

Supporting Information

Cobalt Carbonate Hydroxides Anchored on Nanoscale Pyrenely-Graphdiyne Nanowalls toward Bifunctional Electrocatalyst with Highly Performance and Stable for Overall Water Splitting

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1. Materials and Methods.

Reagents and chemicals are used as received without further purification. Dichloromethane and diethyl ether were used as received. Tetrahydrofuran was dried by passing through a column of activated molecular sieves using a solvent purification system. All water used was purified with a Millipore system (typically 18.2 M Ω cm resistivity).

Reaction conditions was conducted under inert atmosphere by nitrogen when using a standard Schlenk line technique. All other reactions were performed employing standard organic synthesis protocols.

Thin layer chromatography (TLC) was performed using Merck aluminium-backed plates of TLC Silica gel 60 F₂₅₄; the plates were revealed using UV light.

Column chromatography was accomplished using silica gel (60 Å pore size, 230-400 μ m mesh size).

Nuclear Magnetic Resonance (NMR) Spectrum were recorded using Bruker Avance 400 spectrometers (Analysis & Testing Center, Beijing Institute of Technology).

2. Material Characterization

Scanning electron microscopy (SEM) images and **energy dispersive X-ray spectroscopy (EDS)** data were obtained through Zeiss Supra 55 SAPPHIRE SEM equipment with an EDS detector.

Transmission electron microscopy (TEM) and **high-resolution transmission electron microscopy (HRTEM)** images and corresponding **element mapping** were acquired by JEOL JEM-2100F transmission electron microscope

Powder X-ray diffraction (PXRD) data were detected on a Rigaku XRD-6000 diffractometer under the following conditions: 40 kV, 40 mA, Cu K α radiation ($\lambda = 0.154$ nm).

Raman spectroscopy is recorded on a Renishaw Raman spectrometer at a laser excitation wavelength of 532 nm.

X-ray photoelectron spectroscopy (XPS) plots are obtained by monochromatized Al K α exciting X-radiation (PHI Quantera SXM).

Electrochemical techniques are carried out on a CH instruments CHI 760E electrochemical workstation with a standard three-electrode cell, where CCH@Pyr-GDY-NWs as the working electrode, graphite rod as the counter electrode and saturated calomel electrode (SCE) as the reference electrode.

2. DFT calculation

The Calculation of Hydrogen Electrode model (CHE) based on free energy change (ΔG) for OER is estimated to estimate the reaction activity, which can be calculated by the following expression:^[1]

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH} + \Delta G_{field} \quad (1)$$

where ΔE is the total energy change from initial states to final states of the reaction obtained by DFT calculations. ΔZPE is the change in zero-point energy. T is room temperature (298.15 K). ΔS is the change in entropy. $\Delta G = -eU$, where U is the electrode potential with respect to standard hydrogen electrode, and e is the transferred charge. $\Delta G_{pH} = k_B T \ln 10 \times pH$ where k_B is the Boltzmann constant, and $pH = 0$ for acid medium.^[2,3] ΔG_{field} is the free energy correction due to the electrochemical double layer and is neglected as in previous studies.^[1,3] Gas-phase H_2O at 0.035 bar was used as the reference state, which is the equilibrium point of the gas-phase and liquid water at 298.15 K. The free energy of O_2 is obtained from the free energy change of the reaction $O_2 + 2H_2 \rightarrow 2H_2O$, which is -4.92 eV at 298.15 K and a pressure of 0.035 bar [1]. The free energy of $(H^+ + e^-)$ in solution at standard conditions of $pH=0$ and $U=0$ is equal to that of $1/2H_2$ according to a computational hydrogen electrode model suggested by Nørskov et al.^[1] The entropy of the H_2 is taken from the National Institute of Standards and Technology (NIST) database,^[4] while the entropies of the OER intermediates were calculated from the vibrational frequencies.

The working potential is the potential that keeps all the elementary reactions to be exothermic. It is defined as:

$$U_{OER} = \max[-\Delta G_x] / ne \quad (2)$$

where n is the number of electrons transferred for each reaction, and e is the elementary charge.^[5,6]

3. Synthetic procedures

3.1 Synthesis of 1,3,6,8-Tetrakis(trimethylsilylethynyl)pyrene

1,3,6,8-Tetrabromopyrene (1.0 g, 1.93 mmol), $[\text{PdCl}_2(\text{PPh}_3)_2]$ (67 mg, 0.096 mmol), CuI (18 mg, 0.096 mmol), PPh_3 (50 mg, 0.193 mmol), and trimethylsilylacetylene (1.14g, 11.6 mmol) were added to a degassed solution of diisopropylamine (20 mL) and THF (20 mL) under N_2 . The resulting mixture was stirred at 60°C for 12h. The reaction mixture was then cooled to room temperature and solvent was removed to give the crude reaction mixture. Column chromatographic purification of the crude product on silica gel with hexane as the eluent yielded 1,3,6,8-Tetrakis(trimethylsilylethynyl)pyrene (0.33 g, 29 %) as a red orange solid.

