Electronic Supplementary Information

Experimental Section

Materials: N,N-dimethylformamide (DMF), p-phenylenediamine (PPD), pyromellitic dianhydride (PMDA), $CoCl_2 \cdot 6H_2O$, $(NH_4)_2SO_4$, $C_6H_5Na_3O_7 \cdot 2H_2O$, NaH_2PO_2 and KOH were purchased from Aladdin Ltd. (Shanghai, China). Pt/C (10 wt% Pt) was purchased from Alfa Aesar (China) Chemicals Co. Ltd. Nafion (5 wt%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Carbon cloth (CC) was provided by Hongshan District, Wuhan Instrument Surgical Instruments Business. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Synthesis of PI on CC : In a typical synthesis process, PPD (0.270 g) and PMDA (0.545 g) were dissolved in 30.0 mL DMF. After continuously stirring for 30 min, the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave with a piece of CC (2 cm × 3 cm). Then autoclave was sealed and maintained at 210 °C for 20 h in an oven. After the autoclave cooled down to room temperature, the PI/CC was taken out and thoroughly washed with deionized water and ethanol several times alternatively, then dried at 60 °C for 6 h in air.

Synthesis of PI-derived carbon on CC: After that, the PI/CC was further thermally treated at 800 °C for 2 h with a heating speed of 2 °C min^{-1} under Ar flow and then cooled down to room temperature naturally to obtain PI-derived carbon sample, designated as NC/CC.

Synthesis of Co-P@NC/CC: $CoCl_2 \cdot 6H_2O$ (1.19 g), $(NH_4)_2SO_4$ (3 g), $C_6H_5Na_3O_7 \cdot 2H_2O$ (3 g) and NaH_2PO_2 (3 g) were dissolved in 50 mL ultrapure water as the electroplating solution. Then, NC/CC (0.5 × 0.5 cm^2) as the working electrode was polarized at −1.0 V (vs. SCE) in the above solution for 100 s, with the use of a carbon rod as the auxiliary electrode and a SCE as the reference electrode to obtain Co-P@NC/CC.

Characterizations: SEM images and energy dispersive X-ray (EDX) spectra were collected from the tungsten lamp-equipped SU3500 scanning electron microscope at

an accelerating voltage of 20 kV (HITACHI, Japan). XPS measurements were performed using an ESCALABMK II X-ray photoelectron spectrometer with the exciting source of Mg. XRD data were collected on a Rigaku X-ray diffractometer equipped with a Cu Kα radiation source.

Electrochemical measurements: All the electrochemical measurements were conducted using a CHI660E potentiostat (CH Instruments, China) in a typical three-electrode setup with an electrolyte solution of 1.0 M KOH, a graphite rod as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. IR correction was determined using electrochemical impedance measurements. All potentials measured were calibrated on a reversible hydrogen electrode (RHE) scale (E (vs RHE) = E (vs SCE) + 0.0591 × pH + 0.242 V) except specifically explained. Polarization curves were obtained using LSV with a scan rate of 2 mV s^{-1}. The long-term durability test was performed using chronopotentiometric measurements. All currents presented are corrected against the ohmic potential drop and all LSV curves subtracted the capacitance current (average of anodic and cathodic scans). These Tafel plots are fitted to equation: $\eta = b \log j + a$ (η for overpotential, b for Tafel slope, j for current density and a for Tafel constant).

