Electronic Supplementary Information

Experimental Section

Materials: CC was provided by Hongshan District, Wuhan Instrument Surgical Instruments business. Pt/C (20 wt% Pt on Vulcan XC-72R) and Nafion (5 wt%) were purchased from Sigma-Aldrich. $Co(NO_3)_3 \cdot 6H_2O$, $(NH_4)_2SO_4$, KOH, HNO_3 and ethyl alcohol were purchased from Chengdu Kelong Chemical Regent Co. Ltd. $NaH_2PO_2 \cdot H_2O$ was bought from Shanghai Macklin Biochemical Co., Ltd. $Na_3(C_6H_5O_7) \cdot 2H_2O$ was bought from Beijing Chemical Corporation. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of Co_3O_4/CC and Co-P@Co_3O_4/CC: Co_3O_4/CC was prepared as follows. Typically, a piece of clean CC (2 cm × 3 cm) was immersed into a 40 mL aqueous solution containing 8 mmol $Co(NO_3)_2 \cdot 6H_2O$ and 16 mmol NH_4F and 40 mmol urea in a 50 mL Teflon-lined stainless steel autoclave. Then autoclave was sealed and maintained at 120 °C for 6 h in an oven. After the autoclave cooled down to room temperature, the precursor was washed with water several times and dried in 60 °C for 12 h and then annealed at 350 °C for 3 h under air atmosphere. The resulting Co_3O_4/CC was then used as a working electrode in a three-electrode setup and cathodically polarized (-1.2 V vs. Ag/AgCl, 60 min) at room temperature to obtain Co-P@Co_3O_4/CC. The electrolyte was made by adding 10 mmol $Na_3(C_6H_5O_7) \cdot 2H_2O$, 23 mmol $(NH_4)_2SO_4$ and 28 mmol $Na(H_2PO_2) \cdot H_2O$ in 50 mL H_2O.

Preparation of Co-P/CC: A piece of CC (1 cm × 2 cm) was exposed to the deposition solution (5 mmol $Co(NO_3)_2·6H_2O$, 10 mmol $Na_3(C_6H_5O_7)·2H_2O$, 23 mmol $(NH_4)_2SO_4$ and 28 mmol $NaH_2PO_2·H_2O$ in 50 mL water). A platinum wire was used as the counter electrode and a Ag/AgCl electrode as the reference electrode. Then, the Co-P film with the same loading of Co-P in Co-P@Co_3O_4/CC was deposited by constant current electrodeposition based on the transferred charge for Co-P@Co_3O_4 preparation.

Characterizations: XRD data were obtained from a LabX XRD-6100 X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (Shimadzu, Japan). XPS spectra were recorded on a PHI quantera II (Ulvac-Phi, Japan) under ultra-high vacuum using monochromated Al Kα source (1486.6 eV) at 42.1 W. The measurements were performed at 20 eV pass energy, 0.1 eV step and 0.15 dwelling time. SEM measurements were performed on a HITCHI S-4800 scanning electron microscope at an accelerating voltage of 25 kV. TEM measurements were carried out on a Zeiss Libra 200 FE transmission electron microscope operated at 200 kV.

Electrochemical measurements: Electrochemical measurements were performed with a CHI-660E electrochemical analyzer (CH Instruments, Shanghai, China) in a standard three-electrode system using a Co-P@Co_3O_4/CC (catalyst loading: ~3.02 mg cm^{-2}) as the working electrode, a graphite sheet as the counter electrode and a Hg/HgO as the reference electrode. The potentials reported in this work were calibrated to RHE in 1.0 M KOH, using the following equation: E (RHE) = E

(Hg/HgO) + (0.098 + 0.059 pH) V. Polarization curves were obtained using linear sweep voltammetry with a scan rate of 5 mV s^{-1}. All experiments were carried out at room temperature (25 °C).

To acquire the ECSA of the working electrodes, their roughness factor (R_f) were obtained firstly according to the equation: ECSA = R_fS, where S was generally equal to the geometric area of electrode (here S=1.0 cm^2). The R_f was determined by the relation $R_f = C_{dl}/20\ \mu F\ cm^{-2}$ based on the double-layer capacitance (C_{dl}) of a smooth oxide surface (60 μF cm^{-2}),[1] where C_{dl} could be acquired by cyclic voltammetry measurement within the potential windows of 0.124~0.224 V vs. RHE (1.0 M KOH solution). The various scan rates were utilized, such as 5, 20, 40, 80, 100, 120, 160, and 200 mV s^{-1}. The C_{dl} was estimated by plotting the $j_a - j_c$ at 0.174 V (where j_c and j_a are the cathodic and anodic current densities, respectively) vs. RHE against the scan rate, in which the slope was twice that of C_{dl}.