^1H NMR (CDCl_3 , 400 M Hz): $\delta = 8.60$ (s, 4 H), 8.31 (s, 2 H), 0.39 (s, 36 H) ppm.

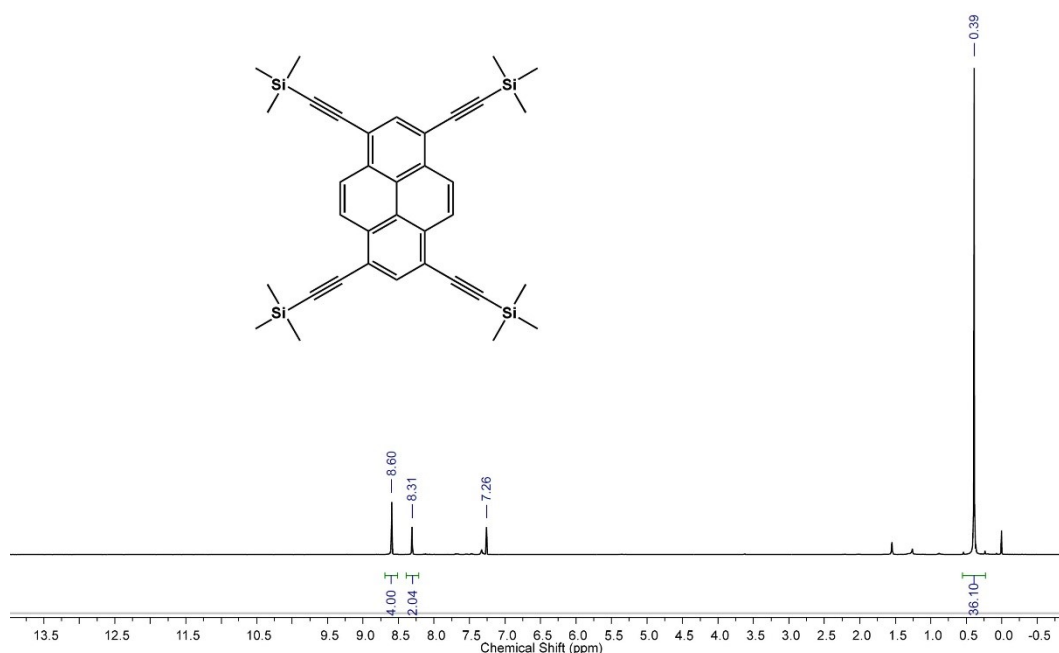


Fig. S1. ^1H NMR spectrum of 1,3,6,8-Tetrakis(trimethylsilylethynyl)pyrene

3.2 Synthesis of 1,3,6,8-Tetraethynylpyrene

A red orange solution of 1,3,6,8-Tetrakis(trimethylsilylethynyl)-pyrene (0.5 g, 0.85 mmol) in degassed THF (30 mL) was treated with *n*-Bu₄NF (26 mg, 0.085 mmol) and the resulting mixture was stirred at 30 °C for 1 h. The reaction mixture was then poured into ice cold water (100 mL) and the solid obtained was filtered, washed with water (2 × 100 mL), and dried to yield 3g (0.24 g, 93 %) as a pale-yellow solid.

3.2 Synthesis of Pyrenyl-Graphdiyne nanowalls (Pyr-GDY-NWs) on carbon cloth

Several (2) pieces of carbon cloth (2 × 2 cm²) with H-Cu MPs were charged in a three-neck flask (250 mL), and then a mixed solution of acetone (50 mL), pyridine (2.5 mL), and tetramethylethylenediamine (TMEDA) (0.5 mL) was added to above flask. TEP (40 mg) was dissolved in 150 mL of acetone and the solution was added dropwise into the reaction mixture mentioned above. Then the mixture was heated at 50 °C under Ar atmosphere for 12 hours. The reaction flask was covered with Al foil and protected from light. Finally, two pieces of carbon cloth were washed with acetone and THF to remove unreacted TEP followed by drying under nitrogen. Pyr-GDY-NWs grown on the carbon cloth were further used to prepare CCH@Pyr-GDY-NWs.