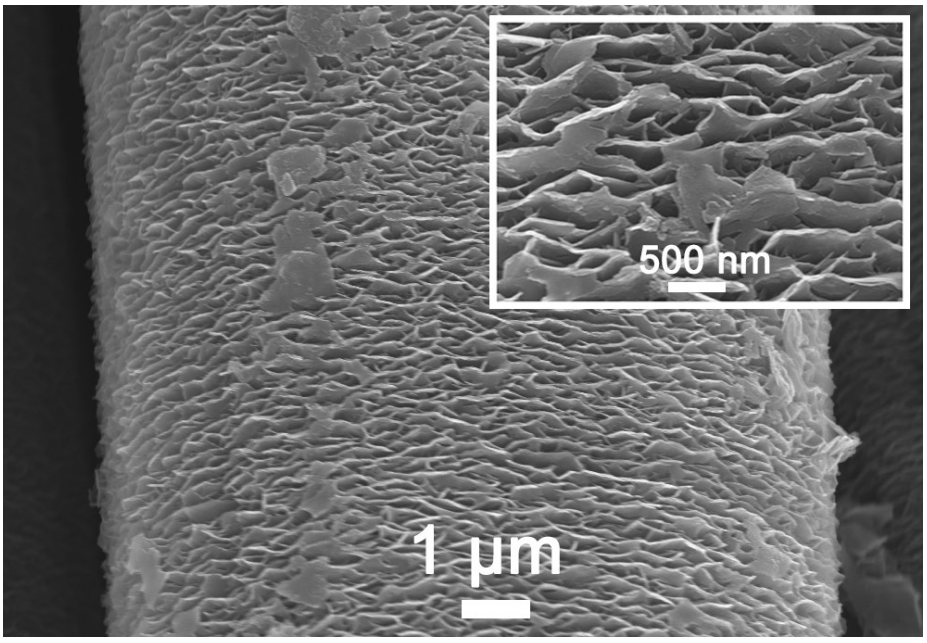

Fig. S1. SEM images for PI on CC.

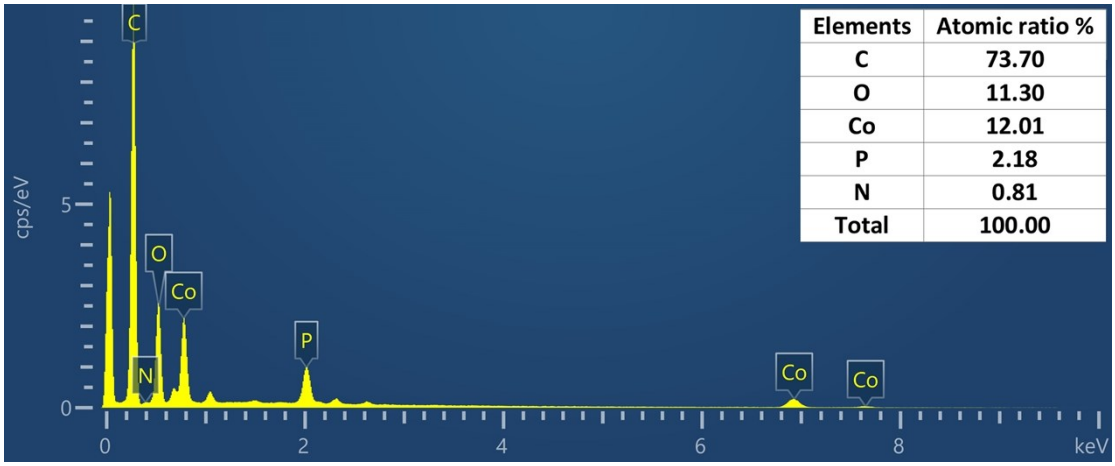

Fig. S2. EDX spectrum of Co-P@NC/CC.

