Supporting Information

In situ anchoring of metal nanoparticles in N-doped carbon framework derived

from metallophthalocyanine-based conjugated microporous polymers towards

## efficient oxygen reduction reaction

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#### **Experimental Section**

## 1. Materials

*N*, *N*-dimethylacetamide (DMAc, AR), *N*, *N*-dimethylformamide (DMF, AR), chloroform (AR), acetone (AR), tetrahydrofuran (THF) and sodium hydroxide (NaOH) were purchased from Tianjin Fuyu Fine Chemical Co. Ltd. Hydrochloric acid (HCl) was purchased from Beijing Chemicals Co. Ltd. 4-nitrophthalonitrile, 1, 4-benzenedicarboxaldehyde (BDA), ammonium molybdate, urea, Na<sub>2</sub>S·9H<sub>2</sub>O, FeCl<sub>2</sub> 4H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O and CuCl<sub>2</sub> were purchased from Aladdin Chemical Reagent Co. Ltd. All materials are used without further purification. The water used in our present work was deionized.

#### 2. Synthesis of samples

2.1 Synthesis of tetraaminometallophthalocyanines ((MPc(NH<sub>2</sub>)<sub>4</sub>, M=Fe, Co, Cu) <sub>S1</sub>



Scheme S1. The Schematic illustration for the synthesis process of MPc(NH<sub>2</sub>)<sub>4</sub>.

4-nitrophthalonitrile (20.0 mmol) was mixed with metal salts (5.0 mmol), urea (160.0 mmol) and amount of ammonium molybdate as catalytic, then the mixture was reacted in solid state at 160 °C for 5 h. The obtained crude product was further stirred in 200 mL 1 M HCl solution and 200 mL 1 M NaOH solution at 90 °C for 1 h, respectively. After cooling to room temperature, the aqueous was removed and the residue was poured into 1000 mL water, then the residue was filtered, washed with water for several times and dried under vacuum oven to get metal

tetranitrophthalocyanine (MPc(NO<sub>2</sub>)<sub>4</sub>).

The MPc(NH<sub>2</sub>)<sub>4</sub> was obtain by a simple reduce process of MPc(NO<sub>2</sub>)<sub>4</sub>. Briefly, MPc(NO<sub>2</sub>)<sub>4</sub> (2.0 mmol) and Na<sub>2</sub>S·9H<sub>2</sub>O (74 mmol) were dissolved in 30 mL DMF and then reacted at 60 °C for 1 h. Then, the product was collected by centrifugation and washed with water until neutral. Corresponding data are shown as follows.

**FePc(NH<sub>2</sub>)**<sub>4</sub>: Yield: 47%. UV-Vis (DMF,  $\lambda_{max}/nm$ ): 711, 268. FT-IR (KBr,  $v_{max}/cm^{-1}$ ): 3348 ( $v_{N-H}$  of NH<sub>2</sub>), 3205 ( $v_{N-H}$  of NH<sub>2</sub>), 1493 ( $v_{C=N}$  of Pc macrocycles), 1406 ( $v_{C=C}$  of Pc macrocycles), 1113 (vibration and characteristic band of Pc macrocycles), 826 ( $v_{Fe=N}$ ), 749 (vibration and characteristic band of Pc macrocycles).

**CoPc(NH<sub>2</sub>)**<sub>4</sub>: Yield: 56%. UV-Vis (DMF,  $\lambda_{max}/nm$ ): 706, 278. FT-IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3339 ( $\nu_{N-H}$  of NH<sub>2</sub>), 3218 ( $\nu_{N-H}$  of NH<sub>2</sub>), 1502 ( $\nu_{C=N}$  of Pc macrocycles), 1423 ( $\nu_{C=C}$  of Pc macrocycles), 1096 (vibration and characteristic band of Pc macrocycles), 829 ( $\nu_{Co=N}$ ), 748 (vibration and characteristic band of Pc macrocycles).

**CuPc(NH<sub>2</sub>)**<sub>4</sub>: Yield: 72%. UV-Vis (DMF,  $\lambda_{max}/nm$ ): 723, 340. FT-IR (KBr,  $\nu_{max}/cm^{-1}$ ): 3352 ( $\nu_{N-H}$  of NH<sub>2</sub>), 3217 ( $\nu_{N-H}$  of NH<sub>2</sub>), 1502 ( $\nu_{C=N}$  of Pc macrocycles), 1416 ( $\nu_{C=C}$  of Pc macrocycles), 1096 (vibration and characteristic band of Pc macrocycles), 824 ( $\nu_{Cu=N}$ ), 747 (vibration and characteristic band of Pc macrocycles).

