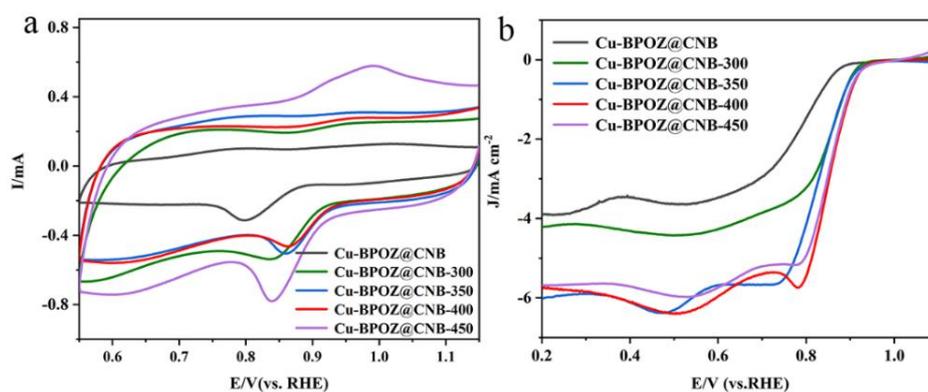


Fig S7. (a) CV curves and (b) LSV curves of Cu-BPOZ@CNB-T (T= 0, 300, 350, 400 and 450 °C, T represents the pyrolysis temperature.)

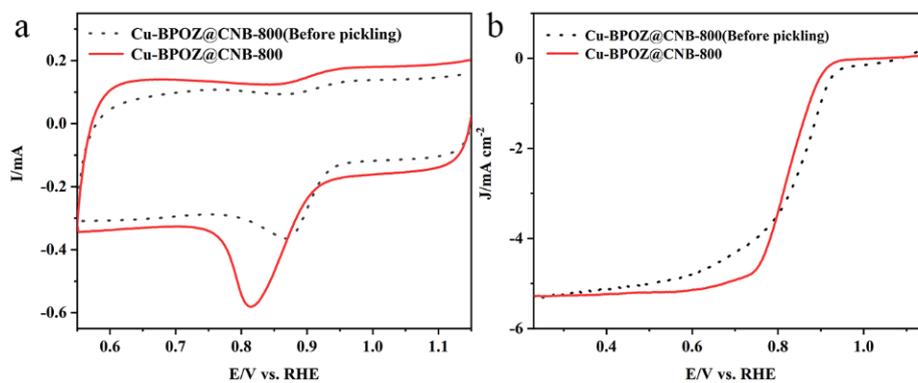


Fig S8. (a) CV curves and (b) LSV curves of Cu-BPOZ@CNB-800 (before acid etching) and Cu-BPOZ@CNB-800

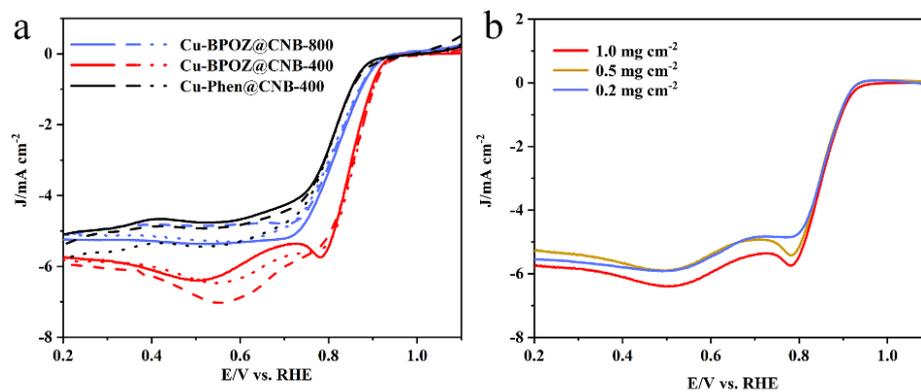


Fig. S9. (a) LSV curves (@ 1600 rpm) of Cu-BPOZ@CNB-800, Cu-BPOZ@CNB-400 and Cu-Phen@CNB-400 from repetition of three tests; and (b) LSV curves (@ 1600 rpm) of Cu-BPOZ@CNB-400 with the mass loading of 1.0 mg cm^{-2} , 0.5 mg cm^{-2} and 0.2 mg cm^{-2} , respectively, in 0.1 M KOH.