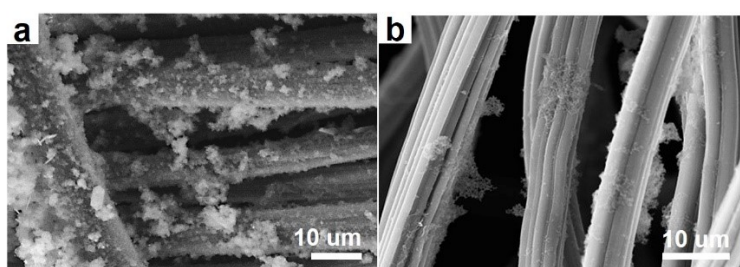


Fig. S2. SEM image of CCH@Pyr-GDY-NWs which was catalyzed by Cu film (a) and CuI (b).

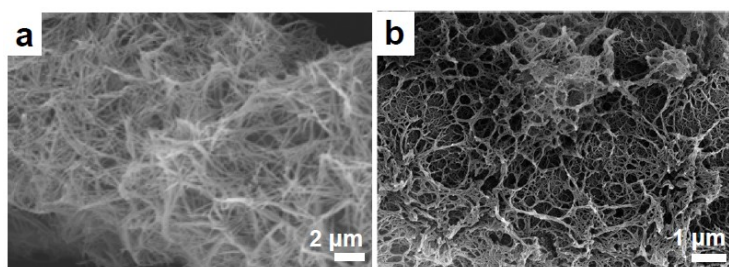


Fig. S3. SEM image of CCH@Pyr-GDY-NWs-25 (a) and CCH@Pyr-GDY-NWs-0.5 (b).

4. Supplementary of XPS spectrum

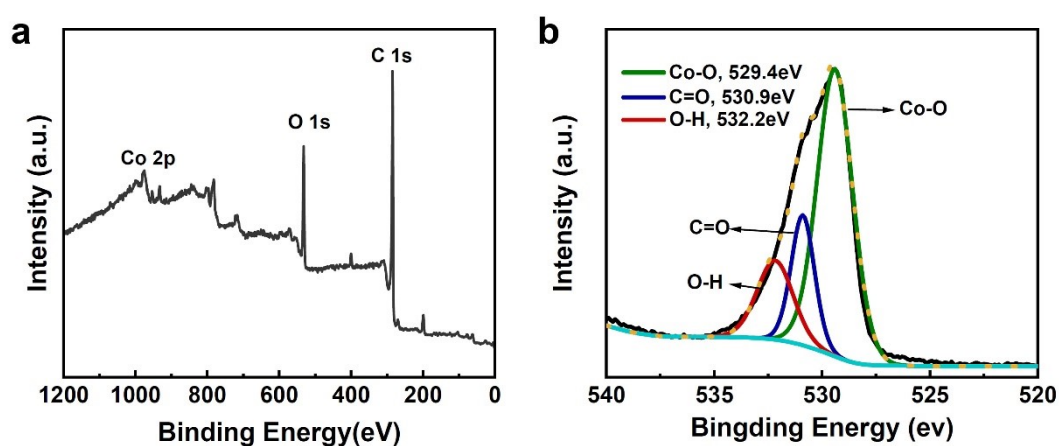


Fig. S4. (a) XPS survey scan of CCH@Pyr-GDY-NWs; (b) High-resolution XPS spectrums of CCH@Pyr-GDY-NWs showing O 1s.

The XPS survey scan as shown in Fig. S1 exhibits the presence of Co, C and O suggesting the formation of CCH and Pyr-GDY-NWs. Meanwhile, the peaks at 529.4 eV, 530.9 eV and 532.2 eV could be ascribed to the C-O, C=O and O-H, which means that the material is composed of CCH and Pyr-GDY-NWs.

