Crystalline/amorphous composite interface of CoP@Ni/Fe-P as boosted electrocatalyst for full water splitting

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Materials characterization

Scanning electron microscopy (SEM) was performed on JSM-6701F (JEOL) scanning electron microscope with the accelerating voltage 10 kV. Samples were prepared by directly sticking on the conductive tape.

Transmission electron microscopy (TEM) was carried out by JEM-2100F (JEOL) microscope working at an accelerating voltage from 120 kV to 200 kV. The CC supporting samples were treated in ethanol by ultrasonicating treatment for 15 min and then the dispersion was dropped onto carbon-coated copper grids and drying at ambient temperature.

The XRD analysis carried out with a scanning rate of 5° min^{-1} in the 2θ range 10-80° using the Rigaku Ultima VI X-ray diffractometer (XRD) with Cu Kα radiation (λ = 1.543 Å) at 40 kV and 20 mA. The CC supporting samples were tested directly.

The X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB 250 (Thermo Scientific Corporation) X-ray photoelectron spectrometer working with a monochromated X-ray source (Al Ka hy¼ 1486.6 eV). The CC supporting samples

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were tested directly.

Electrochemical measurements

Electrochemical measurements were performed on a three-electrode electrochemical workstation (CHI 760E) using Hg/HgO electrode, graphite rod and the prepared samples as the reference electrodes, counter electrodes and working electrodes, respectively. The reference electrode was corrected according to the following reversible hydrogen electrode (RHE) equation: E(RHE) =E(Hg/HgO) + 0.0592×pH + 0.098. N_2-saturated 1 M KOH was used as alkaline electrolyte for HER and OER measurements. Cyclic voltammograms (CV) cycles were performed at a scan rate of 100 mV/s. Linear scan voltammograms (LSV) were recorded at a scan rate of 1 mV/s. EIS plots were obtained at potential of -1.5 V from 100 kHz to 0.1 Hz with a 5 mV AC dither in 1 M KOH. C_{dl} was measured using CV method in the non-Faradaic current region (-0.1-0 V vs. RHE) at scan rate of 30, 50, 70, 100, 150, 200 mV/s.

Determination of number of M sites involved in OER based on redox peak method[1]

Area under MOOH formation peak for Ni/Fe-P = 4.296×10^{-5}A V

Charge associated with MOOH formation = 4.296×10^{-5}A V / 0.005 V s^{-1}

$$= 8.59 \times 10^{-3} \text{ A s}$$

$$= 8.59 \times 10^{-3} \text{ C}$$

Charge of an electron = 1.602×10^{-19} C

Hence,

Number of electrons transferred = 8.59 × 10⁻³ C / 1.602 × 10⁻¹⁹ C

= 5.36 × 10¹⁶

Area under MOOH formation peak for CoP = 3.358 × 10⁻⁵A V

Charge associated with MOOH formation = 3.358 × 10⁻⁵A V / 0.005 V s⁻¹

$$= 6.72 \times 10^{-3} \text{ A s}$$

$$= 6.72 \times 10^{-3} \text{ C}$$

Charge of an electron = 1.602 × 10⁻¹⁹ C

Hence,

Number of electrons transferred = 6.72 × 10⁻³ C / 1.602 × 10⁻¹⁹ C

= 4.19 × 10¹⁶

Area under MOOH formation peak for CoP@Ni/Fe-P = 1.432 × 10⁻⁴A V

Charge associated with MOOH formation = 1.432 × 10⁻⁴A V / 0.005 V s⁻¹

$$= 2.86 \times 10^{-2} \text{ A s}$$

$$= 2.86 \times 10^{-2} \text{ C}$$

Charge of an electron = 1.602 × 10⁻¹⁹ C

Hence,

Number of electrons transferred = 2.86 × 10⁻² C / 1.602 × 10⁻¹⁹ C

= 1.78 × 10¹⁷

Since, the M^{2+} to M^{3+} formation reaction is a single electron transfer reaction, the number of electron transferred during the reaction is exactly equal to the number of M sites involved in the reaction.

Hence,

Number of M sites that actually involved in OER for Ni/Fe-P = 5.36×10^{16}

Number of M sites that actually involved in OER for CoP = 4.19×10^{16}

Number of M sites that actually involved in OER for CoP@Ni/Fe-P = 1.78×10^{17}

Determination of Turnover Frequency (TOF) from OER Current Density TOF in our study was calculated assuming that the surface-active M atoms that had undergone the redox reaction just before onset of OER only participated in OER electrocatalysis. The corresponding expression is,

