Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Two-dimensional graphdiyne analogues porphyrin covalent organic framework nanosheets as stable electrocatalyst for oxygen evolution reaction

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1. Experimental details.

1.1 Materials: 4-Bromobenzaldehyde, ethynyltrimethylsilane, palladium(II) bis(triphenylphosphine) dichloride ($Pd(PPh_3)_2Cl_2$), triphenylphosphine (PPh_3), copper(I) iodide (CuI), pyrrole, tetrabutylammonium fluoride (TBAF), tetramethylethylenediamine (TMEDA) and cobalt chloride ($CoCl_2$) were purchased from Macklin reagent company. Triethylamine (Et_3N), petroleum ether, propionic acid, tetrahydrofuran (THF), pyridine, N,N-dimethylformamide (DMF) and dichloromethane were purchased from Beijing Chemical Reagent Company. All the chemicals used in synthesis are analytical pure and were used as received. Solvents were dried and distilled for synthesis.

1.2 **Synthesis**

4-((trimethylsilyl)ethynyl)benzaldehyde (2) [1]

Under nitrogen atmosphere, 4-bromobenzaldehyde (5.0 g), $Pd(PPh_3)_2Cl_2$ (189 mg), PPh_3 (142 mg), CuI (108 mg) and KOH (800 mg) were dissolved in 150 ml Et_3N. The mixture was stirred for about 10 min. Then ethynyltrimethylsilane (5.7 ml) was added via syringe. The solution was refluxed for 8 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica gel, petroleum ether). Yellow solid was obtained.

5,10,15,20-(tetra-4-(trimethylsilyl)ethynylphenyl)porphyrin (3)

Compound 2 (2.5 g) was dissolved in 60 ml propionic acid, the mixture was heated to 80 °C and stirred. Then pyrrole (1.3 ml) was added via syringe, which was dried and distilled before synthesis. The solution was refluxed for 2.5 h and cooled to room temperature. The dark violet precipitate was collected by filtration and washed with methanol. The purple solid was obtained by recrystallization twice from $CHCl_3$/MeOH.

Cobalt(II) 5,10,15,20-(tetra-4-(trimethylsilyl)ethynylphenyl)porphyrin (4)

$CoCl_2$ (850 mg) and Compound 3 (400 mg) were dissolved in 40 ml DMF. The solution was refluxed for 6 h and cooled to room temperature. The solvent was removed under reduced pressure and added 100 ml deionized water, the precipitate was filtered and washed with MeOH and a brown solid was obtained.

Cobalt(II) 5,10,15,20-(tetra-4-ethynylphenyl)porphyrin (5)

Under nitrogen atmosphere, compound 4 (400 mg) was dissolved in 40 mL THF and added TBAF (2.4 mL, 1 M in THF) and stirred in room temperature overnight. The solution was then diluted with dichloromethane and washed with distilled water and dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield brown monomer.

Co-PDY/CF electrode

Prior to growth, CF (30 mm × 10 mm) were first ultrasonicated in acetone, 2 M HCl and ethanol for 15 min to remove impurities on the surface. Under nitrogen atmosphere, the copper foam was added into 50 ml acetone and 50 ml pyridine, and the solution was heated to 70 °C. Then compound 5 (40 mg) was dissolved in 20 mL acetone and added via syringe. The solution was refluxed for 48 h and cooled to room temperature. Upon completion copper foams were washed with acetone and DMF in turn and the copper foam turned to dark brown.

PDY/CF

The typical process for synthesis was similar to Co-PDY/CF except omitting the coordination process between cobalt ions and compound 3.

1.4 Theoretical Computation:

In our calculations, density of states (DOS) of Co-PDY and PDY slabs were computed by using DFT within the local density approximation (LDA). A plane-wave energy cutoff of 500 eV was used together with norm-conserving pseudopotentials,[2] and the Brillouin zone is sampled with a 4 × 4 × 1 Monkhorst-Pack grid. The structure was fully optimized until the force on each atom is less than 10^{-5} eV/Å.

