

# **Systematic study of the transition-metal (Fe, Co, Ni, Cu) phthalocyanine as electrocatalyst for oxygen reduction and its evaluation by DFT**

Zhengping Zhang, Shaoxuan Yang, Meiling Dou, Haijing Liu, Lin Gu and Feng Wang\*

State Key Laboratory of Chemical Resource Engineering, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing University of Chemical Technology, Beijing 100029, P. R. China

Tel./fax: +86 10 64451996. Email: wangf@mail.buct.edu.cn

## **Materials Synthesis**

### **materials**

FeCl<sub>3</sub>, CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, urea, NH<sub>4</sub>Cl, (NH<sub>4</sub>)<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>, phthalic anhydride, acetone, methanol, ethanol, KOH were purchased from Sinopharm. Vulcan XC-72 was CABOT Corporation. 5% Nafion were bought from DuPont, respectively. High-purity nitrogen and oxygen gas was provided from Beijing AP BAIF Gases Industry Co., Ltd. All chemicals were of analytical grade and applied without further purification. Distilled ultrapure water was used for all solution preparation and cleaning products.

### **Preparation of graphitized carbon black (GCB)**

In a typical process, 10 g of Vulcan XC-72 was placed in a graphite container and sealed, and then heated in a furnace at 2600 °C for 1 h under an argon atmosphere, followed by cooling to room temperature.

### **Synthesis of iron phthalocyanine (FePc)**

FePc was prepared by a solid phase synthesis method in a muffle furnace. Briefly, a mixture of 0.71 g FeCl<sub>3</sub>, 4.10 g urea, 1.00 g NH<sub>4</sub>Cl, 0.025 g (NH<sub>4</sub>)<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>, and 2.10g phthalic anhydride was ground. Next, it was transformed in a 250 mL crucible, heated in a muffle furnace at 210 °C for 3 h. After cooling to room temperature, the product was washed with water, acetone, and ethanol. The precipitates were dried under vacuum at 70 °C overnight.

### **Synthesis of cobalt phthalocyanine (CoPc)**

CoPc was prepared by a solid phase synthesis method in a muffle furnace. Briefly, a mixture of 1.60 g CoCl<sub>2</sub>·6H<sub>2</sub>O, 4.10 g urea, 1.00 g NH<sub>4</sub>Cl, 0.025 g (NH<sub>4</sub>)<sub>2</sub>Mo<sub>2</sub>O<sub>7</sub>, and 2.10g phthalic anhydride was ground. Next, it was transformed in a 250 mL crucible, heated in a muffle furnace at 210 °C for 3 h. After cooling to room temperature, the product was washed with water, acetone, and ethanol. The precipitates were dried under

vacuum at 70 °C overnight.

### **Synthesis of nickle phthalocyanine (NiPc)**

NiPc was prepared by a solid phase synthesis method in a muffle furnace. Briefly, a mixture of 1.60 g  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , 4.10 g urea, 1.00 g  $\text{NH}_4\text{Cl}$ , 0.025 g  $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ , and 2.10g phthalic anhydride was ground. Next, it was transformed in a 250 mL crucible, heated in a muffle furnace at 210 °C for 3 h. After cooling to room temperature, the product was washed with water, acetone, and ethanol. The precipitates were dried under vacuum at 70 °C overnight.

### **Synthesis of copper phthalocyanine (CuPc)**

CuPc was prepared by a solid phase synthesis method in a muffle furnace. Briefly, a mixture of 1.16 g  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , 4.10 g urea, 1.00 g  $\text{NH}_4\text{Cl}$ , 0.025 g  $(\text{NH}_4)_2\text{Mo}_2\text{O}_7$ , and 2.10g phthalic anhydride was ground. Next, it was transformed in a 250 mL crucible, heated in a muffle furnace at 210 °C for 3 h. After cooling to room temperature, the product was washed with water, acetone, and ethanol. The precipitates were dried under vacuum at 70 °C overnight.

### **Oxygen reduction reaction (ORR) measurements**

#### **Rotating disk electrode (RDE) measurements**

The glassy carbon rotating disk electrode is 4 mm in diameter. The Koutecky–Levich (K-L) plots reflecting the relation of  $I^{-1}$  vs.  $\omega^{-1/2}$  were constructed according to:

$$I^{-1} = i_k^{-1} + (0.2nFC_{\text{O}_2} D_{\text{O}_2}^{2/3} \gamma^{-1/6})^{-1} \omega^{-1/2}$$

where  $I$  is the measured current,  $i_k$  is the kinetic-limiting current,  $n$  is the number of electrons transferred per oxygen molecule,  $F$  is the Faraday constant (96,500 C mol<sup>-1</sup>),  $C_{\text{O}_2}$  is the concentration of oxygen in 0.1 M KOH,  $D_{\text{O}_2}$  is the diffusion coefficient of oxygen in 0.1 M KOH,  $\gamma$  is the kinematic viscosity of the 0.1 M KOH and  $\omega$  is the electrode rotation rate.

