

Electronic Supplementary Material (ESI)

A reduced graphene oxide/covalent cobalt porphyrin framework for efficient oxygen reduction reaction

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Experimental section

Materials

Acetic anhydride, propanoic acid, pyridine, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (AR), HCl (37%), $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ (AR), terephthalaldehyde, chloroform, n-Hexane, methanol, isopropanol, n-butyl alcohol and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd (China). Pyrrole was purchased from Aladdin reagent (Shanghai) Co. Ltd. 4-Nitrobenzaldehyde and o-dichlorobenzene was purchased from Inno chemical Co. Ltd (China). All the reagents were used without further purification. Nafion (5 wt% in isopropanol) was purchased from Sigma-Aldrich. The commercial catalyst 20% Pt/C-JM was purchased from Johnson-Matthey (UK).

Preparation of cobalt(II) porphyrin

4-nitrobenzaldehyde (22.0 g, 145 mmol) and acetic anhydride (24.0 mL, 254 mmol) were dissolved in 600 mL of stirring propionic acid. After the resulting solution was refluxed, freshly distilled pyrrole (10.0 mL, 144 mmol) in propionic acid (20 mL) was slowly added. Then, the mixture was refluxed for 30 min. After the resulting mixture

was allowed to cool, a dark solid was collected by centrifugation, washed with water (100 mL×6) and dried in vacuum. The dark solid was added to pyridine (160 mL). The suspension was refluxed for 1 h with stirring, and cooled to room temperature. The resulting mixture was centrifuged to get the solid product 5,10,15,20-tetrakis(4-nitrophenyl) porphyrin [H₂(p-NO₂)TPP, yield 4.65 g, 16.3%], which was washed repeatedly with acetone until its color was no longer dark.

H₂(p-NO₂)TPP (4.65 g, 5.85 mmol) was added to 250 mL of concentrated HCl, and the solution was bubbled with N₂ for 1 h. A solution of SnCl₂·2H₂O (18 g, 79.8 mmol) in concentrated HCl (250 mL), also bubbled with N₂, and was added to the above mixture. Then the stirring mixture was heated at 75 °C for 30 min. After the mixture was cooled to 0 °C, the reaction mixture was then neutralized with concentrated NH₄OH (250 mL) under N₂, taking care to maintain a low temperature throughout the very exothermic reaction. The resulting mixture was centrifuged to get the solid, which was added to 5% NaOH (500 mL). The resulting solution was stirred vigorously for 30 minutes. Then the solid product was again centrifuged, washed with water, dried, and extracted with chloroform (300 mL) by Soxhlet extractor. The Soxhlet extracting solution was reduced to 50 mL by rotary evaporation, then ethanol (150 mL) was added to the above solution, and crystalline product 4,4',4",4""-(porphyrin-5,10,15,20-tetrayl)tetraaniline [H₂(p-NH₂)TPP, 1.6 g, 40.6%] as purple solid was obtained.¹HNMR(300 MHz, CDCl₃): -2.72 (s, 2H, pyrrole-NH×2), 4.03 (s, 8H, NH₂×4), 7.07 (d, J=7.8 Hz, 8H, Ph-H×8), 7.99 (d, J=7.8 Hz, 8H, Ph-H×8) and 8.90 ppm (s, 8H, pyrrole-H×8).¹

The $\text{H}_2(\text{p-NH}_2)\text{TPP}$ (300 mg, 0.445 mmol) was dissolved in chloroform (75 mL). A solution of $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$ (120 mg, 0.482 mmol) in methanol (30 mL) was added to the above mixture. The resulting mixture was refluxed for 4 h under N_2 . After cooling to room temperature, the resulting mixture was concentrated in vacuum to get the product, which was washed with methanol (100 mL) and chloroform (100 mL) respectively for 2 hours by Soxhlet extractor. Then the product was dried under vacuum to yield cobalt(II) porphyrin as a purple solid.²