5. EIS and relating data

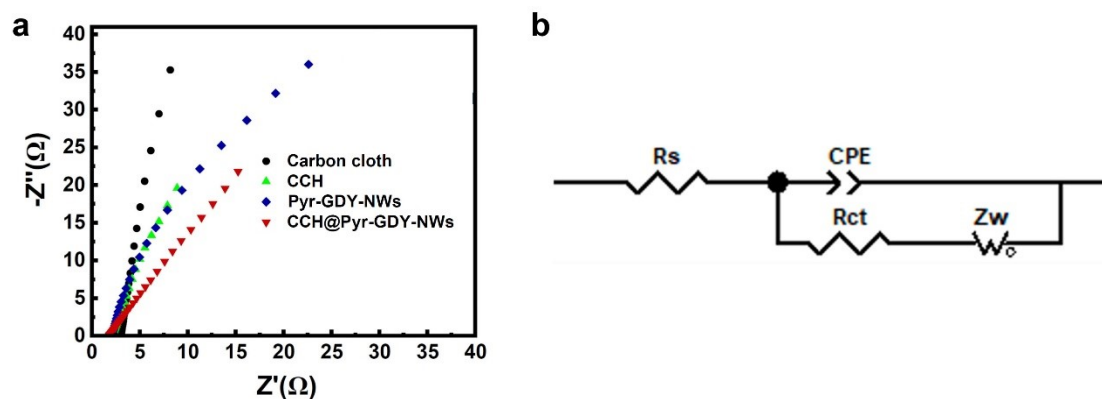


Fig. S5. (a) Nyquist plots of the CCH@Pyr-GDY-NWs, CCH, Pyr-GDY-NWs and Carbon cloth in different scale; (b) the equivalent circuit model used for fitting.

Table S1. R_s and R_{ct} value of CCH@Pyr-GDY-NWs, CCH, Pyr-GDY-NWs and Carbon cloth.

	R_s (Ω)	R_{ct} (Ω)
CCH@Pyr-GDY-NWs	1.68	0.70
CCH	1.89	6.66
Pyr-GDY-NWs	2.45	16.06
Carbon cloth	2.64	73.08

6. Cyclic voltammetry (CV) curve for different electrodes

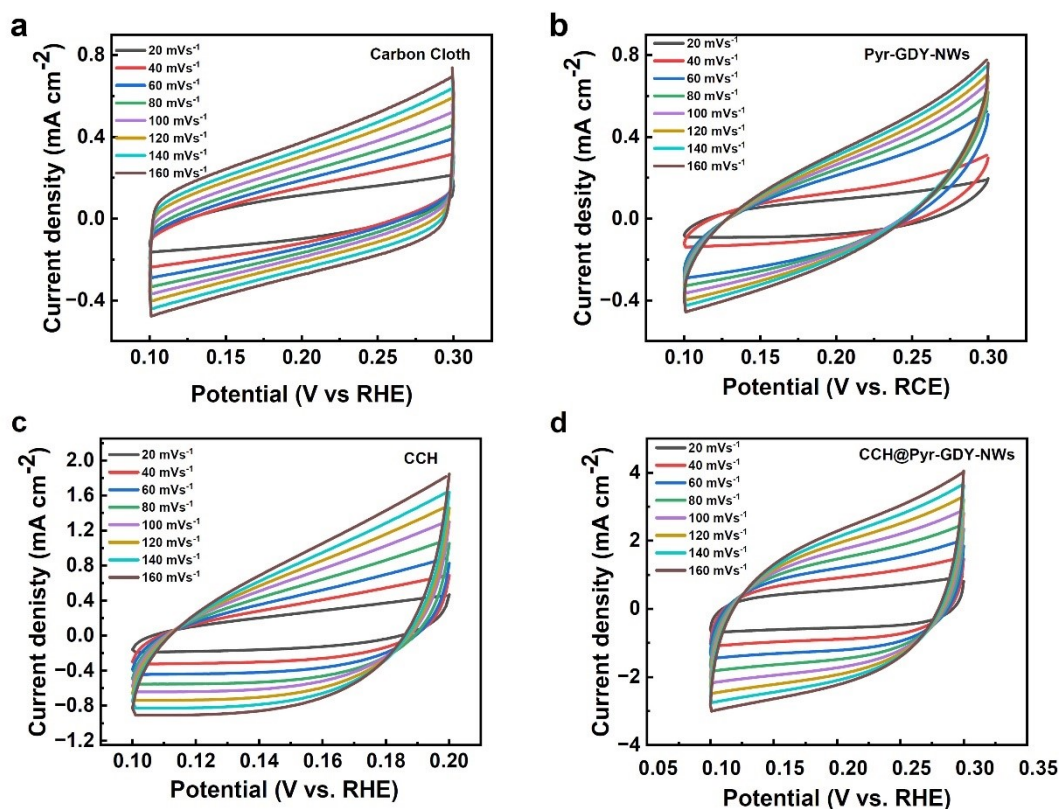


Fig. S6. CV curves of (a) Carbon Cloth, (b) Pyr-GDY-NWs, (c) CCH and (d) CCH@Pyr-GDY-NWs at various scan rates (20-160 mV s⁻¹).