For the Tafel plot, the kinetic current was calculated from the mass-transport correction of RDE by:

$$J_k = \frac{J \times J_L}{J_L - J}$$

#### **Rotating ring-disk electrode (RRDE) measurements**

The disk electrode was scanned cathodically at a rate of 5 mV·s<sup>-1</sup> and the ring potential was constant at 1.5 V vs. RHE. The electron transfer number ( $n$ ) was determined by the followed equation:

$$n = 4 \times \frac{I_d}{I_d + I_r / N}$$

where  $I_d$  is disk current,  $I_r$  is ring current and  $N = 0.4$  is the current collection efficiency of the Pt ring. The peroxide percentage (%  $HO_2^-$ ) was calculated based on the equation<sup>[1]</sup>:

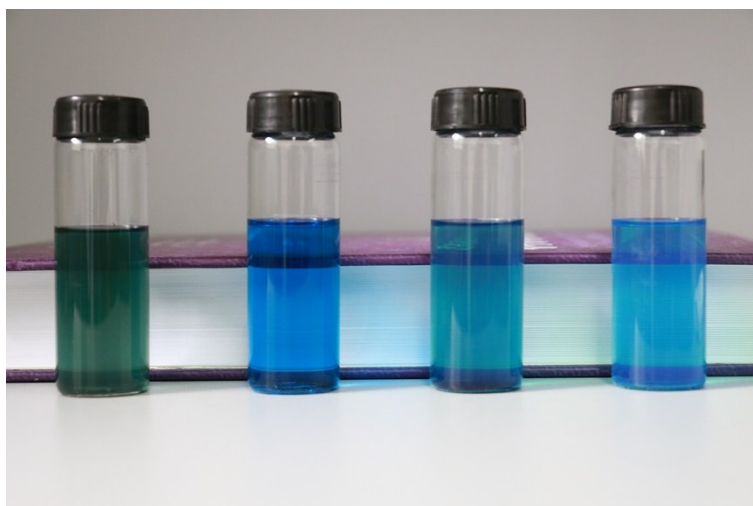
$$\%HO_2^- = 200 \times \frac{I_r / N}{I_d + I_r / N}$$

**Table S1** Calculated properties of TMPc systems.

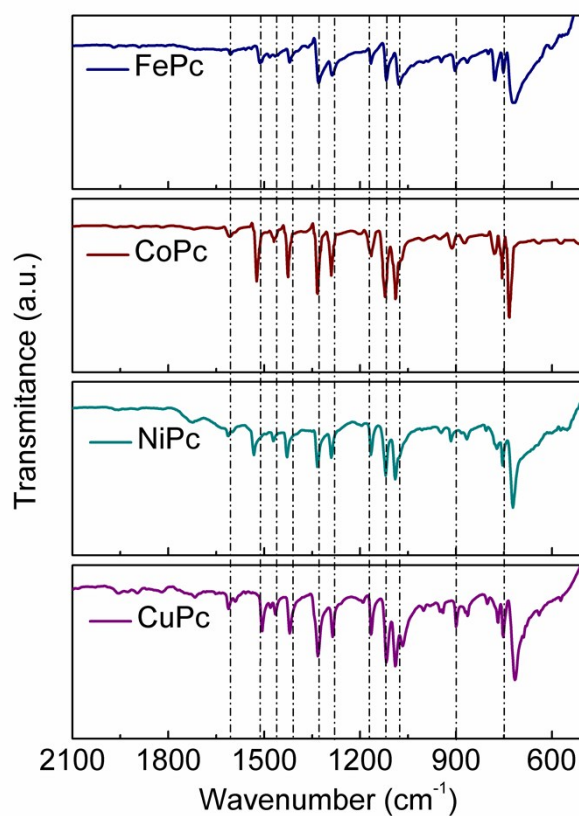
	$R_{TM-N} / \text{\AA}$		
	this work	expt	other works
FePc	1.962	1.928 <sup>[2]</sup>	1.958 <sup>[3]</sup>
CoPc	1.925	1.91 <sup>[4]</sup>	1.930 <sup>[3]</sup>
NiPc	1.938		
CuPc	1.985		