Synthesis of the CoCOF-Py-rGO catalysts

Cobalt(II) porphyrin (0.027 mmol, 20.1 mg), terephthalaldehyde (0.055 mmol, 7.4 mg) and G-dye (1.4 mg) was added to an o-dichlorobenzene / n-butyl alcohol / 6 M acetic acid (1.25 mL/1.25 mL/0.12 mL) solution. The resulting mixture was degassed in a Pyrex tube (20 mL) by three freeze-pump-thaw cycles. The tube was sealed off and heated at 120 °C for 3 days. The precipitate was filtered and extracted with anhydrous THF for 2 hours by Soxhlet extractor to get CoCOF-Py-0.05rGO catalyst, which was dried at 80 °C under vacuum overnight.³ Therein, G-dye was synthesized according to the literatures.⁴⁻⁵

Other CoCOF-Py-rGO catalysts were synthesized by the same way. Therein, CoCOF does not contain G-dye, CoCOF-Py-0.1rGO contains 2.8 mg of G-dye, CoCOF-Py-0.1rGO contains 6.9 mg of G-dye, CoCOF-0.05rGO contains 1.4 mg of reduced graphene oxide (rGO).

Physical characterization

Fourier transform infrared spectroscopy (FT-IR) measurements were recorded at

room temperature on the NICOLET 5700 FTIR spectrometer. Ultraviolet-visible spectroscopy (UV-Vis) spectroscopic data was collected using the TU-1810 UV-Vis Spectrometer with N,N-Dimethylformamide as the solvent and a path length of 1 cm. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was performed on an IRIS Intrepid II XSP (Thermo Fisher Scientific, USA). Scanning electron microscopy (SEM) images were got using a SIGMA scanning electron microscope of German Zeiss company. Transmission electron microscopy (TEM) images were performed on a Tecnai G20 U-Twin. N₂ adsorption desorption isotherms were measured at the temperature of 77 K on a Quantachrome NOVA 4200e adjusting the temperature by liquid nitrogen. X-ray photoelectron spectroscopy (XPS) spectra of catalysts were obtained using a Kratos XSAM 800 spectrophotometer. Powder X-ray diffraction (PXRD) was carried out using a MiniFlex 600 instrument (Rigaku) with Cu K α radiation, and the tests were performed at a scan rate of 2° min⁻¹. Thermogravimetric analysis (TGA) was recorded by diamond DSC STA7300 instrument under N₂ with a heating rate of 10 °C /min. Raman spectra were recorded by using a Renishaw in Via Plus. ¹HNMR of samples were tested by Varian Mercury VX-300 Nuclear magnetic resonance spectrometer. Rotating disk electrode (RDE), rotating ring disk electrode (RRDE), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) investigations were performed to evaluate the electrochemical properties by using a CHI760e work station with a three electrode system.

Electrochemical measurements

To carry out the activity of the as-synthesized catalysts for ORR, three electrode system was selected, the reference electrode was the Hg/HgO electrode (MOE) in an alkaline system or the Hg/Hg₂Cl₂ electrode (SCE) in an acid system, the counter electrode was platinum sheet (dimension: 1 cm × 1 cm × 0.02 cm), the working electrode was glassy carbon (GC, $\phi = 5$ mm). And all electrochemical tests temperature was room temperature.

Every sample (4 mg) and XC-72 (1.2 mg) was dispersed in isopropanol solvent (0.8 mL, 0.1% Nafion) for preparing the catalytic ink, which (36 μ L, loading amount: 0.18 mg) was deposited onto the GC rotating disk electrode (RDE), and then dried naturally. Pt/C catalyst ink was prepared from Pt/C (5 mg) dispersed in isopropanol solvent (1 mL, 0.1% Nafion) by the same procedure, then 6 μ L ink suspension (loading amount: 0.03 mg) was cast onto the GC RDE.

