

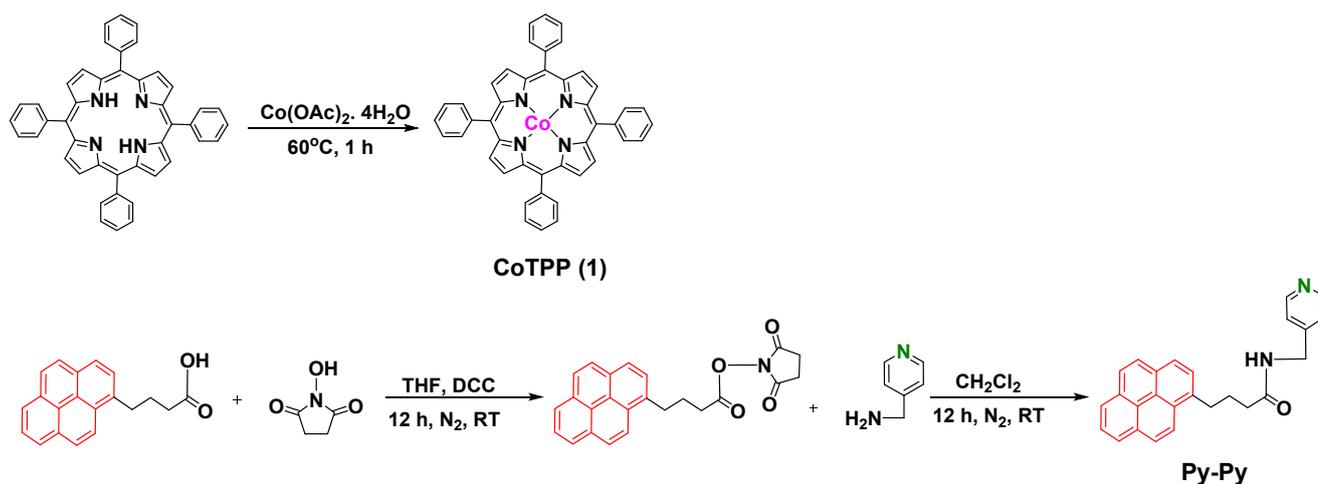
Supporting Information

Noncovalent Immobilization of Co(II)porphyrin through Axial Coordination as an Enhanced
Electrocatalyst on Carbon Electrode for Oxygen Reductions and Evolutions

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Scheme 1. Synthesis of Co(II)porphyrin (**1**) and pyrene-pyridine hybrid (**Py-Py**).

General

All reagents were purchased from commercial suppliers and used without any further purification unless otherwise stated. Multiwalled carbon nanotubes of diameter 8-15 nm were purchased from Tanfeng Tech. Inc. (China). All aqueous solutions were prepared freshly using Milli-Q water. Moisture sensitive reactions/ synthesis were performed under N_2 . 5,10, 15, 20-tetraphenylporphyrin ligand and its' metal complex was synthesized using modified methods as described in **scheme 1**. ^1H NMR spectra were recorded on Bruker AVANCE II spectrometer (operating at 400.13MHz) using CDCl_3 as the internal reference. Absorption spectra were obtained using Shimadzu UV 3600 spectrophotometer. Fluorescence measurement was performed at room temperature on Varian-Cary Eclipse Fluorescence Spectrophotometer model number EL01064834. HR-MALDI-TOF-mass spectra was recorded on a Bruker Daltonics solariX workstation. Fourier transform infrared spectrum (FT-IR) was taken using KBr pellet method on Nicolet Nexus 470 FT-IR spectrophotometer from Thermo Electron Corporation. XRD diffraction patterns were measured on HITACHI-6000. EPR were recorded on Electron Paramagnetic Resonance Spectrometer; model number A300.10/12 from Brooke BRUKER, Germany. Surface morphologies of composites were characterized using JEOL JSM-7001F Field Emission Scanning Electron Microscope (FE-SEM). Cyclic and linear sweep voltammetries were performed using Chi-730D electrochemistry workstation. It consists of a three-electrode-compartment

cell; a GCE of 3 mm as working electrode while platinum wire and Ag/AgCl electrodes were used as the counter and reference electrodes respectively. ORR and OER experiments were conducted in aqueous solutions saturated by bubbling high purity O₂ and N₂ for 30 min before analysis. Bulk electrolysis was conducted using an “H” type cell with a fritted glass layer that separates the cathodic and anodic sections of the cell. The working electrode used was GC coated with 1/MWCNT and 1/MWCNT/Py-Py materials. The counter and reference electrodes were made from platinum wire and SCE respectively. Both the working and reference electrodes were placed in one compartment while the counter electrode was in another compartment of the cell. Potentials observed using Ag/AgCl and SCE were converted to reversible hydrogen electrode (RHE) using the following Nernst equations.