**Table S2** Experimental results and calculated properties of TMPc systems.

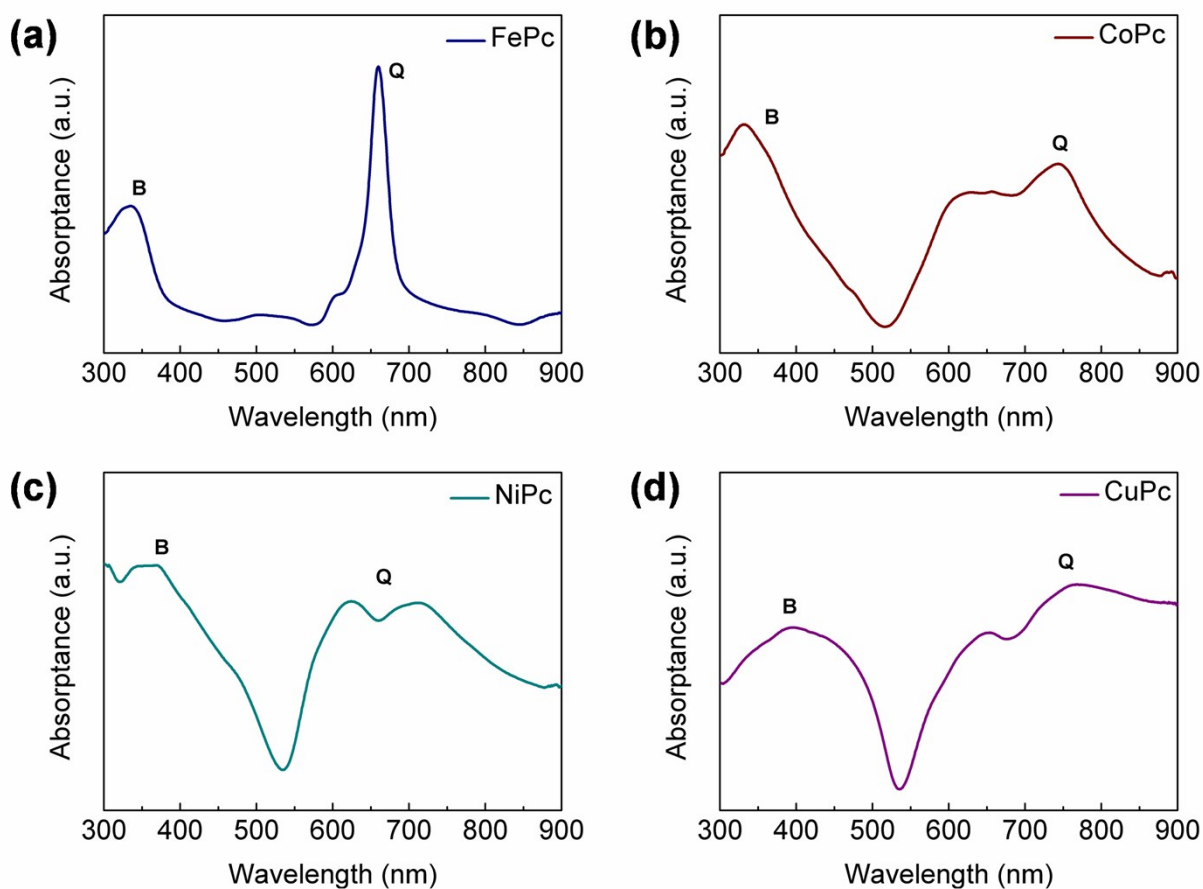
	$E_{onset}/E_{1/2}$	$\%HO_2^-$	Solution/Reference electrode/ Scan rate/Rotation rate	$\Delta E_{TM-OO}$	
FePc	0.98/0.90 V	1.1 %	0.1 M KOH/ vs. RHE/5 mV s <sup>-1</sup> /1600 rpm	-2.032 eV	This work
	0.05/-0.07 V	ca. 1%	0.1 M NaOH/ vs. Hg/HgO/10 mV s <sup>-1</sup> /1600 rpm <sup>5</sup>	-1.16 eV <sup>5</sup>	Other works
	-0.094/-0.14 V	ca. 5%	0.1 M NaOH/ vs. SCE /5 mV s <sup>-1</sup> /500 rpm	-0.454 eV <sup>3</sup>	
CoPc	0.86/0.76 V	45.4 %	0.1 M KOH/ vs. RHE/5 mV s <sup>-1</sup> /1600 rpm	-1.294 eV	This work
	-0.05/-0.17 V	ca. 40%	0.1 M NaOH/ vs. Hg/HgO/10 mV s <sup>-1</sup> /1600 rpm <sup>5</sup>	-0.402 eV <sup>5</sup>	Other works
	-0.1/-0.168 V	ca. 85%	0.1 M NaOH/ vs. Hg/HgO/20 mV s <sup>-1</sup> /2500 rpm <sup>6</sup>	-0.287 eV <sup>3</sup>	
NiPc	0.76/0.55 V	83.7 %	0.1 M KOH/ vs. RHE/5 mV s <sup>-1</sup> /1600 rpm	-0.180 eV	This work
CuPc	0.78/0.58 V	52.5 %	0.1 M KOH/ vs. RHE/5 mV s <sup>-1</sup> /1600 rpm	-0.271 eV	This work
	0.02/0.21 V	ca. 53.5 %	0.1 M KOH/ vs. SCE/5 mV s <sup>-1</sup> /1500 rpm <sup>7</sup>		Other work