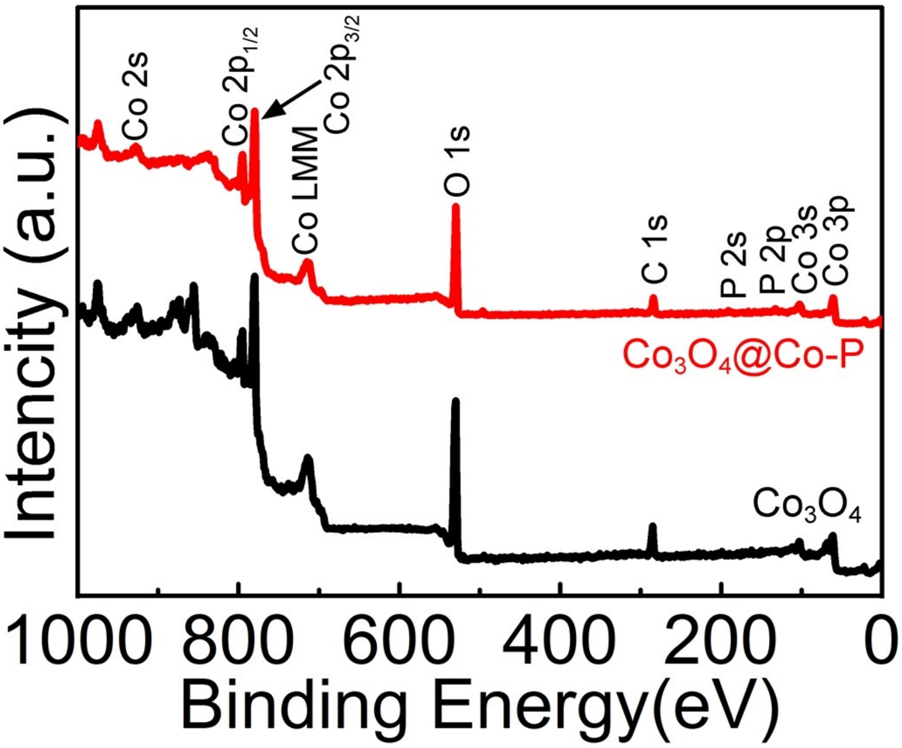

Fig. S1. XPS survey spectra of Co_3O_4 and Co-P@Co_3O_4.

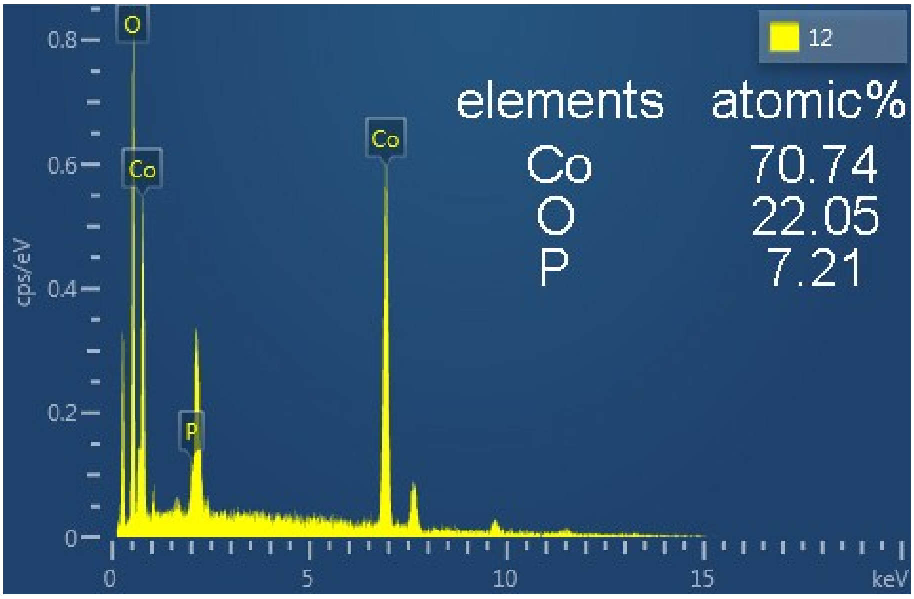

Fig. S2. EDX spectrum of Co-P@Co_3O_4/CC.