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591\text{pH} + E^{\circ}_{\text{Ag/AgCl}} \quad [1]$$

$$E_{\text{RHE}} = E_{\text{SHE}} + 0.0591\text{pH} + E^{\circ}_{\text{SHE}} \quad [2]$$

Where $E_{\text{Ag/AgCl}}$ is the experimentally determined potential using Ag/AgCl reference electrode; $E^{\circ}_{\text{Ag/AgCl}}$ is 0.199V at 25°C. Similarly, E_{SHE} is the experimentally determined potential using SCE reference electrode with $E^{\circ}_{\text{SHE}} = 0.241$ at 25°C.

Synthesis of Co(II)-5,10,15,20-tetraphenylporphyrin (**1**)

5,10,15,20-tetraphenylporphyrin^[1] (0.5 g, 0.813 mmol) was dissolved in 80 mL CHCl₃ and a 20 mL CH₃OH solution of Co(OAc)₂·4H₂O (2.025 g, 8.13 mmol) added and refluxed at 60 °C for 1 h. The solvent mixture was evaporated to dryness on rotary, dissolved in 50 mL CHCl₃, washed with distilled water (50 x 3) and dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography using Al₂O₃ with CHCl₃ as the eluent and dried under vacuum for 2-3 h. The yield found was 90% (0.45g, 0.699 mmol). MS: *m/z* calcd for C₄₄H₂₈CoN₄ = 671.67; found 671.75. Molar absorption coefficients (ε) of **1** was determined in CH₂Cl₂; (λ_{max} in nm, ε in M⁻¹cm⁻¹); as λ = 410 (814601), 527 (47156) (Fig. *S1a*).

Synthesis of 4-(pyren-1-yl)-N-(pyridin-4-ylmethyl)butanamide (Py-Py)

This compound was synthesized through a known procedure [2]. 4-(pyren-1-yl)butanoic acid (300 mg, 1.0 mmol) and N-hydroxysuccinimide (120 mg, 1.0 mmol) were mixed together and dissolved in 40 mL dried THF at room temperature and labelled as **1**. N,N'-Dicyclohexyl carbodiimide (210 mg, 1.0 mmol) was dissolved in 10 mL THF and labeled **2**. Solutions **1** and **2** were mixed together at a temperature of 0 °C and under nitrogen atmosphere stirred overnight (12 h) at room temperature. The resulting mixture was filtered, and filtrate subjected to reduced pressure to remove solvent (THF). A yellowish product (2,5-dioxopyrrolidin-1-yl 4-(pyren-1-yl)butanoate) [2] of yield 51.94% was obtained (200 mg, 0.519 mmol) and labelled **3**. A known mass of **3** (150 mg, 0.389 mmol) was dissolved in dried CH₂Cl₂ (10 mL) and added dropwise to a 10 mL CH₂Cl₂ solution of 4-aminomethylpyridine (42 mg, 0.389 mmol). The resulting mixture was stirred overnight at room temperature under nitrogen atmosphere and the filtrate collected and dried to obtain a crude yellow solid as reported by Li and co-workers [3]. It was purified on silica gel using CH₂Cl₂/CH₃OH mixture (30:1 v/v) as eluent. The desired product obtained was whitish powder of yield 64% (95 mg, 0.251 mmol). Molar absorption coefficients (ϵ) for Py-Py was determined in CH₂Cl₂; (λ_{\max} in nm, ϵ in M⁻¹cm⁻¹); as $\lambda = 257$ (27500), 267 (53620), 277 (93640), 313 (24380), 328 (56735), 345 (83154) (**Fig. S1b**); Florescence emission in CH₂Cl₂ was determined (λ_{\max} in nm, intensity in a.u.) as $\lambda = 374$ (321.06), 393 (256.22), 416 (90.05) (*Fig. S1b*); ¹H NMR (400 MHz, Chloroform-*d*): $\delta_{\text{H}} = 8.49$ (2 H, d, $J = 5.1$), 8.28 (1 H, d, $J = 9.3$ Hz), 8.17 (2 H, d, $J = 7.7$ Hz), 8.12 – 8.08 (3 H, m), 8.02 (2 H, d, $J = 4.8$ Hz), 8.00 – 7.97 (1 H, m), 7.85 (1 H, d, $J = 7.8$ Hz), 7.15 – 7.13 (2 H, m), 4.40 (2 H, d, $J = 6.0$ Hz), 3.43 (2 H, d, $J = 7.4$ Hz), 2.34 (2 H, d, $J = 6.8$ Hz), 2.26 (2 H, t, $J = 7.5$ Hz) (**Fig. S2b**); MS: m/z calcd for C₂₆H₂₂N₂O = 378.48; found 378.50 (**Fig. S3**). The schematic representation of the above synthesis is shown in **Scheme S1**.