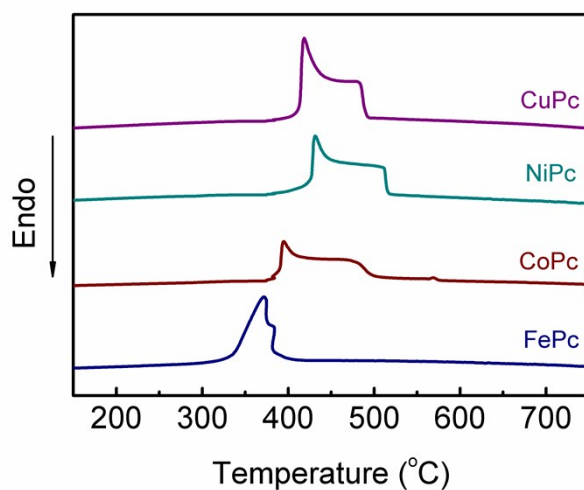
**Fig. S1** Digital photograph of TMPc (TM: Fe, Co, Ni and Cu) / tetrahydrofuran mixed solutions.



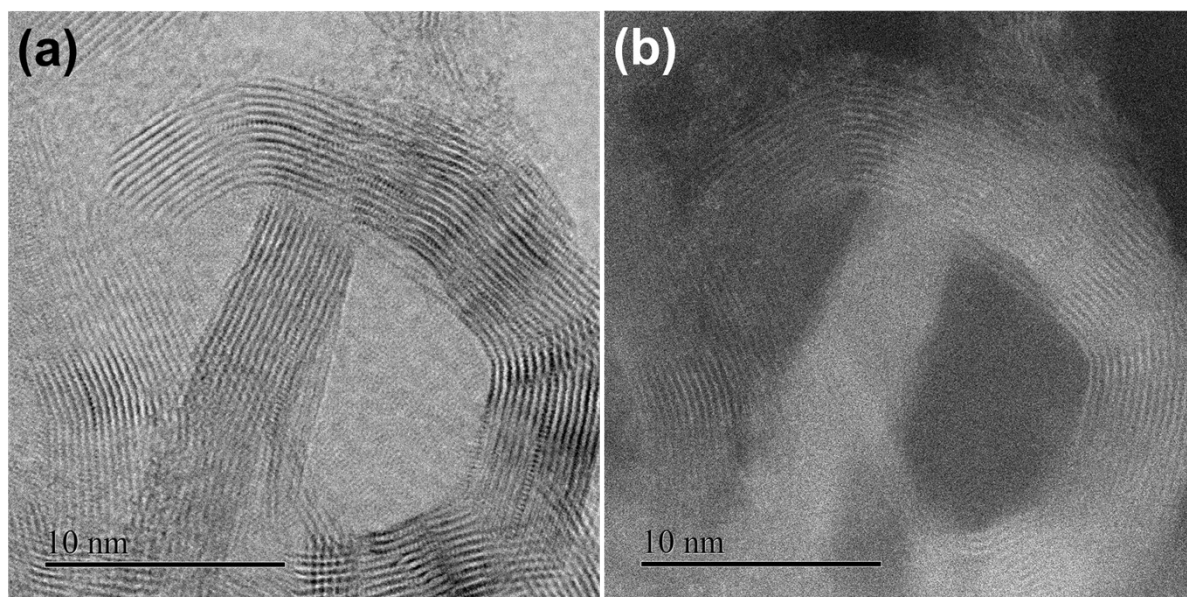
**Fig. S2** FT-IR spectra of FePc, CoPc, NiPc and CuPc. The characteristic signals of the phthalocyanine frameworks ( $\sim 1606\text{ cm}^{-1}$ ,  $\sim 1510\text{ cm}^{-1}$ ,  $\sim 1332\text{ cm}^{-1}$  and  $\sim 1287\text{ cm}^{-1}$ ), the stretching vibration of C-N ( $\sim 1287\text{ cm}^{-1}$ ), metal ligand vibration ( $\sim 900\text{ cm}^{-1}$ ) can be preserved in the TMPc samples, revealing the formation of TMPc.<sup>[8]</sup>