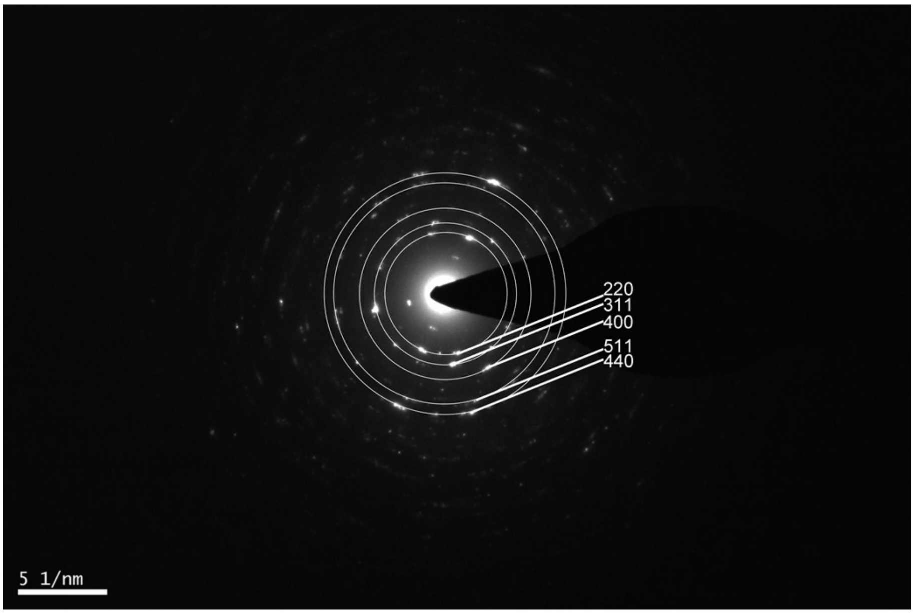

Fig. S3. SAED pattern taken from Co-P@Co_3O_4.

Table S1. Comparison of HER performance for Co_3O_4@Co-P/CC with other reported Co-based electrocatalysts in 1.0 M KOH.

Catalyst	Tafel slope (mV dec^{-1})	j (mA cm^{-2})	η (mV)	Ref.
Co-P@Co_3O_4	85	10	73	This work
		100	151	
Co_3O_4 NCs	115	10	155	2
Co_3O_4-MTA	98	20	190	3
CoO_x@CN	N/A	10	232	4
Co/Co_3O_4	44	10	~90	5
Co@CoO/NG	119	10	112	6
Co-B@CoO	78	10	61	7
Co_2B	136.2-177.0	10	127	8
CoP/G	57	10	154	9
Co-NRCNTs	N/A	10	370	10
Co-P	42	10	94	11
CoP	129	10	209	12
O-Co_2P-3	61.1	10	160	13
P-Co_3O_4	50	10	120	14
Fe-CoP	75	10	78	15
CoP@BCN-1	52	10	215	16
Co/CoP	64	10	135	17
$CoSe_2$	52	10	95	18
CoSe	175.6	10	78	19
CoN	79	10	~180	20
$Ni(OH)_2$-CoS_2	118	20	99	21

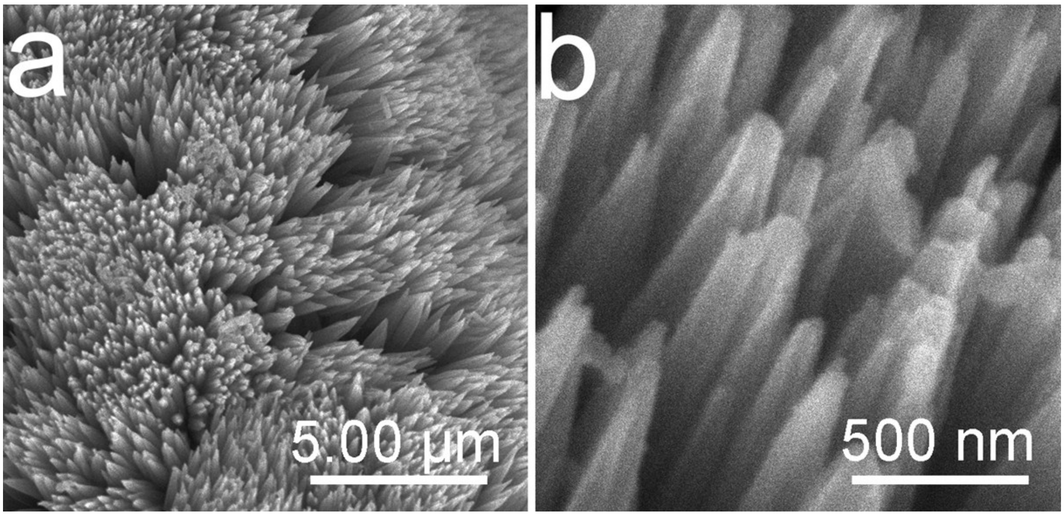

Fig. S4. (a) Low- and (b) high-magnification SEM images of post-HER Co-P@Co_3O_4/CC.