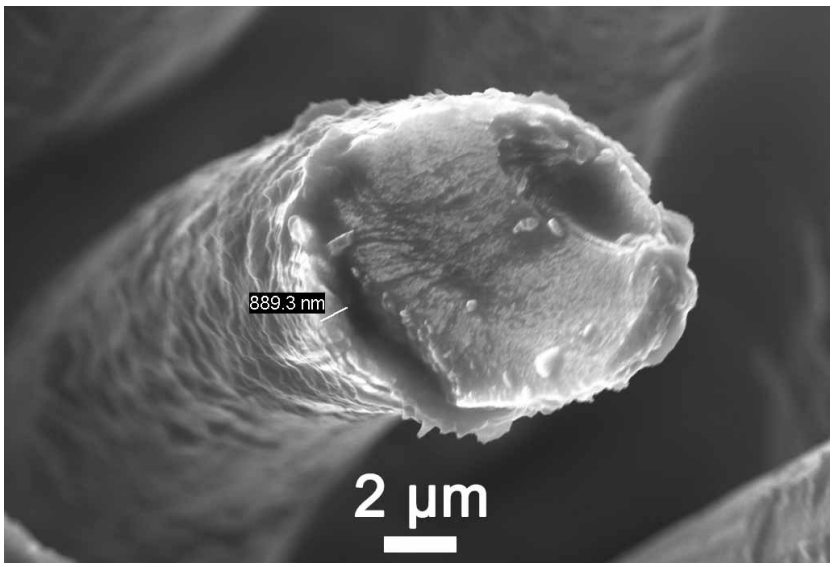

Fig. S3. Cross-section SEM image for Co-P@NC/CC.

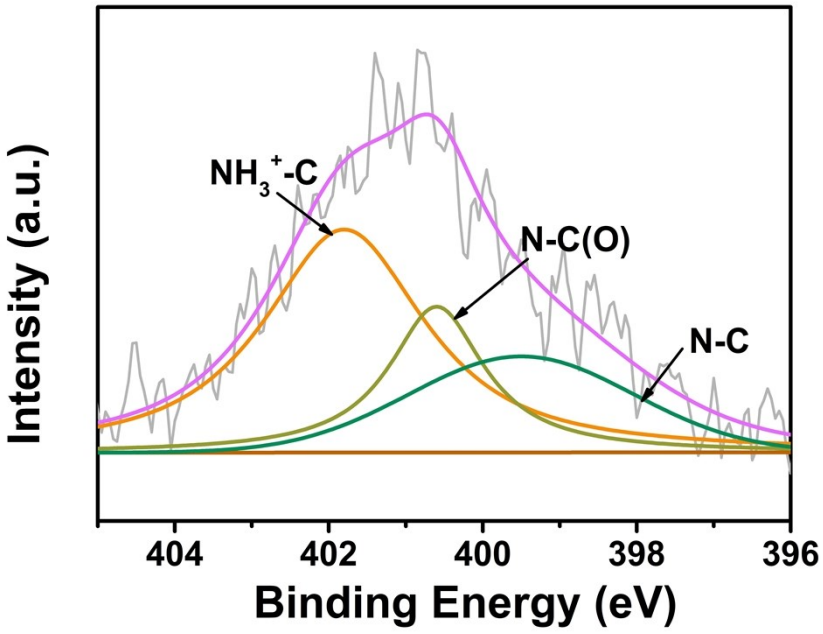

Fig. S4. High-resolution XPS spectrum of Co-P@NC/CC in the N 1s region.