2. Characterizations.

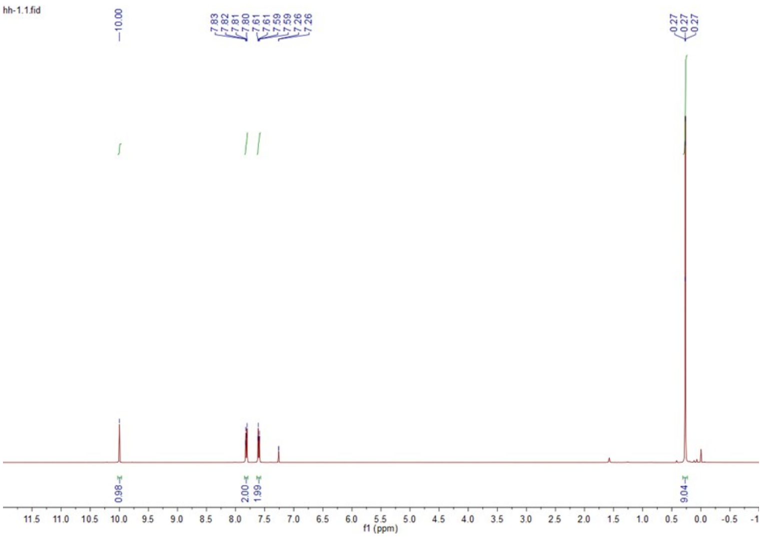
2.1 Physical Characterization:

NMR spectra were recorded on a 400 MHz Bruker ASCEND 400 MHz NMR Spectrometer. The field-emission SEM images and EDS analysis were conducted on a HITACHI SU8020 at 10 and 20 kV accelerating voltage, respectively. TEM images, and elemental distributions mapping, were obtained with FEI Tecnai G2 F20 microscope. The XRD patterns were recorded with D/Max-3cX′Pert diffractometer using a Cu Kα source. XPS measurement was performed on a PHI-5000 X-ray photoelectron spectrometer with Al Kα radiation as the excitation source.

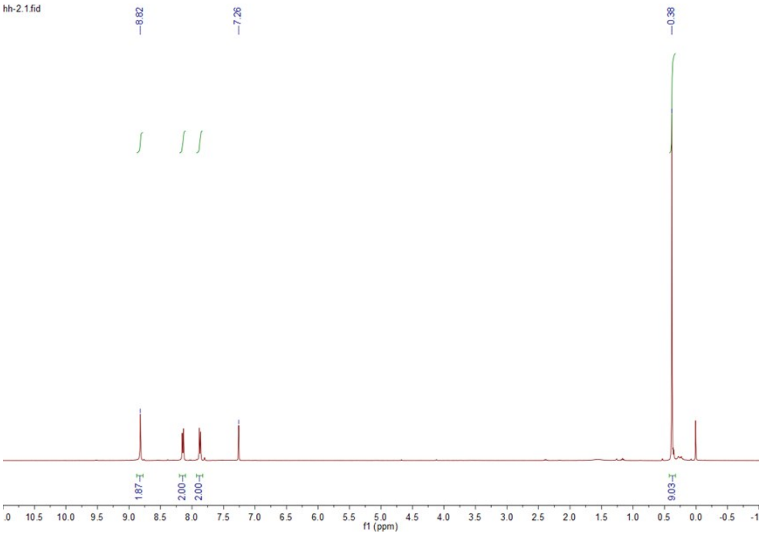
2.2 Electrochemical Characterization:

All electrochemical measurements were carried out with a CHI 760E electrochemical workstation 1 M KOH solution (pH = 14). The as-obtained Co-PDY/CF, PDY/CF and CF were directly used as the working electrode without further treatments. The electrochemical characterizations were conducted in a standard three-electrode electrochemical cell employing a graphite rod counter electrode and a saturated calomel reference electrode, respectively. All potentials measured were calibrated to RHE according to the following equation $E_{\mathrm{RHE}} = E_{\mathrm{SCE}} + 0.243\ \mathrm{V} + 0.059\ \mathrm{pH}$, and the current density was normalized to the effective geometrical surface area of CF. All the LSV measurements for HER were carried out at a scan rate of 5 mV s^{-1} with 95% iR-corrections. Tafel plots derived from HER polarization curves obtained were fitted to the equation $\eta = b \log j + a$ (overpotential η, current density j, Tafel slope b, and Tafel constant a). EIS was carried out at the potential of 1.50 V (*vs.* RHE) from 10^5 Hz to 0.01 Hz with an AC voltage of 5 mV. Chronopotentiometric measurements were conducted continuous for OER and HER electrolysis 10 h.