For translating all the potential to the potential versus the reversible hydrogen electrode (RHE), the reference electrode (MOE or SCE) was used. To calibrate the MOE or SCE to the RHE scale, the system was firstly saturated with H₂, and Pt/C was applied on the surface of the GC electrode, which was used as the working electrode. The test was performed at a scanning rate of 5 mV s⁻¹, using a platinum sheet as the counter electrode to record the hydrogen electrode reactions' (HERs) polarization curve, then the RHE potential was chosen from the potentials at which the current crossed zero.

The impurities of the GC RDE surface was removed by gamma alumina powders with the average sizes of 1, 0.5 and 0.05 μ m, which were used as the polishing agent,

and then ultrapure water and ethanol were used in turn to remove the alumina powders. H_2 (for HER polarization curves), O_2 (for ORR polarization curves, CV curves and Nyquist plots), high-purity Ar (for ORR polarization curves) and high-purity N_2 (for CV curves) were bubbled into the electrolyte for about 30 minutes before each measurement. For RDE measurements, the test system was scanned from 1.0 V to 0.2 V at a rate of 5 mV s^{-1} with 1600 rpm rotating speed in 0.1 M KOH solution. For RRDE experiments, the same conditions as RDE measurements were used. For CV measurements, the test system was scanned from 1.0 V to 0.2 V at a rate of 10 mV s^{-1} in 0.1 M KOH solution. For EIS measurements, the test system was at open circuit potential for initial potential in 0.1 M KOH from 200 kHz to 0.01 Hz with 5 mV of single sine wave with 1600 rpm rotating speed. The $\text{H}_2\text{O}_2\%$ and the electron transfer number (n) were calculate by the following equations: $\text{H}_2\text{O}_2\% = 200 \times I_r/(N \times I_d + I_r)$; $n = 4 \times N \times I_d/(N \times I_d + I_r)$, where I_r is the ring current, I_d is the disk current and N is the current collection efficiency of the Pt ring. In this system, N was determined to be 0.37.