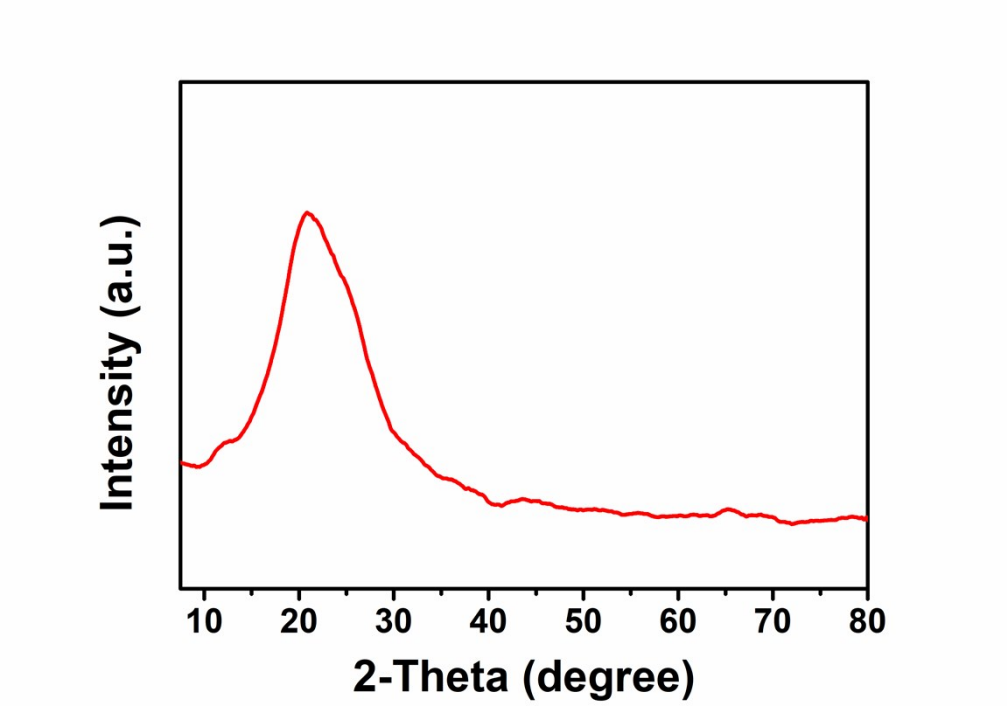

Fig. S5. XRD pattern of Co-P@NC/CC.

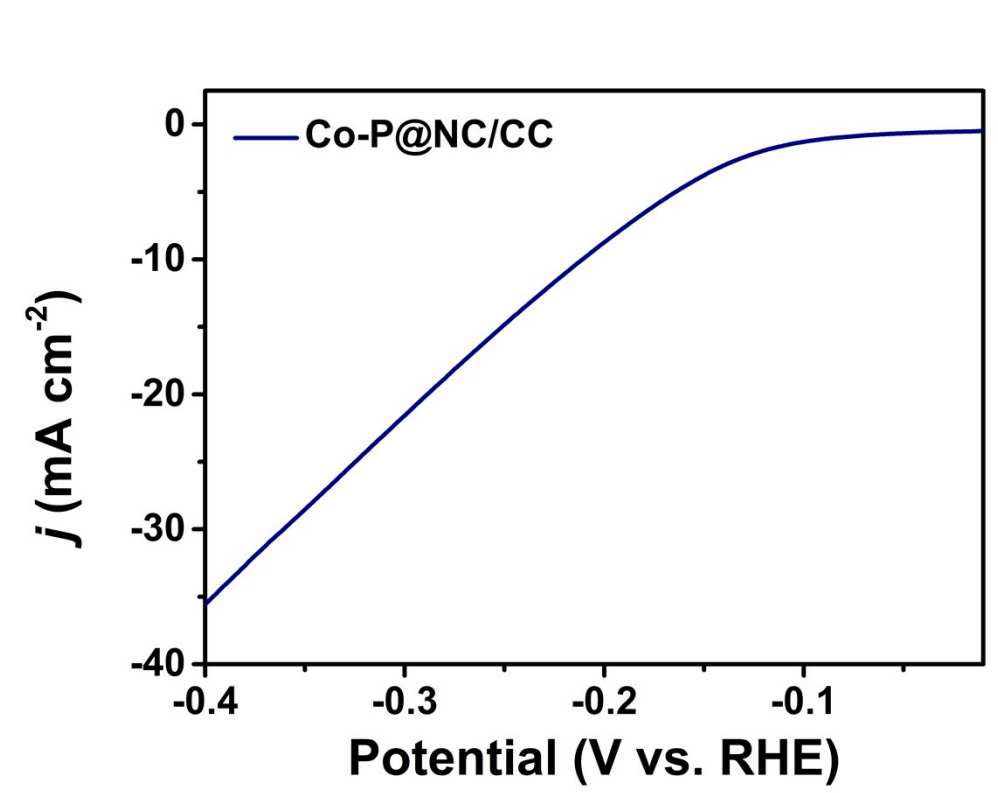

Fig. S6. LSV curve of Co-P@NC/CC in 0.1 M KOH.