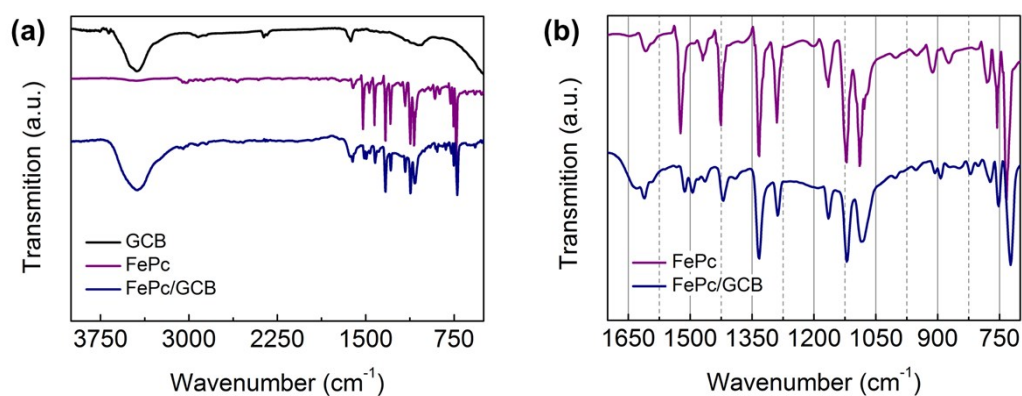
**Fig. S3** UV spectra of a) FePc, b) CoPc, c) NiPc and d) CuPc. The TMPc (TM: Fe, Co, Ni and Cu) showed the characteristic absorption *B* and *Q* bands at 300~400 nm and 600~800 nm.<sup>[9]</sup>



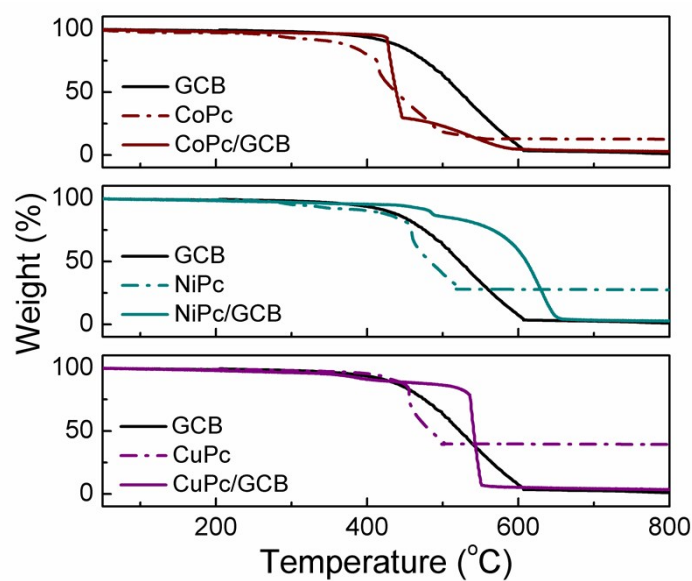
**Fig. S4** Differential Thermal Analysis (DTA) curve of FePc, CoPc, NiPc and CuPc in air atmosphere. DTA curve reveals maximum change in mass occurring at 372 °C for FePc, 395 °C for CoPc, 431 °C for NiPc and 419 °C for CuPc, suggesting the thermal stability of TMPc.<sup>[10]</sup>