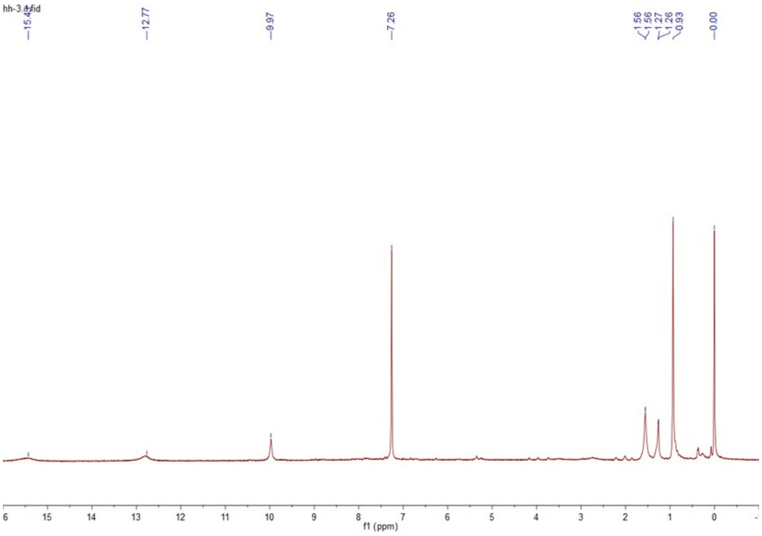
3. Figure S1. ^{1}H NMR spectrum of compound 2.



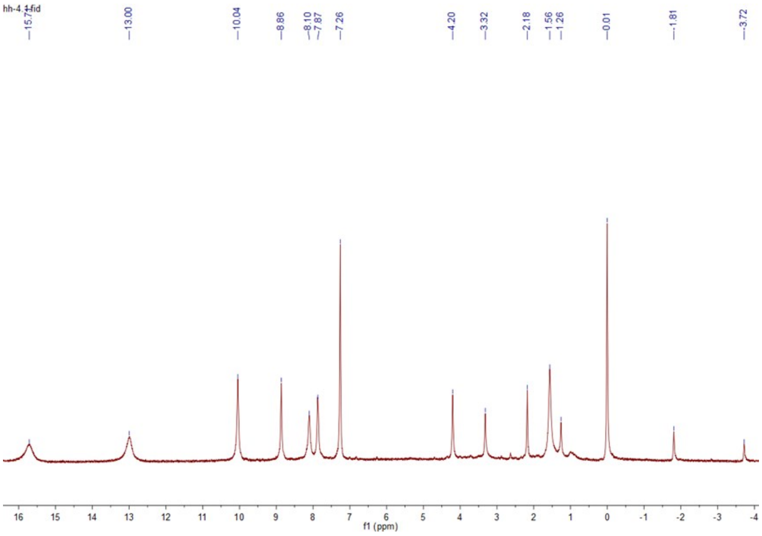
4. Figure S2. ^{1}H NMR spectrum of compound 3.



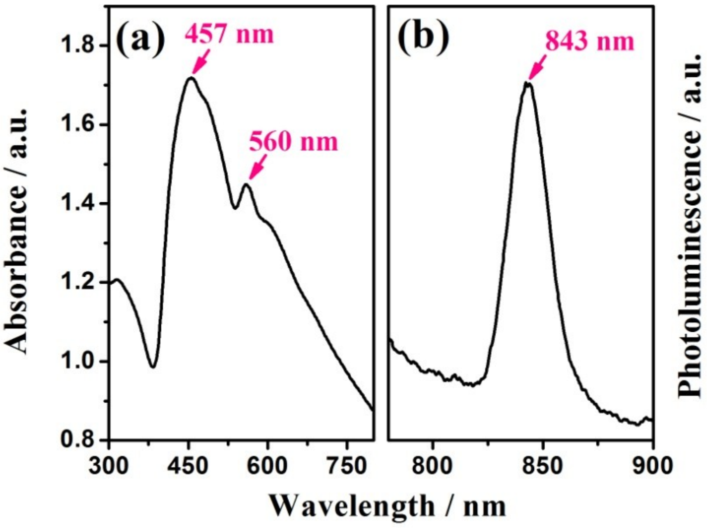
5. Figure S3. ^{1}H NMR spectrum of compound 4.