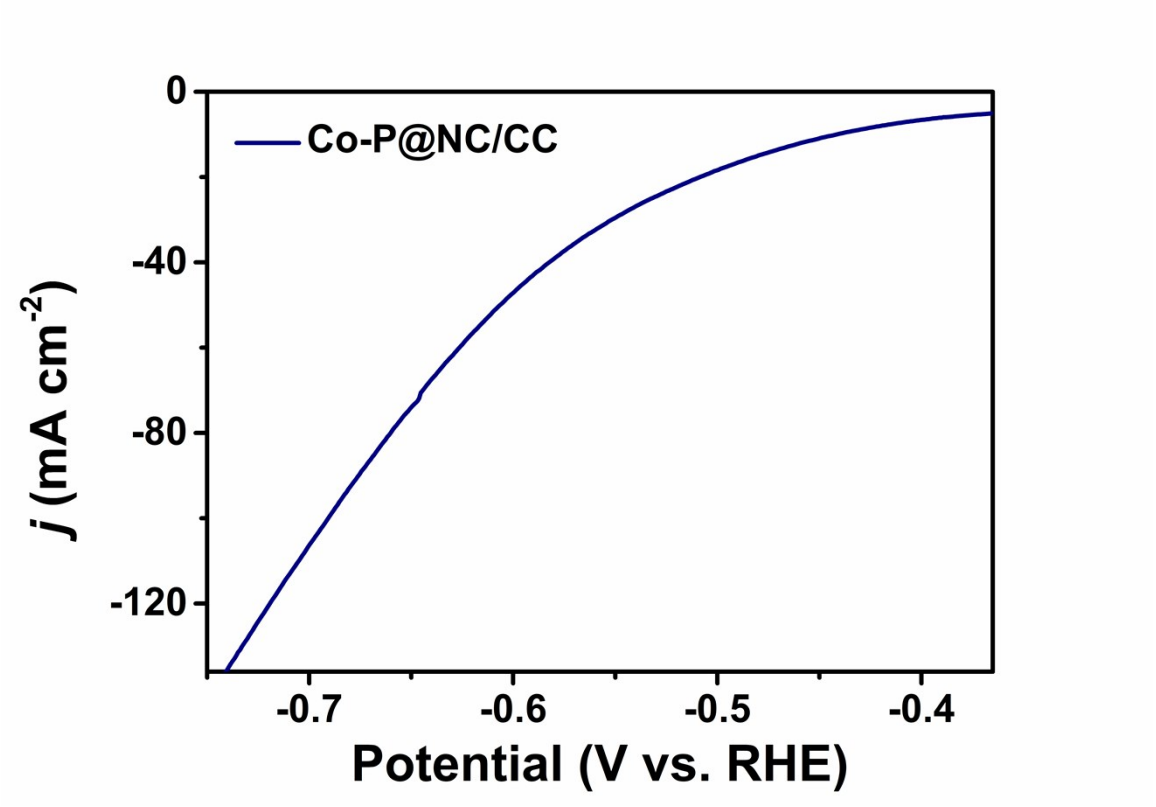

Fig. S7. LSV cruve of Co-P@NC/CC in 0.1 M PBS.