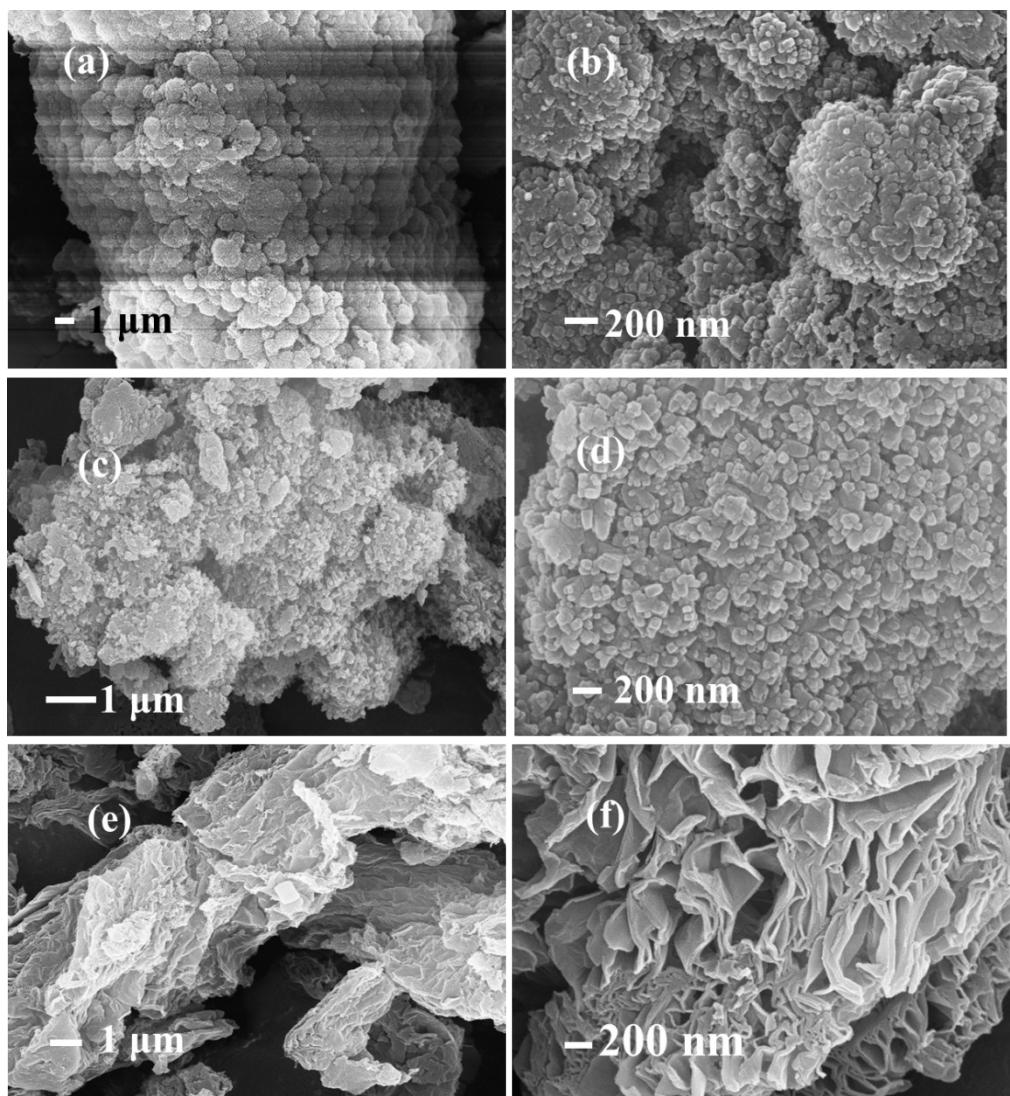


Fig. S1. SEM images of (a, b) CoCOF-Py-0.1rGO, (c, d) CoCOF-Py-0.25rGO and (e, f) G-dye