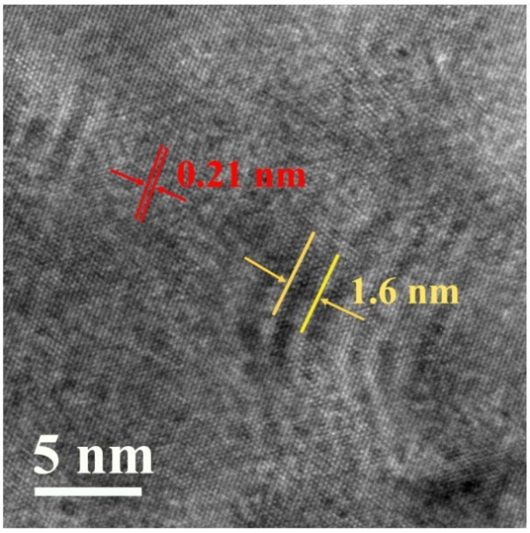
6. Figure S4. ^{1}H NMR spectrum of compound 5.



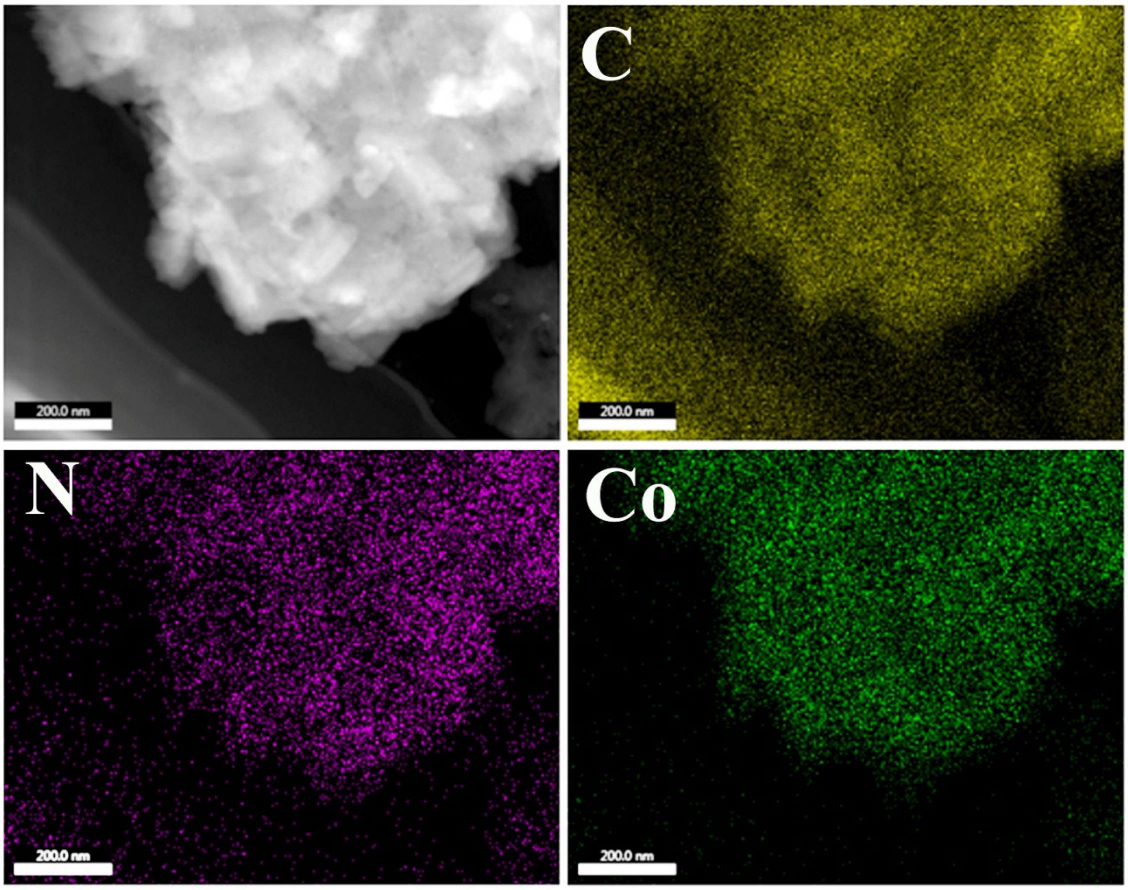
7. Figure S5. (a) UV–Vis absorption spectrum of Co-PDY in aqueous solutions. (b) PL spectrum of CO-PDY with excitation wavelength of 560 nm.