# Supplementary figures



Fig. S1. SEM images of (a) CoNCs700 and (b) CoNCs900.



Fig. S2. FT-IR spectra of (a) CoNCs700 and (b) CoNCs900.



Fig. S3. XRD patterns of (a) CoNCs700 and (b) CoNCs900.



**Fig. S4**. (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of CoPc-CMP.



Fig. S5. TGA curves of CoPc-CMPs under  $N_2$  and Air atmospheres.



Fig. S6. XPS survey spectra of (a) CoNCs700 and (b) CoNCs900.



Fig. S7. High-resolution Co 2p XPS spectra of (a) CoNCs700 and (b) CoNCs900.

![](_page_6_Figure_4.jpeg)

Fig. S8. High-resolution C1s XPS spectra of (a) CoNCs700 and (b) CoNCs900.

![](_page_7_Figure_0.jpeg)

Fig. S9. CV curves of CoNCs700, CoNCs750, CoNCs850 and CoNCs900 in 0.1 M KOH solution saturated by  $O_2$  at a scan rate of 50 mV s<sup>-1</sup>.

![](_page_8_Figure_0.jpeg)

Fig. S10. The CV curves of (a) FeNCs and (b) CuNCs with different pyrolysis temperature in  $O_2$ -saturated 0.1 M KOH solution at a scan rate of 50 mV s<sup>-1</sup>. ORR polarization curves of (c) FeNCs and (d) CuNCs with different pyrolysis temperature at a rotation rate of 1600 rpm in  $O_2$ -saturated 0.1 M KOH solution.

electrocatalysts	$E_{onset} \! / \ V^{(a)}$	$E_{1/2}/V^{(b)}$	n <sup>(c)</sup>	condition
CoNCs800	0.905 V	0.807 V	3.98	0.1 M KOH
Co-W-C/N <sup>S2</sup>	0.960 V	0.774 V	3.89	0.1 M KOH
Co/C-700 <sup>S3</sup>	/	0.76 V	3.81 (0 V)	0.1 M KOH
Co-NCNT/NrGO 800 <sup>S4</sup>	0.91	/	3.88	0.1 M KOH
Co <sub>3</sub> O <sub>4</sub> /Co-N-C <sup>S5</sup>	/	0.798		0.1 M KOH
Co@CoO@Co3O4-N/C <sup>S6</sup>	-0.12 (vs Ag/AgCl)	/	3.85	0.1 M KOH
CoN-HGA-700 <sup>S7</sup>	0.91	0.83	3.89	0.1 M KOH

 Table S1. Summary of the reported Co, N co-doped carbon catalysts for ORR.

(a) onset potential; (b) positive half-wave potential; (c) electron transfer number.

![](_page_10_Figure_0.jpeg)

**Fig. S11.** CV curves of CoNCs800 (a) and 20 wt% Pt-C (b) at a scan rate of 50 mV s<sup>-1</sup> in  $O_2$ -saturated 0.1 M KOH solution containing 3M methanol.

![](_page_11_Figure_0.jpeg)

**Fig. S12.** (a) CV curves of CoNCs800 in 0.5 M  $H_2SO_4$  solution saturated by  $N_2$  or  $O_2$  at a scan rate of 50 mV s<sup>-1</sup>. (b) ORR polarization curves of CoNCs800 and Pt-C at a rotation rate of 1600 rpm. (c) ORR polarization curves of CoNCs800 at different rotation rates at a scan rate of 10 mV s<sup>-1</sup>. (d) K-L plots of CoNCs800 at different potentials, (inset) the electron transfer number (n) against electrode potential.

![](_page_12_Figure_0.jpeg)

Fig. S13. (a) The long-time stability and (b) methanol-tolerance evaluation of CoNCs800 are tested by the current-time chronoamperometric responses with a rotation of 1600 rpm at 0.4 V versus RHE (commercial 20% Pt/C is used for comparison) in  $O_2$ -saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> solution.

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