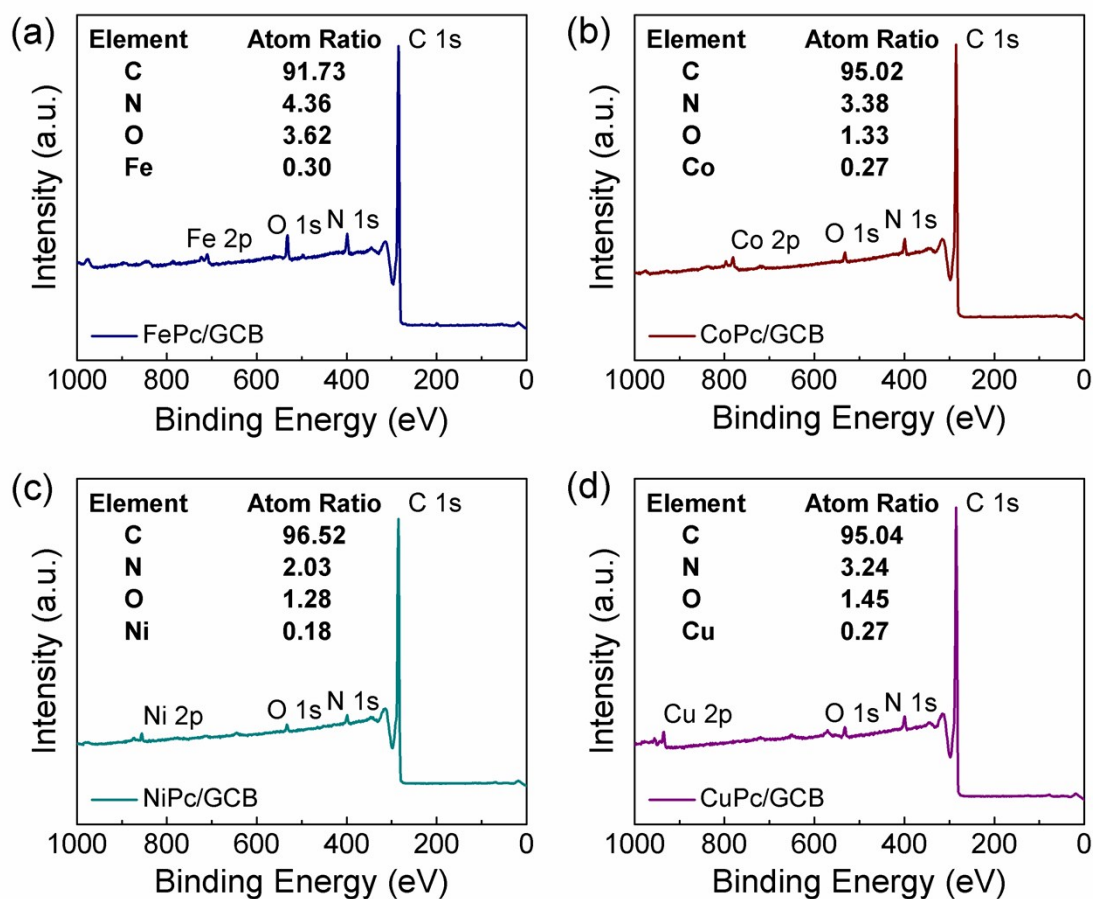
**Fig. S5** a) Aberration-corrected high resolution STEM images and b) the corresponding HAADF-STEM images of FePc/GCB



**Fig. S6** a) FT-IR spectra of GCB, FePc and FePc/GCB, and the corresponding high-magnification image of FePc and FePc/GCB.