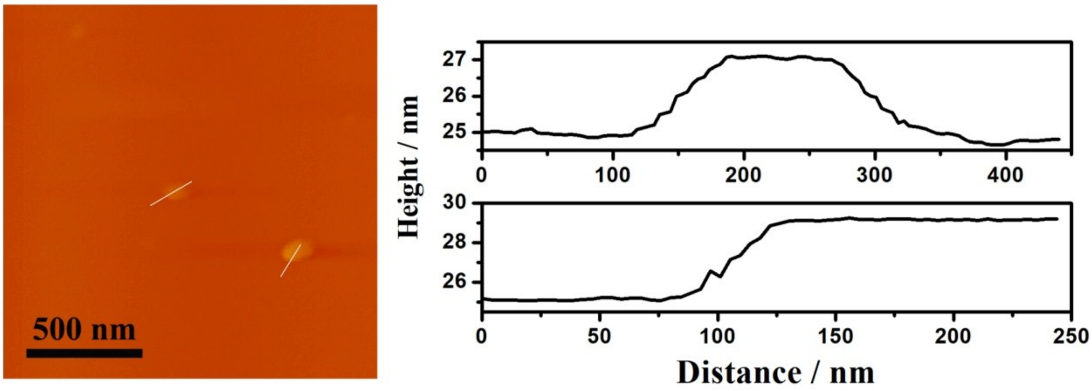
8. Figure S6. HRTEM image of Co-PDY.



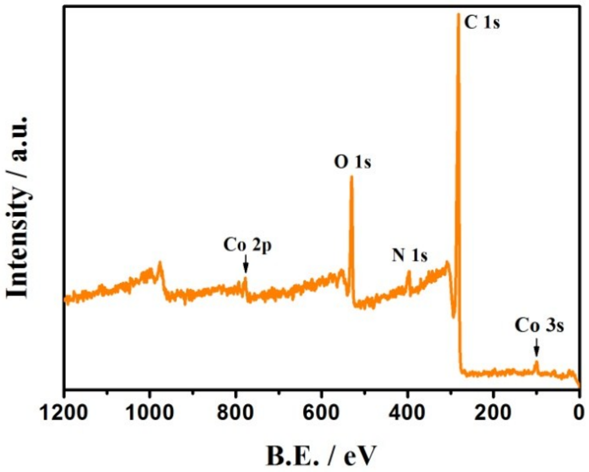
9. Figure S7. HAADF-STEM image and corresponding EDS mapping images of Co-PDY.



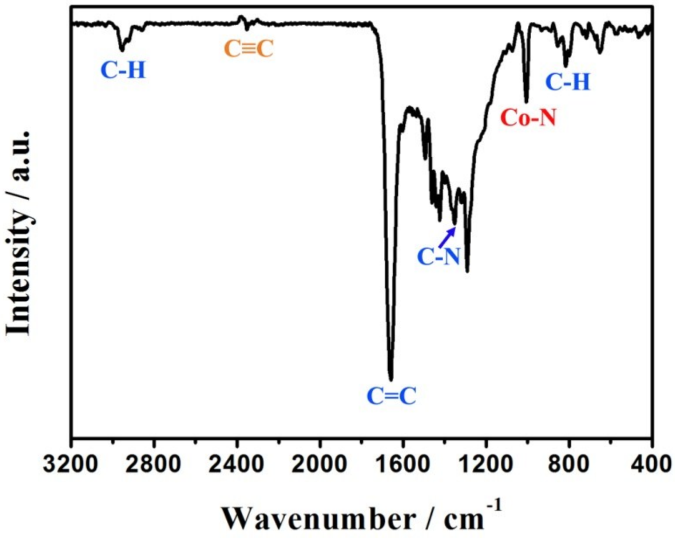
10. Figure S8. AFM image of Co-PDY sample.



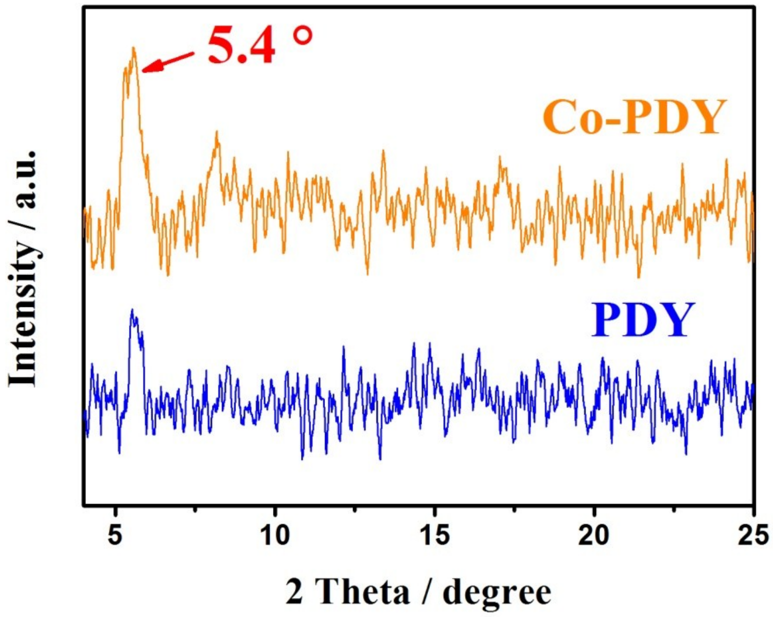
11. Figure S9. XPS survey spectrum of Co-PDY sample.