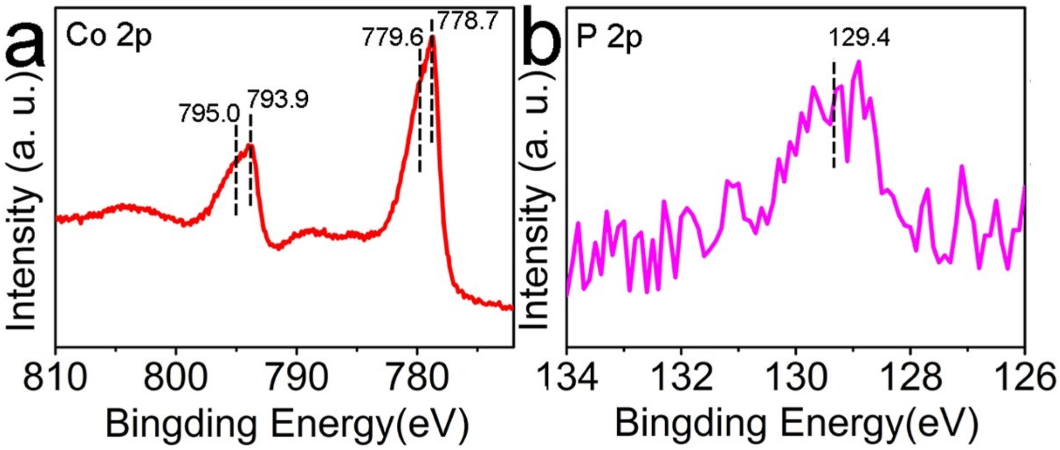

Fig. S5. Co 2p (a) and P 2p (b) core-level XPS spectra for post-HER Co-P@Co_3O_4.

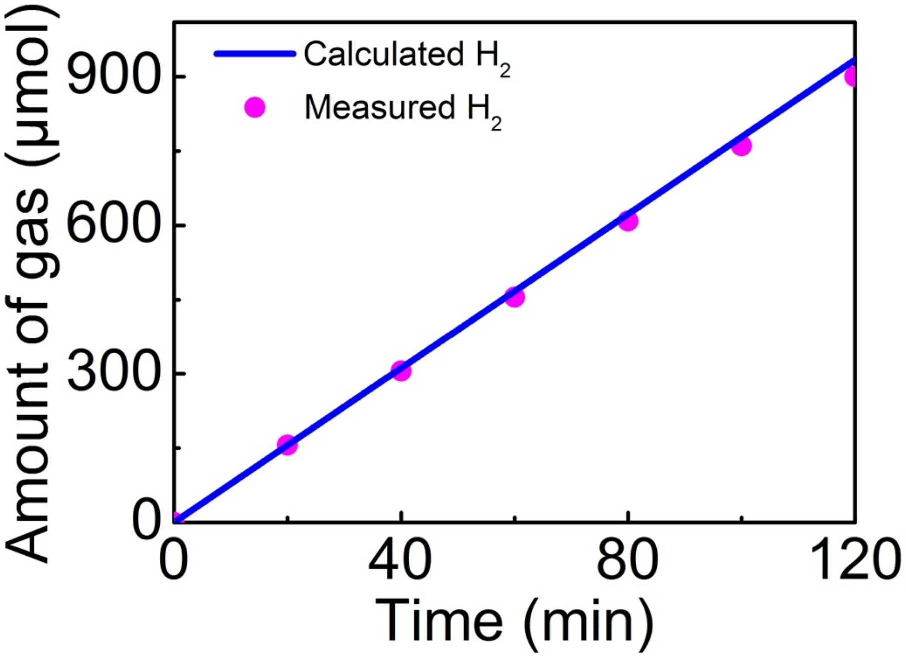

Fig. S6. The amount of gas theoretically calculated and experimentally measured versus time for hydrogen evolution of Co-P@Co_3O_4/CC.