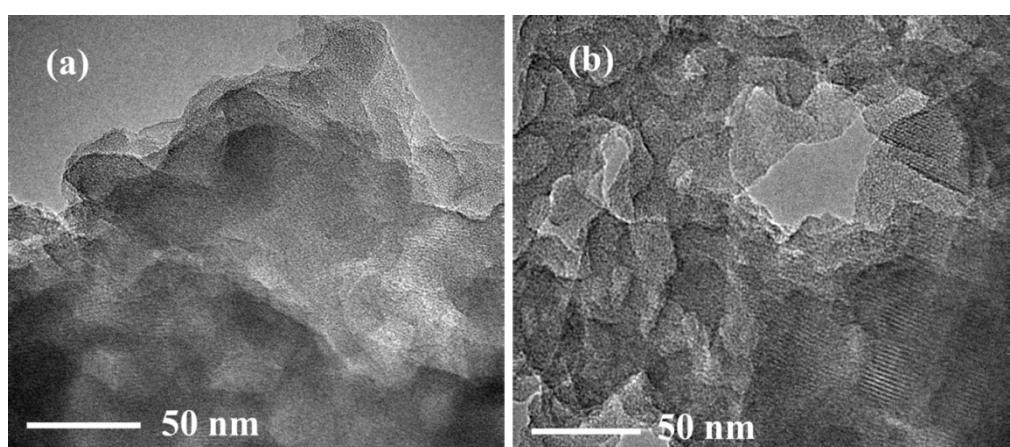


Fig. S2. TEM images of (a) CoCOF, (b) CoCOF-Py-0.05rGO

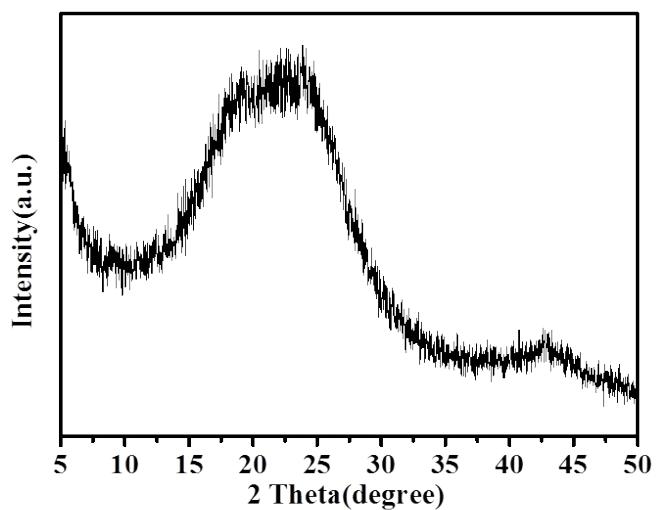


Fig. S3. PXRD of G-dye.

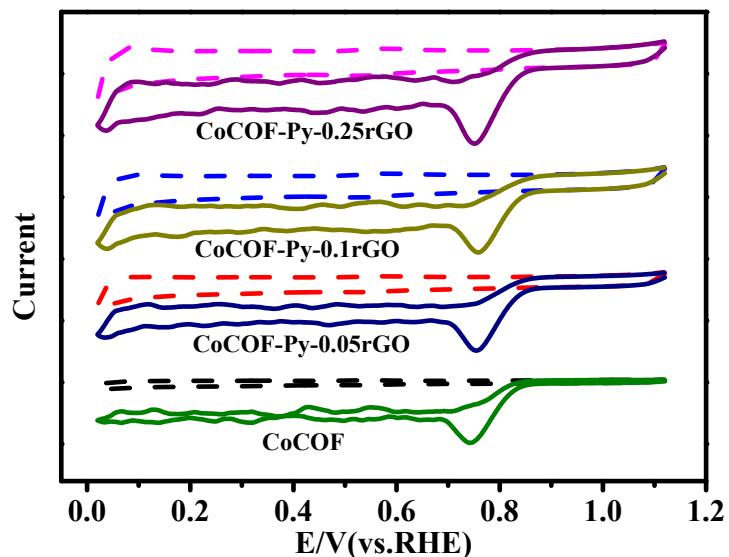


Fig. S4. CV curves of CoCOF-Py-rGo catalysts in N₂⁻ (dotted line) and O₂⁻ (solid line) saturated 0.1 M KOH solution (scanning rate: 10 mV s⁻¹) adding XC-72 (30 wt% of sample).

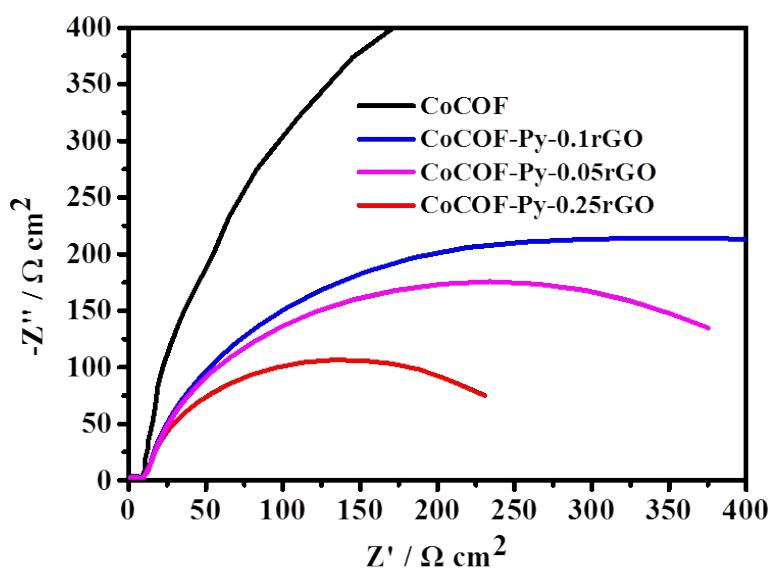


Fig. S5. The Nyquist plots of CoCOF-Py-rGO catalysts adding XC-72 (30 wt% of sample). Impedance spectra were taken at open circuit potential for initial potential in O_2 -saturated 0.1 M KOH from 200 kHz to 0.01 Hz with 5 mV of single sine wave.