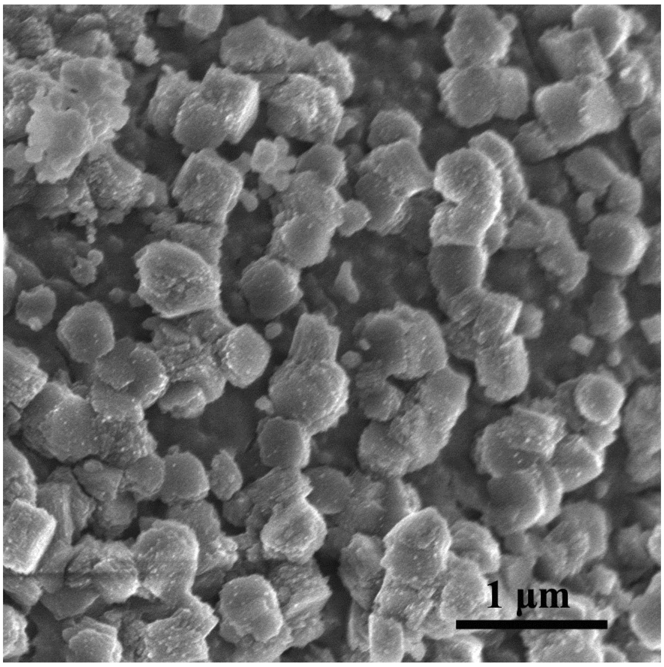
12. Figure S10. The FTIR spectrum of Co-PDY sample.



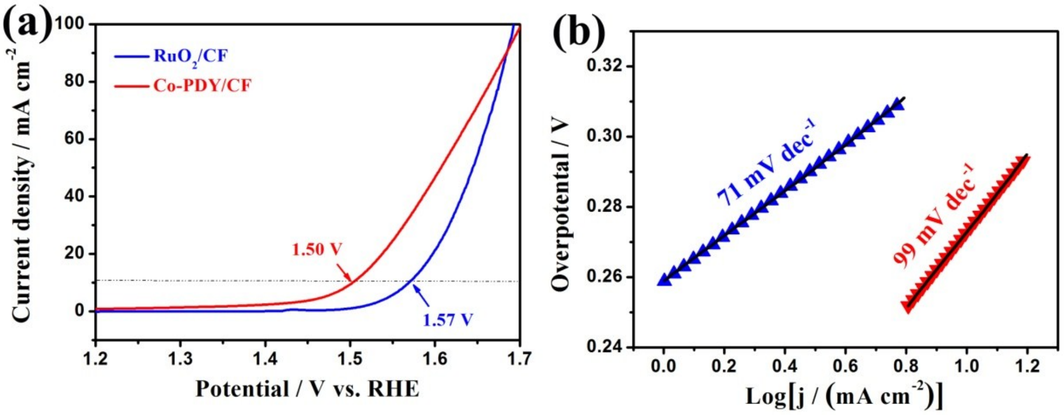
13. Figure S11. The XRD pattern of Co-PDY sample.