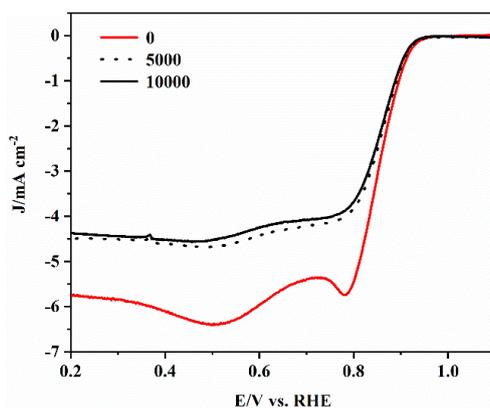


Fig S10. LSV curves of Cu-BPOZ@CNB-400 toward ORR after 0, 5000 and 10,000 potential cycles in O_2 -saturated 0.1 M KOH.

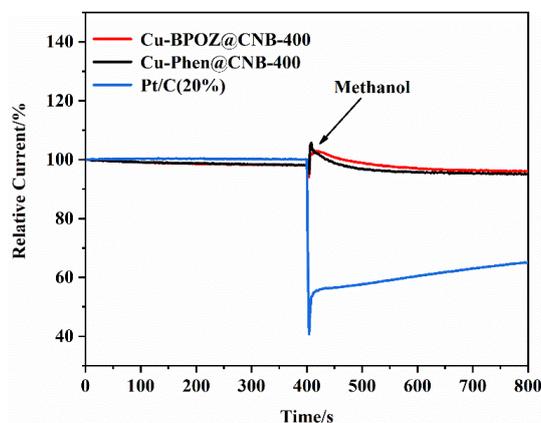


Fig S11. Methanol tolerance of Cu-BPOZ@CNB-400, Cu-Phen@CNB-400 and Pt/C.

Table S1. The content of different N types for the Cu-BPOZ@CNB-400 and Cu-BPOZ@CNB-800 calculated from XPS.

Catalysts	Pyridinic-N	Cu-N	Pyrolic-N	Graphitic-N
Cu-BPOZ@CNB-400	16.6%	27.7%	26.6%	29.1%
Cu-BPOZ@CNB-800	17.1%	19.7%	24.4%	38.8%

Table S2. Comparison of copper content of previously reported atomically dispersed copper-based catalysts.

Catalysts	Cu (wt %)	Reference
Cu-BPOZ@CNB-400	2.3	This work
Cu-NSDC	0.29	S3
Cu/Zn@NC	0.34	S4
CuSA/g-C ₃ N ₄ -1000	0.78	S5
Cu@NG	0.82	S6

Table S3. The R_{Ω} and R_{ct} for Cu-BPOZ@CNB, Cu-BPOZ@CNB-400 and Cu-BPOZ@CNB-800.

Catalysts	R_{Ω}/Ω	R_{ct}/Ω
Cu-BPOZ@CNB	86	503
Cu-BPOZ@CNB-400	85	161
Cu-BPOZ@CNB-800	80	215

Table S4. Comparison of ORR performance in 0.1 M KOH at 1600 rpm of previously reported copper-based catalysts.

Catalysts	$E_{1/2}$ (V vs. RHE)	Reference
Cu-BPOZ@CNB-400	0.86	This work
Cu/Zn@NC	0.83	S4
Cu _{SA} /g-C ₃ N ₄ -1000	0.85	S5
Cu@NG	0.84	S6
Cu/Cu ₂ O-NC	0.8	S7
Cu-ZrO _{3-x} @N-BPCNFs	0.856	S8
Cu-NHC	0.87	S9
Cu SAC	0.81	S10
Cu-S ₁ N ₃	0.84	S3
Cu-N/C	0.813	S11
Cu-N-C-ICHP NDs	0.85	S12
Cu-N ₄ -C	0.84	S13
CoCu-LDH@NC	0.84	S14
Cu@C(N4.13)	0.77	S15

Table S5. Electrocatalytic performance of prepared catalysts in the zinc-air cell.

Catalysts	P_{\max} (mW cm ⁻²)	OCV (V)
Cu-BPOZ@CNB-400	127	1.45
Cu-Phen@CNB-400	105	1.375
Pt/C(20%)	122	1.43

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