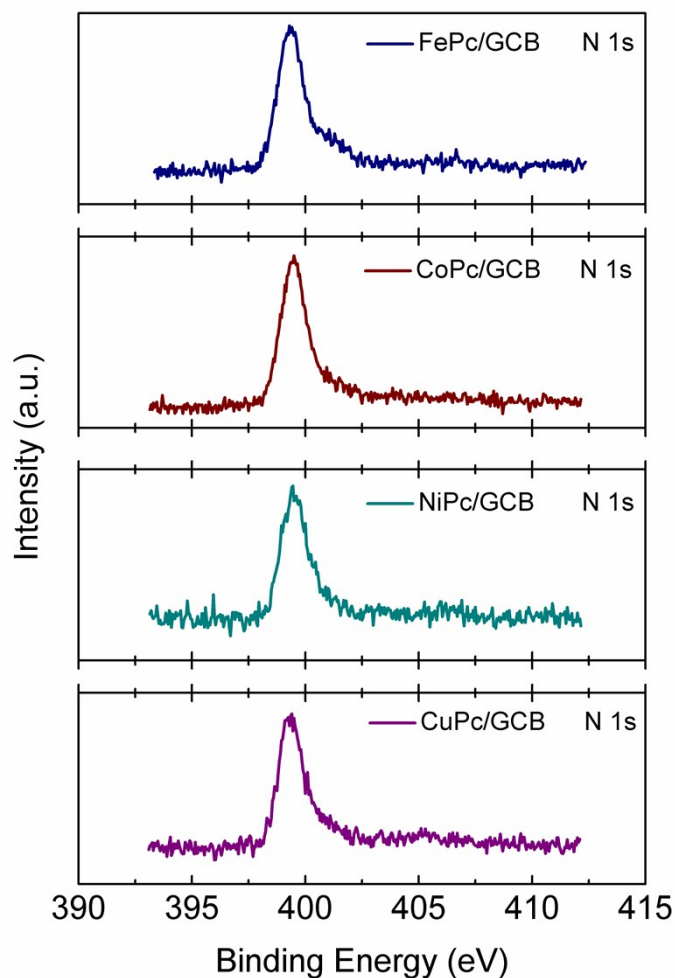


**Fig. S7** Thermalgravimetric analysis (TGA) of GCB, CoPc, NiPc CuPc and the corresponding TMPc/GCB catalysts. Atmosphere: air, Rate: 5 °C min<sup>-1</sup>.

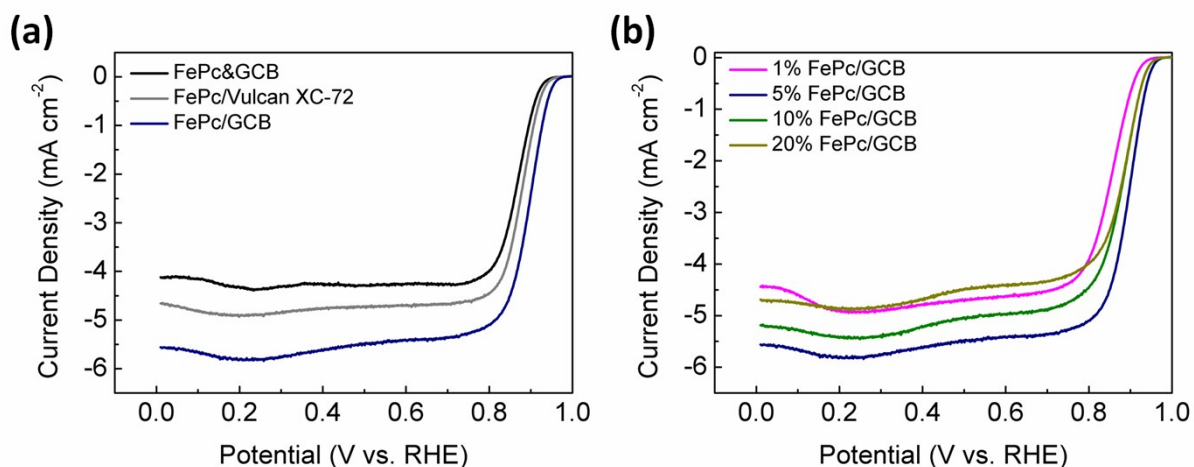


**Fig. S8** X-ray photoelectron spectra (XPS) survey spectra of the a) FePc/GCB, b) CoPc/GCB, c) NiPc/GCB and d) CuPc/GCB catalysts.