Preparation of as-prepared 1/MWCNT/Py-Py and 1/MWCNT electrodes

1.0 mg as-prepared materials were sonicated in 1.0 mL IPA nafion mixture and applied on the surface of well-polished and dried GC electrodes. They were labelled 1/MWCNT/Py and 1/MWCNT kept in the dark and ready for ORR and OER experiments.

Preparation of 1/MWCNT/Py electrode

A 1.0 mM CH₂Cl₂ solution of CoTPP (**1**) was mixed with 10 μL (25 mM) pyridine to form a homogeneous mixture. The mixture was sonicated and stirred for 12 h to facilitate the CoTPP and Py bond coordination. CH₂Cl₂ was removed via rotary and the mixture dried further under pressure. MWCNT was drop casted on a well-polished GCE (3x2μL) and allowed to dry after which 5 μL of CoTPP/Py mixture was added and dried for 1 h. It was labelled **1/MWCNT/Py** and kept in the dark and ready for electrochemical experiment towards ORR and OER.

UV-Vis characterization of 1mg as-prepared 1/MWCNT/Py-Py and 1/MWCNT

1.0 mg of as-prepared **1/MWCNT/Py-Py** and **1/MWCNT** were suspended into 5 mL DCM and filtered to obtain a UV-Vis data devoid of MWCNT noise. The data obtained (**Fig. S8**) revealed a coordination interaction between **1** and MWCNT/Py as well as intercalation between **1** and MWCNT. Also, from Beer-lamberts law, we can predict the amount concentration of CoTPP in **1/MWCNT** is a little more than **1/MWCNT/Py-Py** if not the same.

Electrocatalytic activities of as-prepared 1/MWCNT/Py-Py, 1/MWCNT and 1/MWCNT/Py

Electrochemical experiments towards ORR for as-prepared composites (**1/MWCNT/Py-Py**, **1/MWCNT**) were carried in both acidic and basic media to compare their catalytic activities with the earlier method used as reported in our work. The result presented in **Figs. S9** and **S10** reveals a trend similar to our earlier reported work in this paper where electrocatalytic activities for **1/MWCNT/Py-Py** were more pronounced than that of **1/MWCNT**. OER experiments also reveals same trend as shown in **Fig. S11**. This supports the idea of using either methods for electrochemical experiments. Introduction of pyridine instead of Py-Py (**1/MWCNT/Py**) showed a very low current density (ORR) even at very high pyridine concentration in acidic medium (**Fig. S12a**). In the base media for OER (**Fig. S12b**), onset potential and overpotential at $j = 10 \text{ mA} \cdot \text{cm}^{-2}$ were so high compared to all our system used indicating the introduction of pyridine to our system might not be the best kind for ORR and OER activities.

Figures

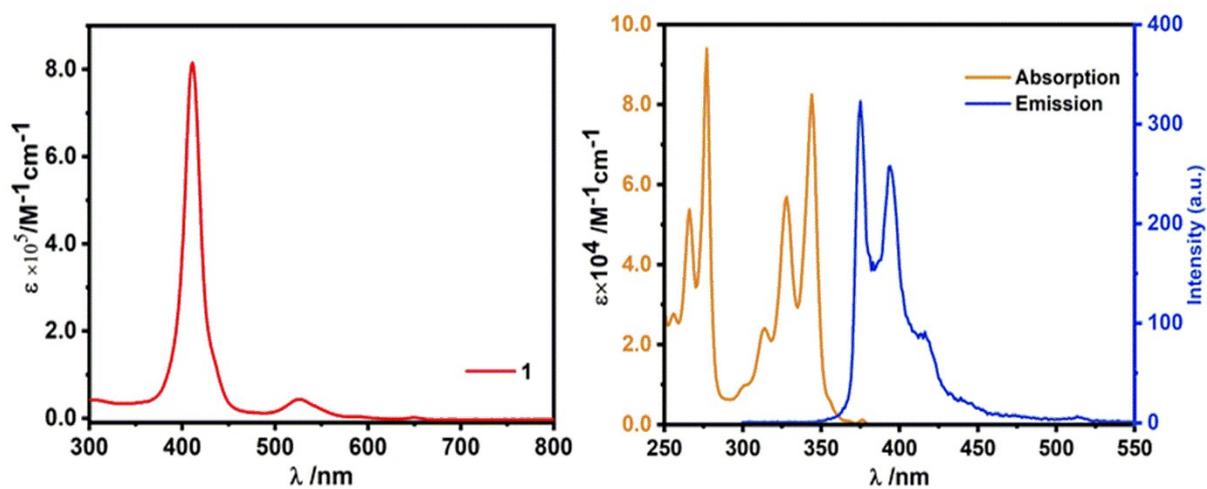


Fig. S1. UV-Vis absorption spectra of **1**(a) and UV-Vis and fluorescence emission spectra of Py-Py (b) in CH_2Cl_2 with 350 nm excitation.