The ECSA of the catalyst was estimated from the electrochemical double-layer capacitance (C_{dl}). C_{dl} was measured via CV curve with a potential range where no apparent Faradaic process was taking place. The double-layer charging current I_C can be related to the scan rates through Equation S1:

$$I_C = C_{dl} \times v \quad (\text{Equation S1})$$

Thus, plotting the charging currents at a specific potential against various scan rates leads to a straight line with the slope equal to C_{dl} . Subsequently, the ECSA value can be obtained by Equation S2:

$$\text{ECSA} = C_{dl} / C_s \quad (\text{Equation S2})$$

where C_S is specific capacitance measured from ideally smooth, planar surfaces of the catalyst, the C_S value is 0.04 mF cm^{-2} in 1 M KOH based on the typical reported values.^[7]

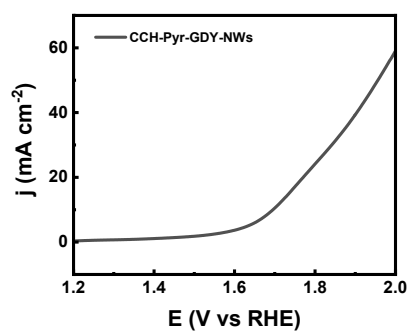


Fig. S7. LSV polarization curve of CCH@Pyr-GDY-NWs for the overall water-splitting.

7. Stability test for CCH@Pyr-GDY-NWs electrodes

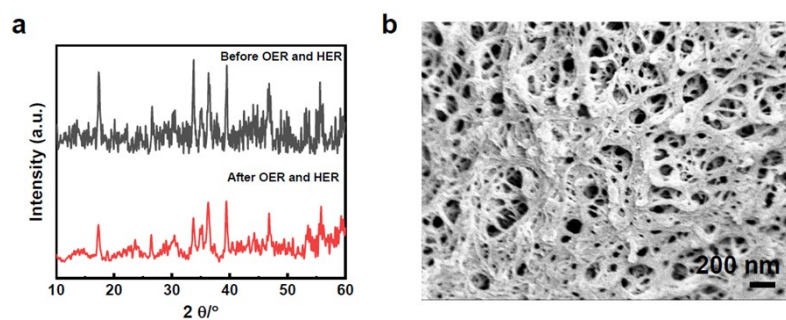


Fig. S8. (a) Powder XRD and (b) SEM image of CCH@Pyr-GDY-NWs before and after 40 h of HER and OER.

Table S2. Literature survey on potential and Tafel slope of the Co-based nanostructures for OER.

Electrocatalysts	Electrolyt e	j [mA cm ⁻²]	Overpotential (V vs RHE) [mV]	Tafel slop [mV dec ⁻¹]	References
CCH@Pyr- GDY-NWs	1.0 M KOH	20	330	66.1	<i>this work</i>
Cu@GDY/Co	1.0 M NaOH	10	350	148	8
Co/CoP-5	1.0 M KOH	10	330	80	9
VN-Co-P	1.0 M KOH	10	320	~	10
Co-P/Co-N- C/NPC	1.0 M KOH	10	374	82	11
Co _{1-x} S	1.0 M KOH	10	311	55	12
2D Co-MOF	1.0 M KOH	10	263	74	13
Co-Ni-P-2	1.0 M KOH	10	350	67	14

Table S3. Literature survey on potential and Tafel slope of the Co-based nanostructures for HER.

Electrocatalysts	Electrolyt e	<i>j</i> [mA cm⁻²]	Overpotential (V vs RHE) [mV]	Tafel slop [mV dec⁻¹]	References
CCH@Pyr-GDY- NWs	1.0 M KOH	20	340	99	<i>this work</i>
Co-N-GDY	1.0 M KOH	10	315	132	15
Co/CoP-5	1.0 M KOH	10	310	95	9
Co-Ni-P-2	1.0 M KOH	10	<200	33	16
NiCo ₂ S ₄ NW/NF	1.0 M KOH	10	280	59	17
Co/N-CNT	1.0 M KOH	10	350	141	18
CoCoOx@CN	1.0 M KOH	10	280	115	19
Co/CoO@NC@CC	1.0 M KOH	10	220	80	10

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