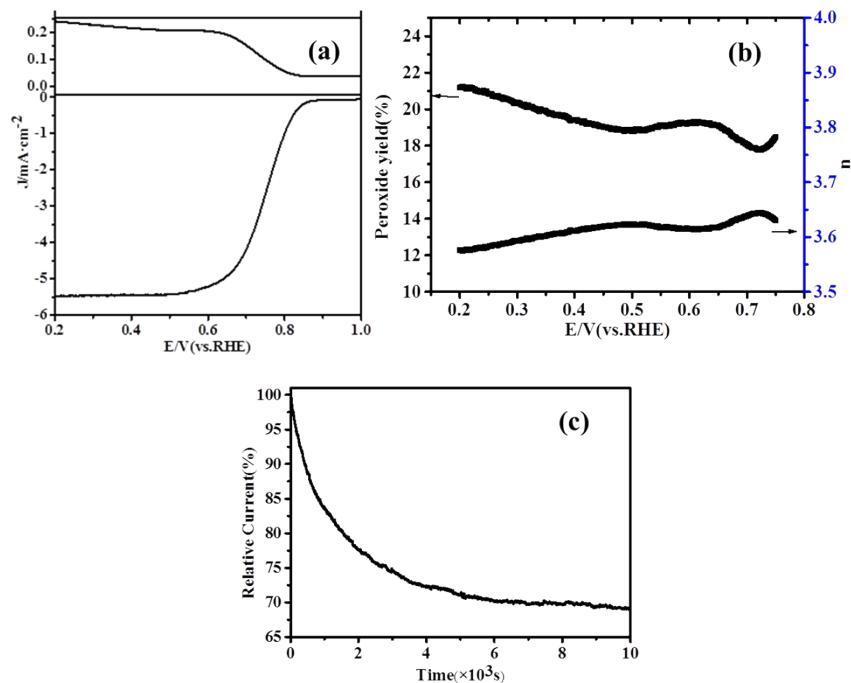


Fig. S6. (a) Steady-state current–potential responses on disk (lower panel) and ring (upper panel) electrodes, (b) H_2O_2 yield and electron transfer number (n) and (c) the stability of the ORR obtained from CoCOF-0.05rGO in O_2 -saturated 0.1 M KOH solution adding XC-72 (30 wt% of sample).

Table S1. Comparison of ORR catalytic performances in alkaline solution between CoCOF-Py-0.05rGO and other non-precious metal-based molecule catalysts reported previously.

Catalyst	Onset potential (V vs. RHE)	Half-wave potential (V vs. RHE)	The diffusion- limited current density (mA/cm ²)	CV redox potential (V vs. RHE)	Ref.
CoCOF-Py-0.05rGO	0.84	0.765	4.72	0.75	This work
FePc/ERGO	-0.05 (V vs SCE)	-0.20(V vs SCE)	5.00	-0.15(V vs SCE)	[6]
FePc/NG	-0.01 (V vs Ag/AgCl)	-0.12 (V vs Ag/AgCl)	4.70	-0.14 (V vs Ag/AgCl)	[7]
rGO/(Ni ²⁺ /THPP/Co ² ⁺ /THPP) ₈	0.84	0.55	3.30	/	[8]
(G-dye 50 wt % - (FeP)n MOF	-0.02 (V vs Ag/AgCl)	-0.50 (V vs Ag/AgCl)	6.20	-0.26 (V vs Ag/AgCl)	[9]
FeP-TIPS/CNTs	0.84	0.71	4.50	0.73	[10]
rGO-TADPyCu	0.951	0.795	5.5	0.80	[11]
(DFTPP)Fe-Im- CNTs	1.0	0.880	7.1	/	[12]

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