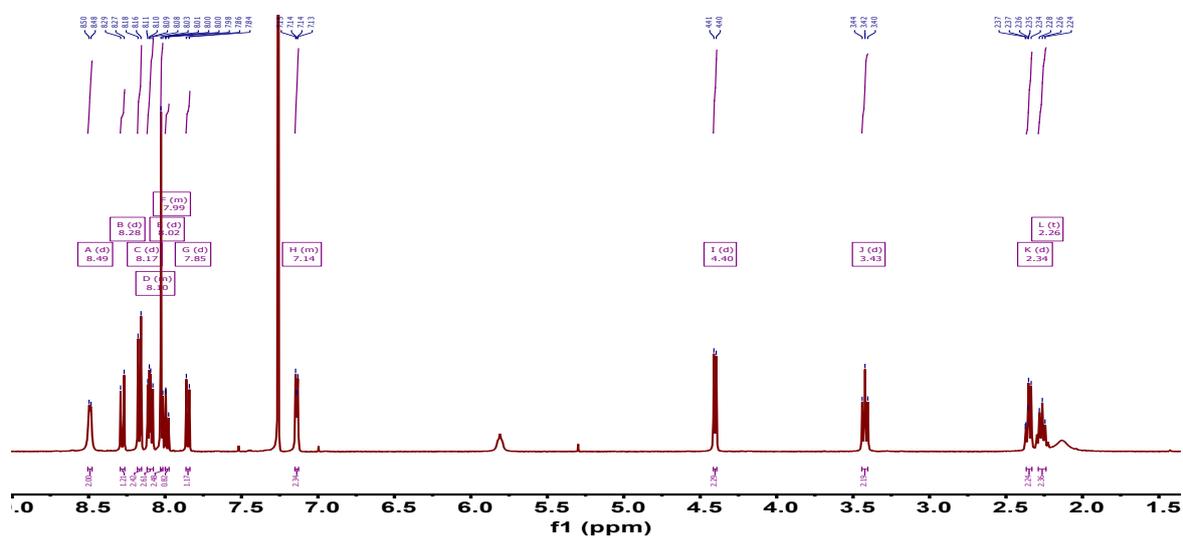


Fig. S2. $^1\text{H-NMR}$ of Py-Py in CDCl_3 .