14. Figure S12. The SEM image of Co-PDY sample without PVP.

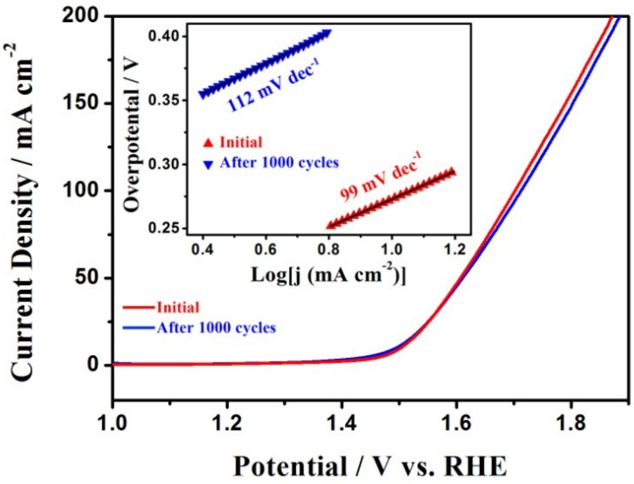


15. Figure S13. OER polarization curves for Co-PDY/CF and RuO_2/CF at 5 mV s^{-1}, (b) the corresponding Tafel plots.

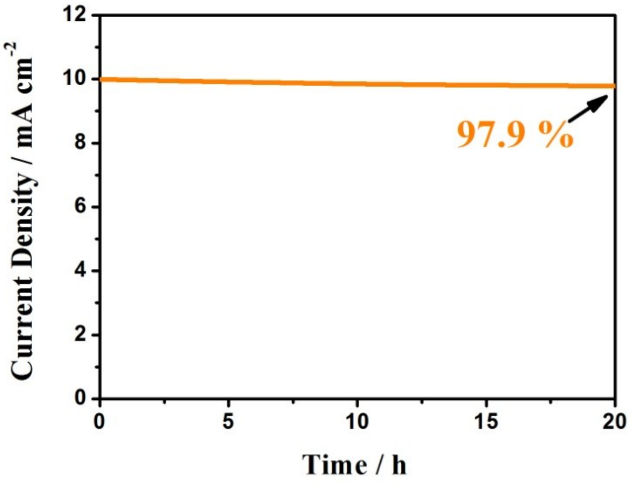


The RuO_2 catalyst was prepared according to a previously reported method.[3] Typically, 0.01 mol $RuCl_3$ was first dissolved in 100 mL ultrapure water. The solution was then heated in air at 100 °C for 10 min. Subsequently, 1 mL KOH solution (1.0 M) was added and the reaction mixture was kept at this temperature for 45 min under stirring. After cooling down to room temperature, the precipitate was collected by centrifugation and washed several times with ultrapure water to remove the remaining chlorides. The resulting powder was dried and calcined in air at 300 °C for 3 h to obtain RuO_2. To prepare RuO_2 catalytic electrodes, 10 mg RuO_2 and 50 mL 5 wt% Nafion solution were dispersed in 1 mL water/ethanol solvent (500 mL ultrapure water and 450 mL ethanol). The mixed solution was then ultrasonically treated for 30 min to form a homogeneously distributed catalyst ink. A suitable amount of the catalyst ink was uniformly drop-cast onto the Cu foam and left to dry in air.

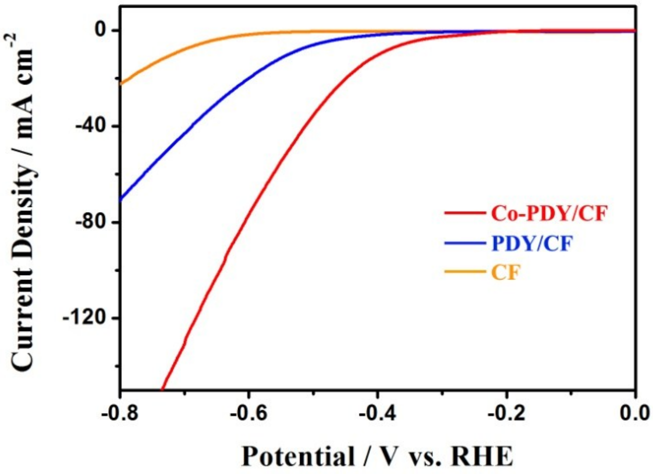
16. Figure S14. Polarization curves and Tafel plots for Co-PDY/CF electrode before and after 1000 cycles.



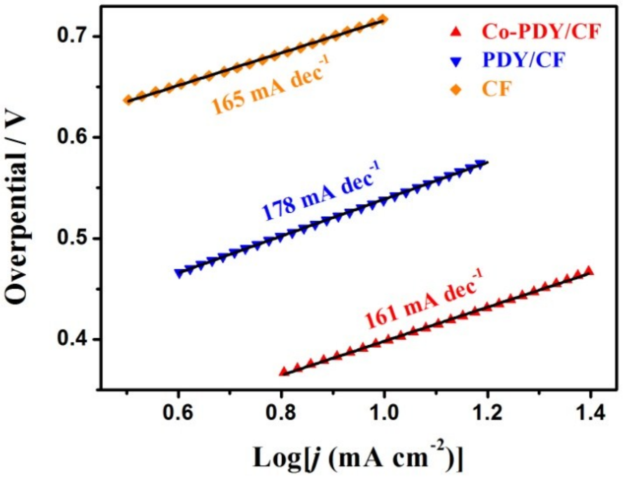
17. Figure S15. chronopotentiometry curve of Co-PDY/CF for OER for 20 hours.