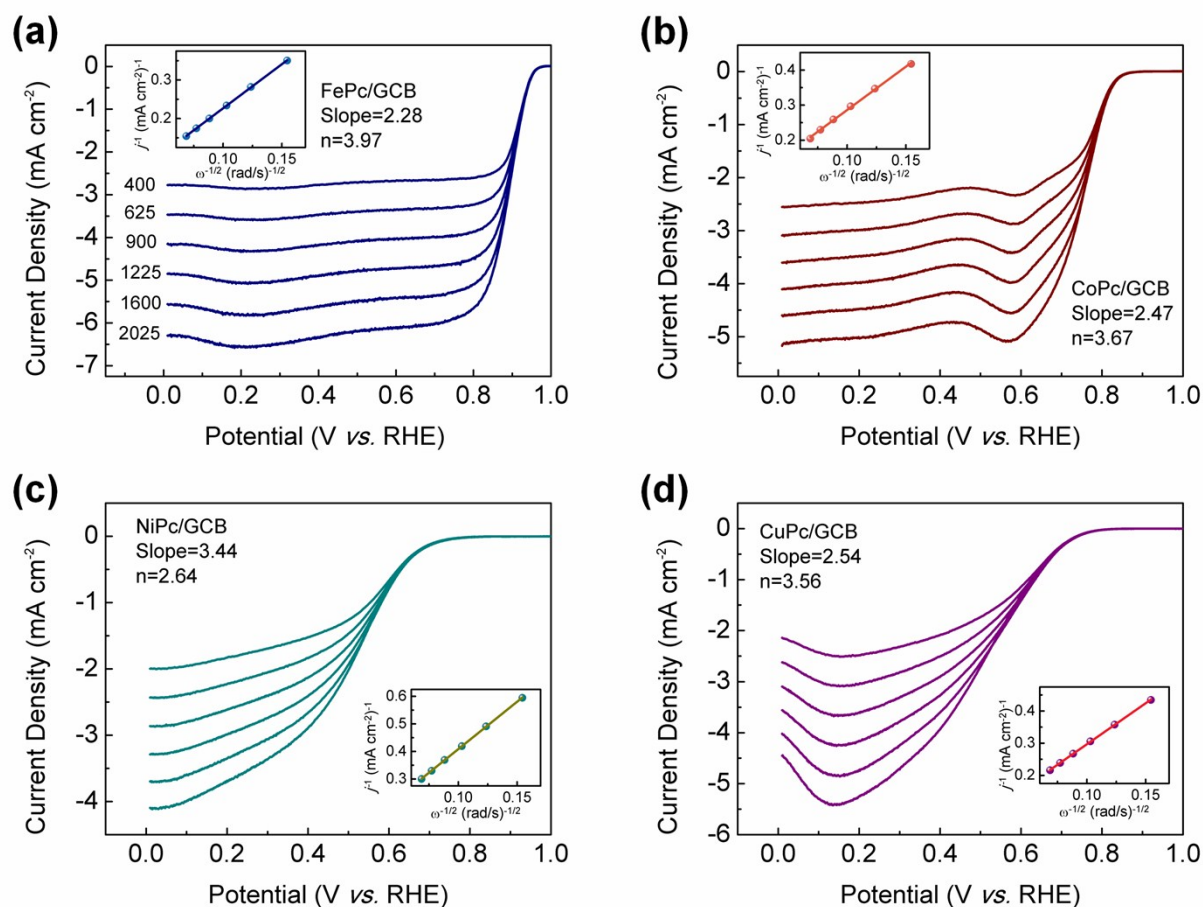


**Fig. S9** X-ray photoelectron spectra (XPS) high-resolution scans of TMPc/GCB N 1s.

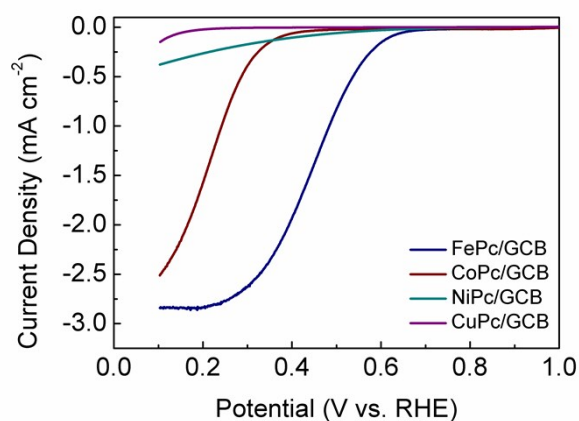


**Fig. S10** Linear polarization curves of a) FePc supported on Vulcan XC-72 (FePc/Vulcan-XC 72), FePc supported on GCB (FePc/GCB) and FePc&C that obtained from a simple mixture of FePc and GCB. b) the FePc/GCB catalysts with different amounts of FePc at rotation rate of 1600 rpm in O<sub>2</sub>-saturated 0.1 M KOH at a scan rate of 5 mV s<sup>-1</sup>. Percentages (w/w) of FePc present: 1%, 5%, 10% and 20%.





**Fig. S11** Linear polarization curves for a) FePc/GCB, b) CoPc/GCB, c) NiPc/GCB and d) CuPc/GCB in  $O_2$ -saturated 0.1 M KOH at a scan rate of 5 mV s<sup>-1</sup> at the different rotation rates (400, 625, 900, 1225, 1600 and 2025 rpm). The insets show K-L plots of TMPc/C at 0.3 V.



**Fig. S12** Linear polarization curves of electrocatalysts with TMPc/GCB at rotation rate of 1600 rpm in  $O_2$ -saturated 0.1 M HClO<sub>4</sub> at a scan rate of 5 mV s<sup>-1</sup>.

## Reference

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