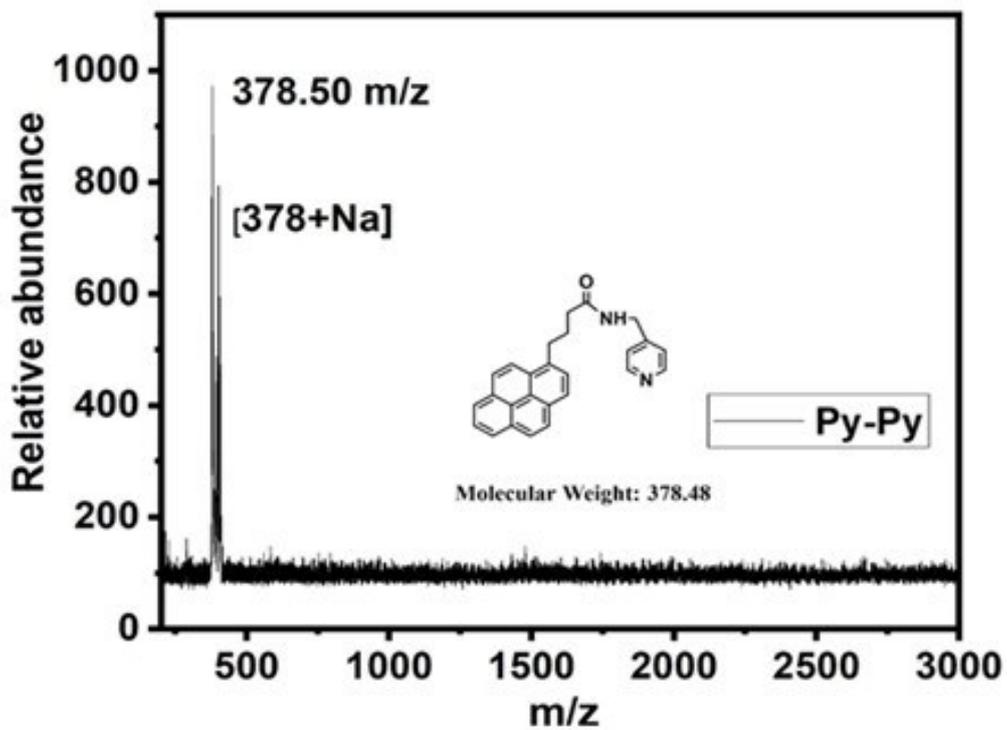


Fig. S3. MALDI-TOF-mass spectra of Py-Py

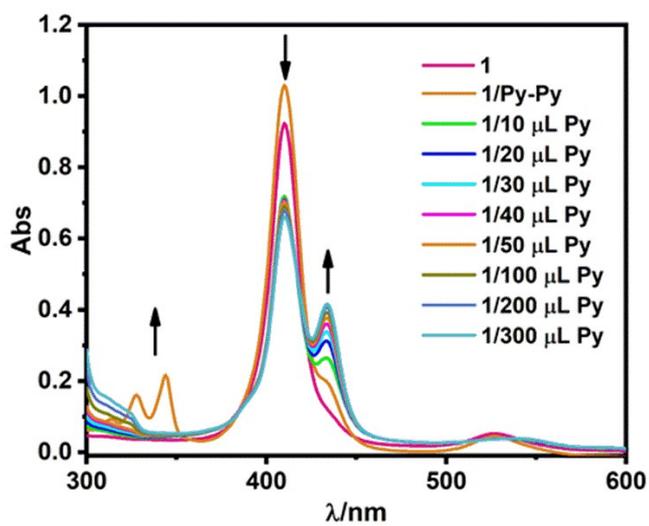


Fig. S4. UV-Vis absorption spectra of 1, 1/Py-Py and 1/Pyridine (varied volumes)

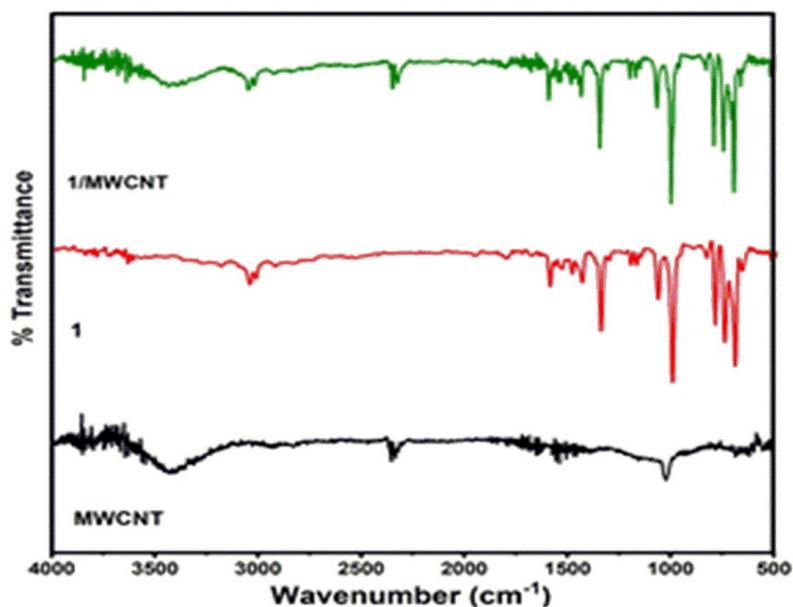


Fig. S5. FT-IR spectra of MWCNT (bottom), 1 (middle) and 1/MWCNT (top) materials.

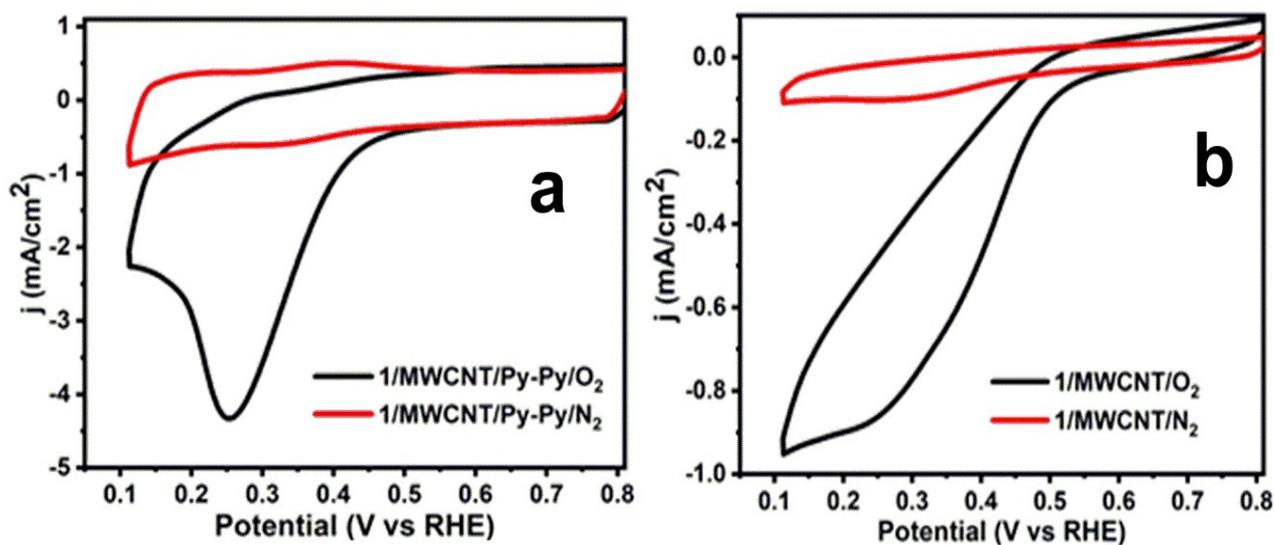


Fig. S6. CVs of GC electrodes coated with 1/MWCNT/Py-Py (a), 1/MWCNT (b) under N_2 or O_2 in 0.1 M $\text{PBS}_{(\text{aq})}$. Conditions: 50 mV s^{-1} scan rate at $25 \text{ }^\circ\text{C}$