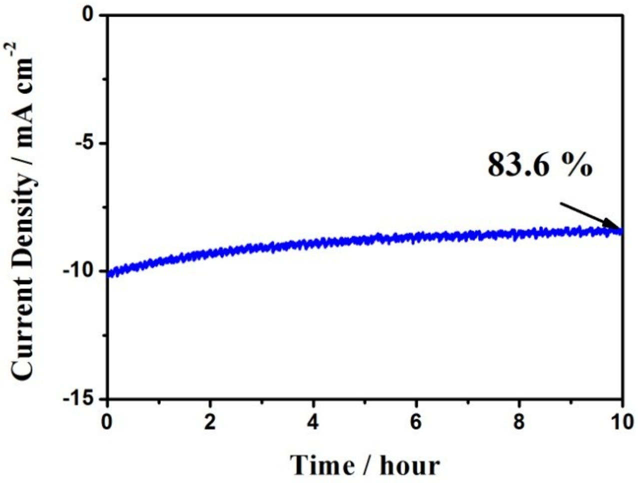
18. Figure S16. Polarization curves of Co-PDY/CF, PDY/CF and CF electrodes.



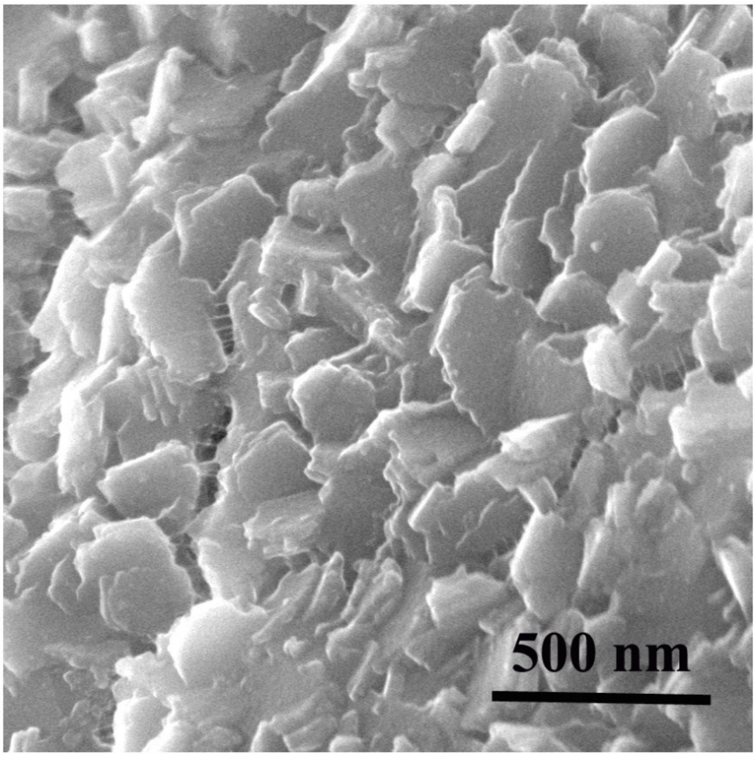
19. Figure S17. Tafel plots for Co-PDY/CF, PDY/CF and CF electrodes.



20. Figure S18. The durability of Co-PDY/CF in 1 M KOH at -0.4 V (*vs.* RHE).



21. Figure S19. The SEM image of Co-PDY/CF electrode after 10 h HER running.



22. Table S1. Comparison of several reported GDY-based materials as OER catalysts.

Catalysts	Overpotential (*vs.* RHE)	Tafel plot	Refs.
GDY	460 mV	282 mV dec^{-1}	[4]
Cu@GDY/Co	350 mV	148 mV dec^{-1}	[5]
$NiCo_2S_4$ NW/CC	344 mV	76 mV dec^{-1}	[6]
GDY@NiFe	260 mV	95 mV dec^{-1}	[4]
Co-PDY/CF	270 mV	99 mV dec^{-1}	This work

References:

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