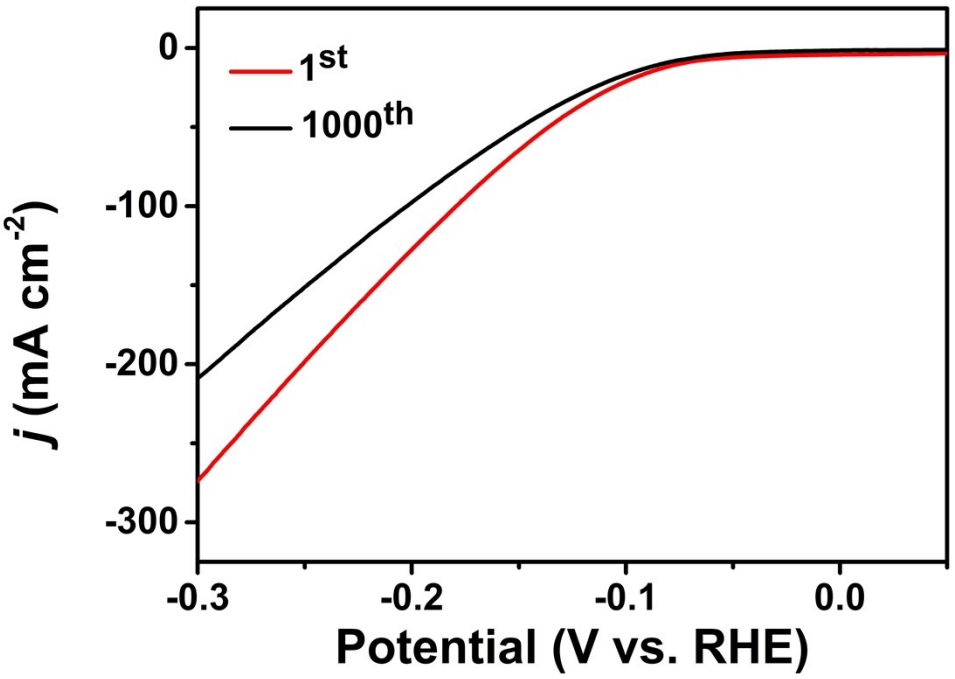

Fig. S8. LSV curves of Co-P@NC/CC before and after 1000 cyclic voltammetry cycles.

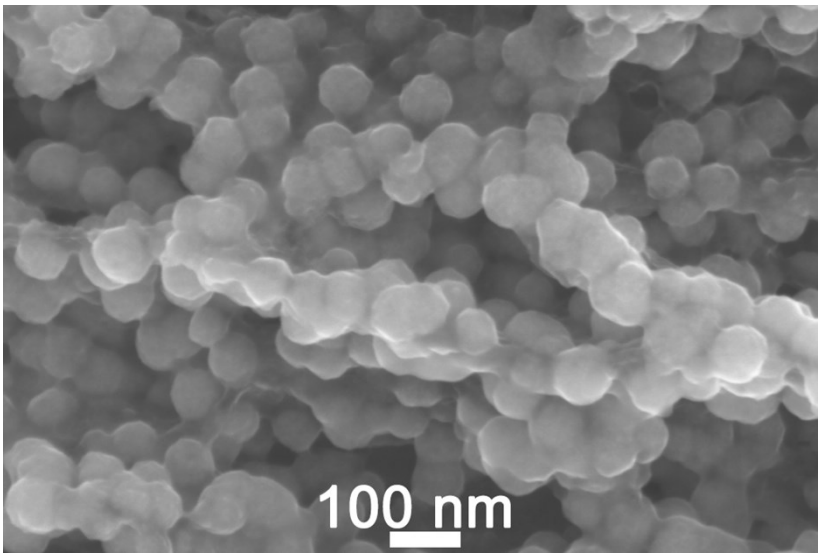

Fig. S9. SEM image for Co-P@NC/CC after long-term stability test.

Table S1. Comparison of HER performance in alkaline media for Co-P@NC/CC with other Co-P-based electrocatalysts.

Catalyst	Electrolyte	j (mA cm^{-2})	Overpotential (mV)	Ref.
Co-P@NC/CC	1.0 M KOH	10	75	This work
Co-P	1.0 M KOH	10	94	1
Co-P/CuO CF	1.0 M KOH	20	95	2
Co-P nanosheets	1.0 M KOH	10	85	3
Co-P foam	1.0 M KOH	10	131	4
Co-P/FTO	1.0 M KOH	10	125	5
Co-P/NC	1.0 M KOH	10	154	6
Co-P-B	1.0 M NaOH	10	145	7
Co-P/Co-N-C/NPC	1.0 M KOH	10	234	8
Co–P@Co_3O_4/CC	1.0 M KOH	10	73	9

References

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