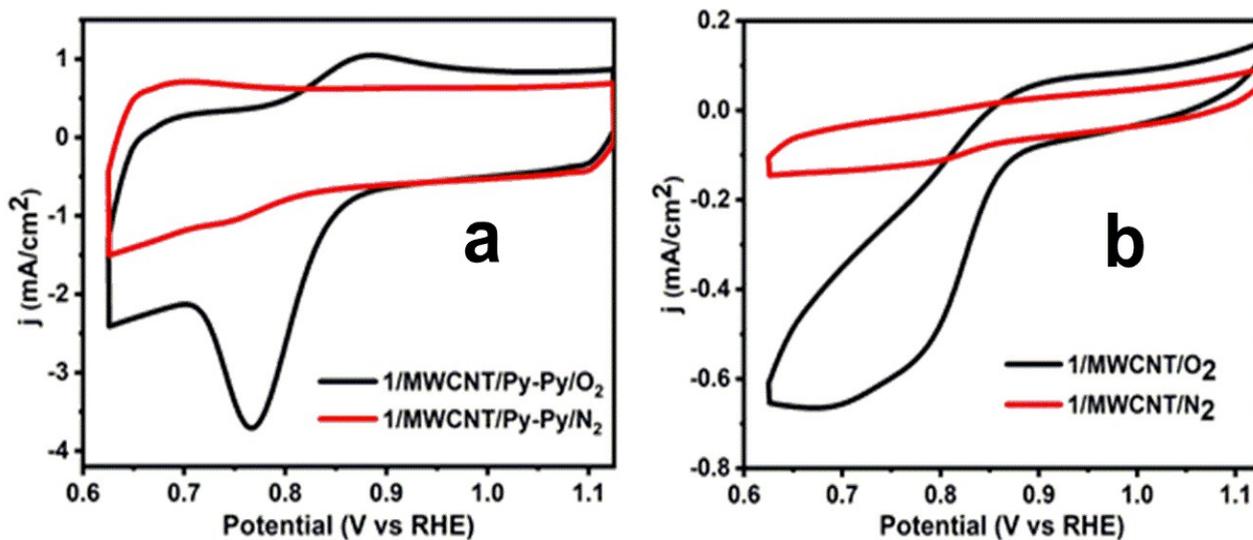


Fig. S7: CVs of GC electrodes coated with 1/MWCNT/Py-Py, (a) and 1/MWCNT (b) under N₂ or O₂ in 1.0 M KOH_(aq). Conditions: 50 mV s⁻¹ scan rate at 25 °C.

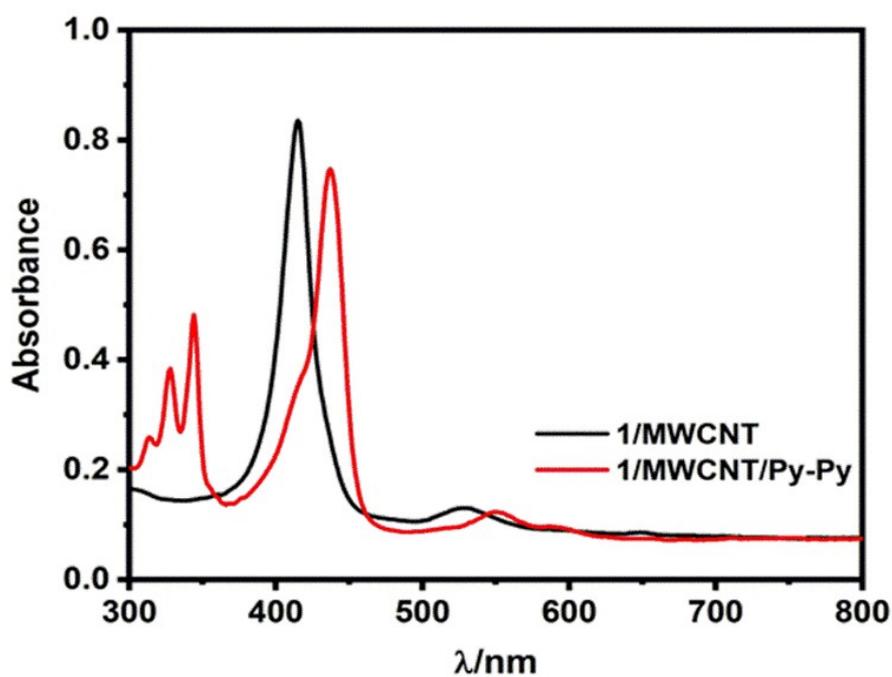


Fig. S8. UV-Vis absorption spectra of as-prepared 1mg 1/MWCNT and 1/MWCNT/Py-Py in CH₂Cl₂