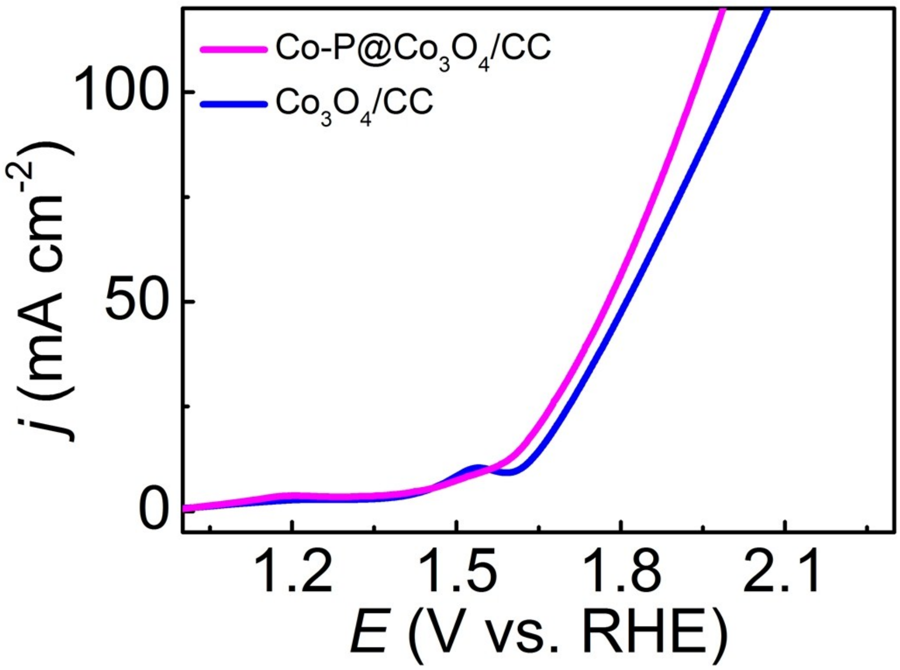

Fig. S7. Polarization curves for Co$_3$O$_4$/CC and Co-P@Co$_3$O$_4$/CC with a scan rate of 5 mV s^{-1} 1.0 M KOH.