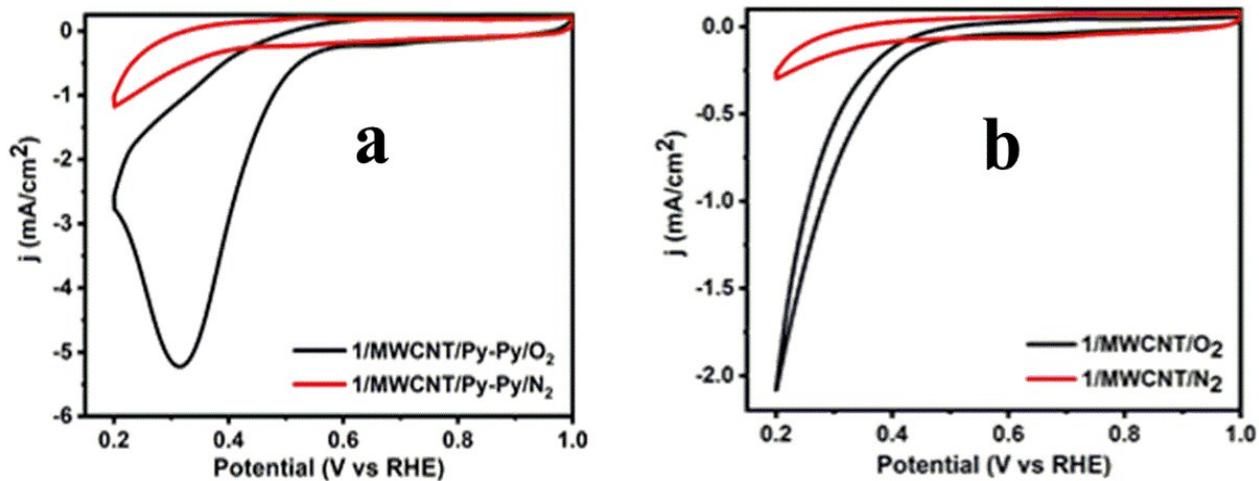


Fig. S9: CVs of GC electrodes coated with as-prepared 1/MWCNT/Py-Py, (a) and 1/MWCNT (b) under N₂ or O₂ in 0.5 M H₂SO_{4(aq)}. Conditions: 50 mV s⁻¹ scan rate at 25 °C.

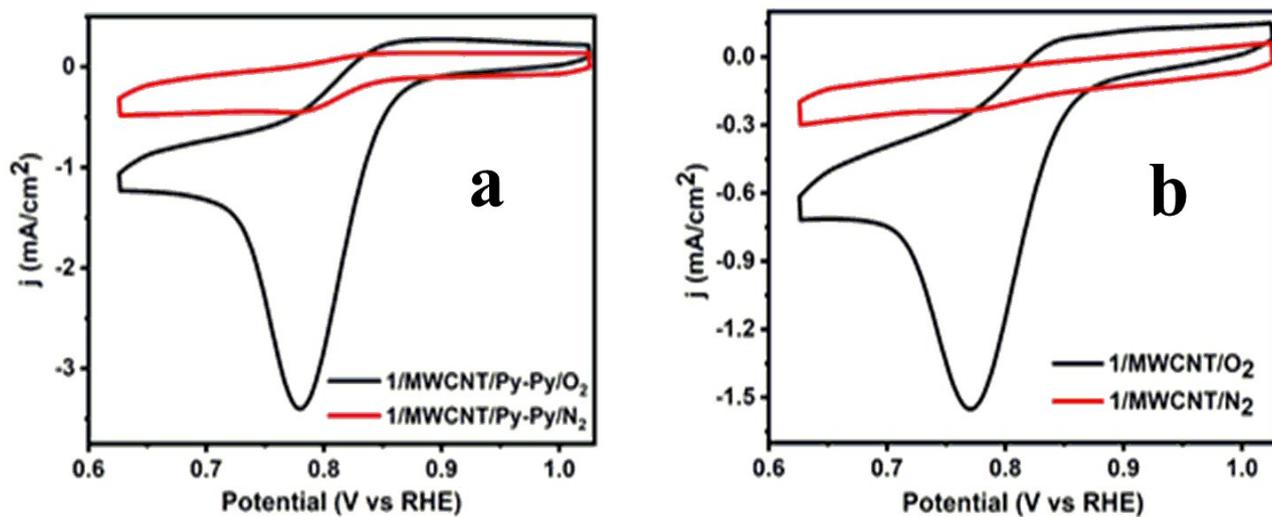


Fig. S10: CVs of GC electrodes coated with as-prepared 1/MWCNT/Py-Py, (a) and 1/MWCNT (b) under N₂ or O₂ in 1.0 M KOH_(aq). Conditions: 50 mV s⁻¹ scan rate at 25 °C.

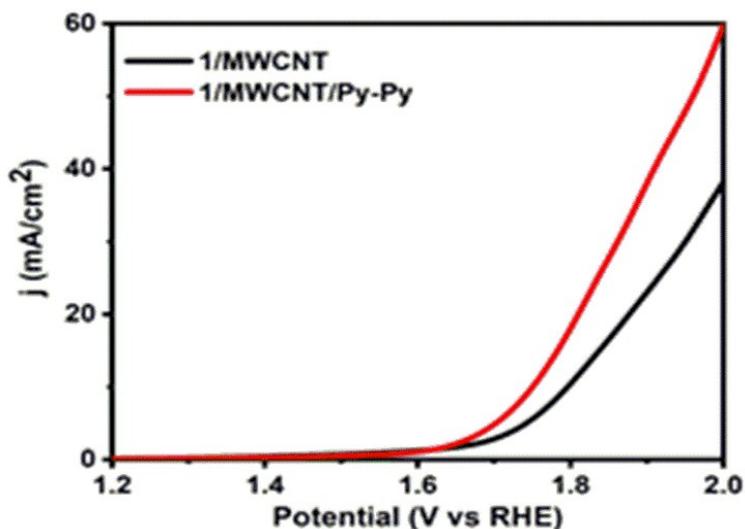


Fig. S11: LSVs of GC electrodes coated with as-prepared 1/MWCNT/Py-Py (red line) and 1/MWCNT (black line) under N_2 in 1.0 M $KOH_{(aq)}$. Conditions: 50 mV s^{-1} scan rate at $25 \text{ }^\circ\text{C}$.

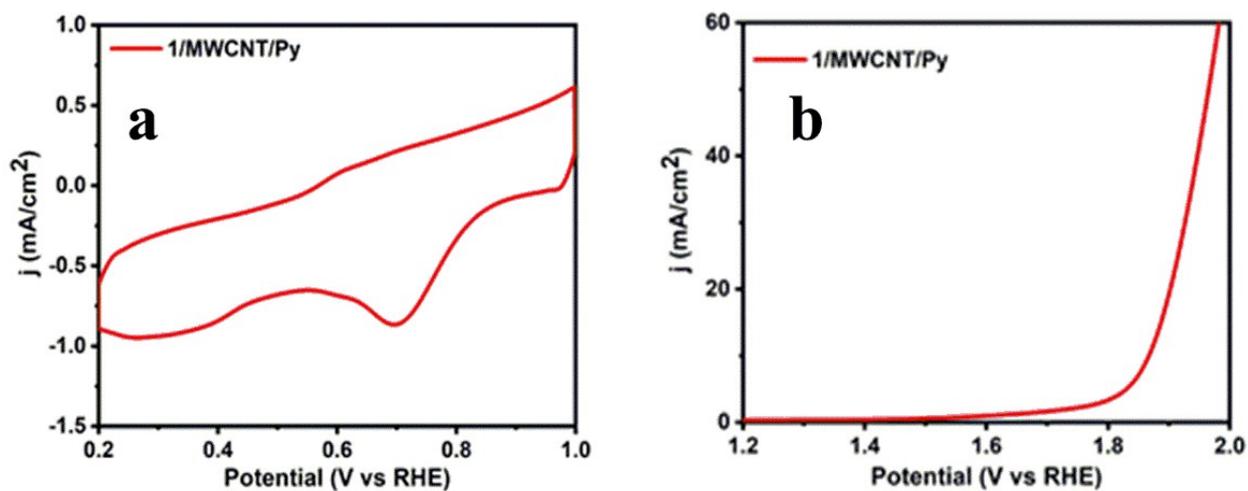


Fig. S12. CV of GC electrodes coated with 1/MWCNT/Py under O_2 atmosphere towards ORR (a) and LSV of GC electrodes coated with 1/MWCNT/Py under N_2 atmosphere towards OER (b). Conditions: 50 mV s^{-1} scan rate at $25 \text{ }^\circ\text{C}$ in $0.5 \text{ M H}_2\text{SO}_{4(aq)}$ for ORR and 1.0 M KOH for OER.

References

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- 3 F. Li, B. Zhang, X. Li, Y. Jiang, L. Chen, Y. Li, L. Sun, *Angew. Chem. Int. Ed.* **50** (2011) 12276–12279.