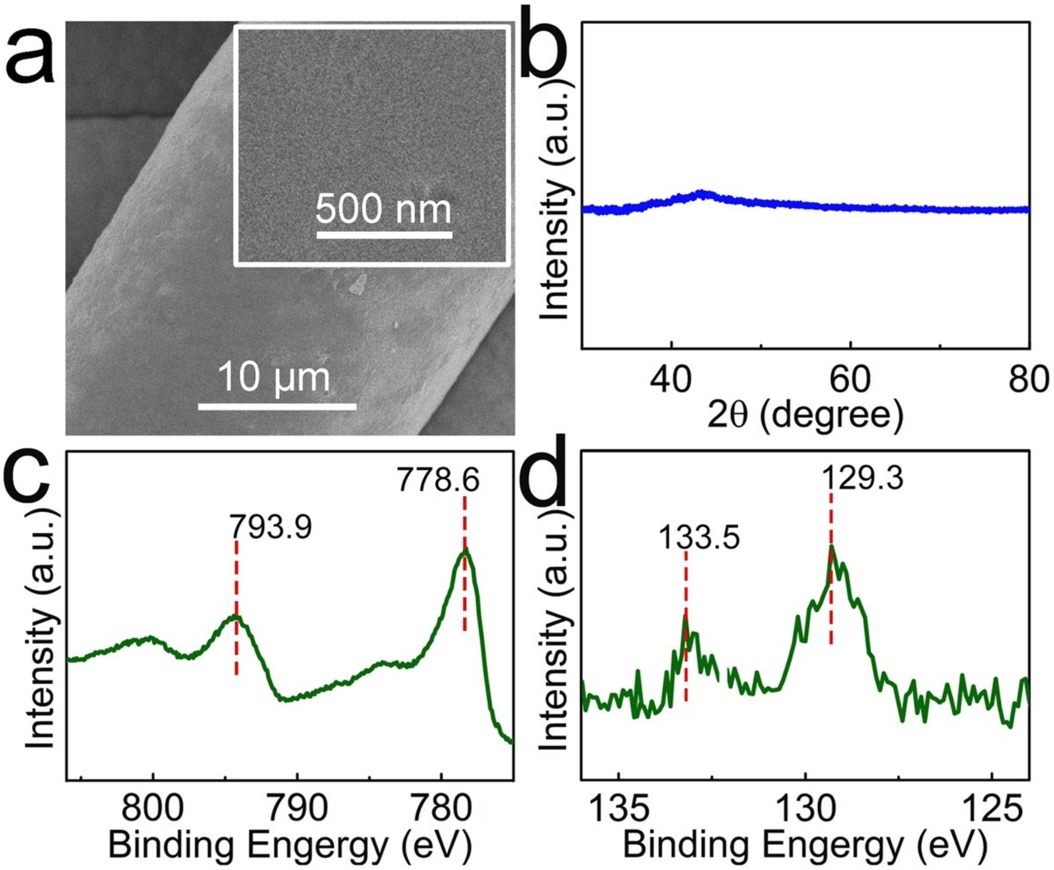

Fig. S8. (a) SEM image and (b) XRD pattern for Co-P/CC. XPS spectra for Co-P in the (c) Co 2p and (d) P 2p regions.

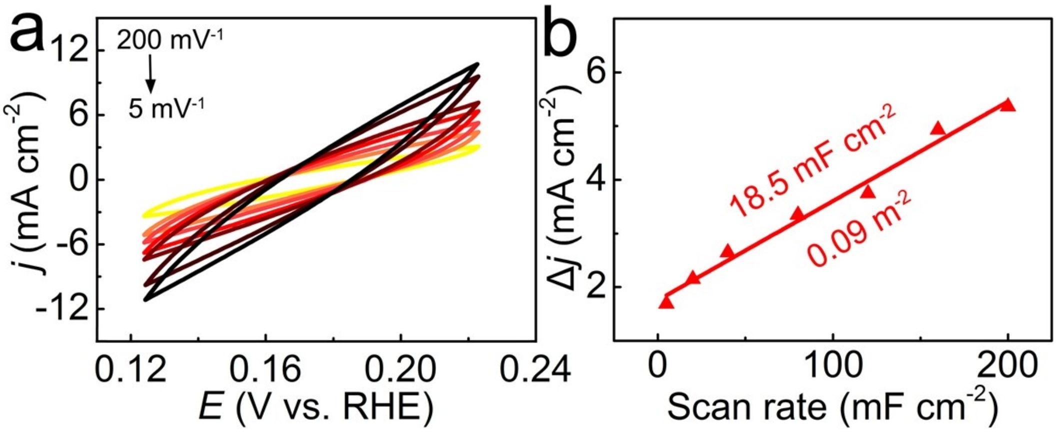

Fig. S9. (a) CVs of Co-P/CC in the non-faradaic capacitance current range in 1.0 M KOH at scan rates of 5, 20, 40, 80 120, 160, and 200 mV s^{-1}. (b) Capacitive curents at 0.174 V as a function of scan rate for Co-P/CC ($\Delta j_0 = j_a - j_c$).

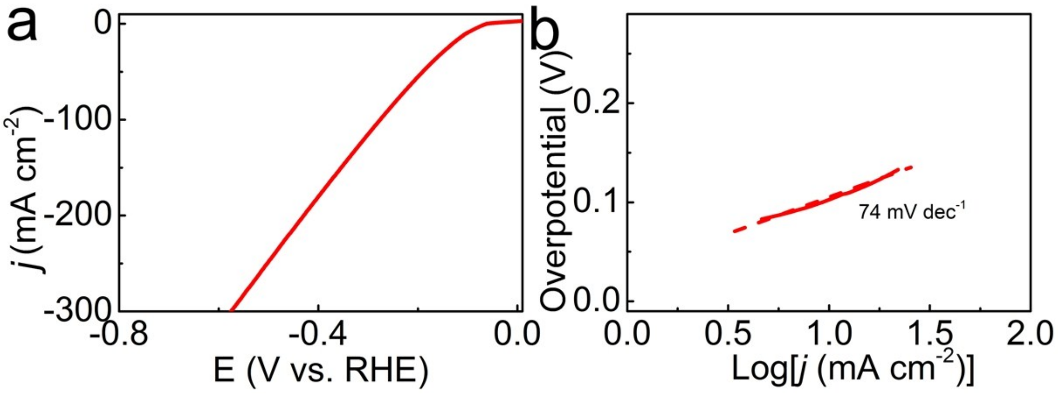

Fig. S10. (a) Polarization curve for Co-P/CC with a scan rate of 5 mV s^{-1} 1.0 M KOH. (b) Tafel plot of Co-P/CC.

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