$$TOF = I \times N_A / (F \times n \times \tau)$$

Where, I = current, N_A = Avogadro number, F = Faraday constant, n = Number of electrons and τ = Surface concentration.
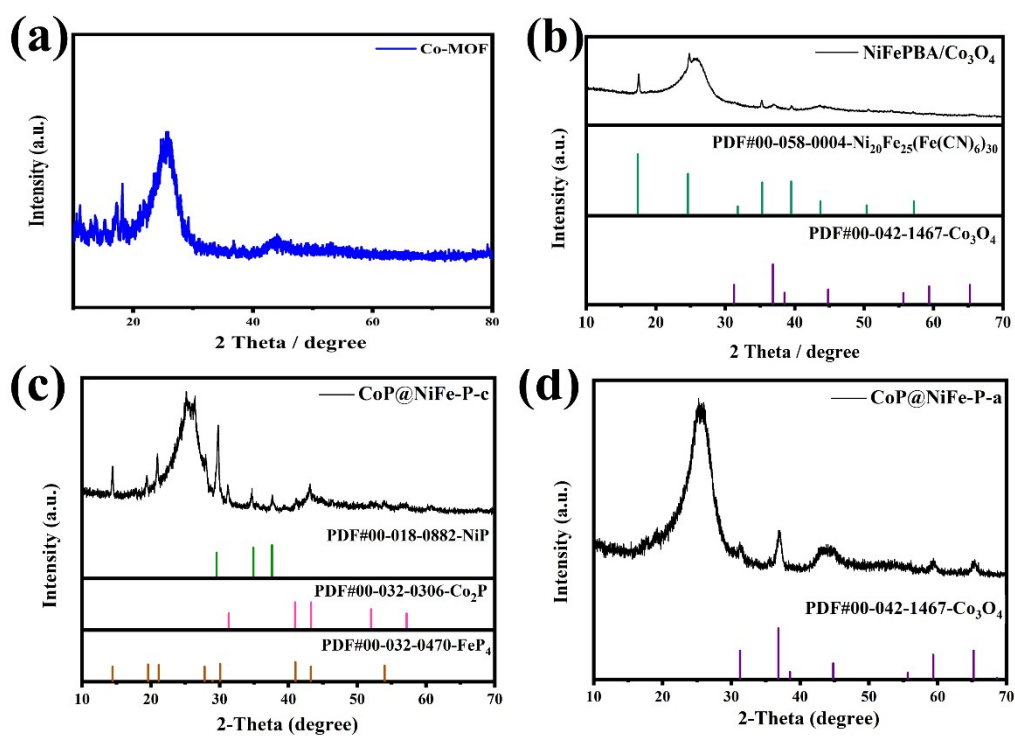
Figure S1. XRD patterns of Co-MOF/CC (a), Co_3O_4@PBA/CC (b), CoP@Ni/Fe-P-c (c) and CoP@Ni/Fe-P-a (d).
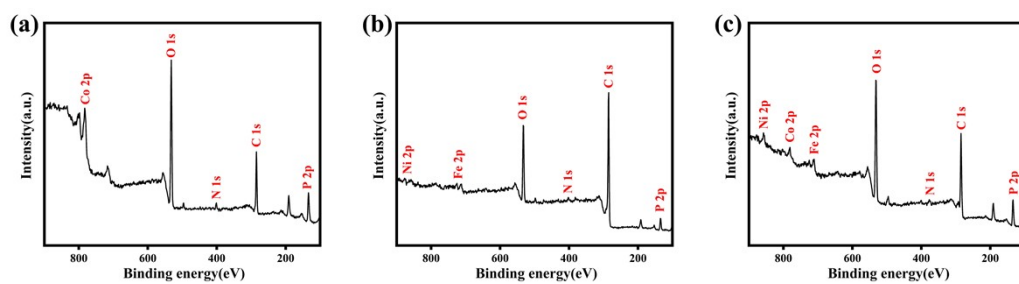

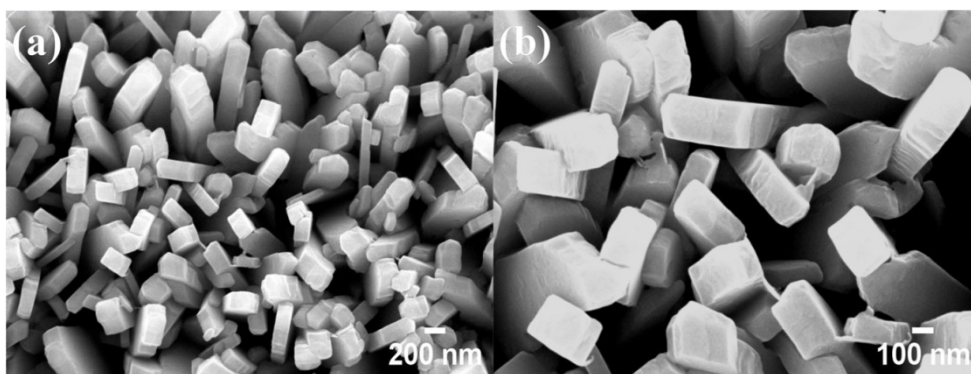**Figure S2.** XPS survey spectrums of Ni/Fe-P/CC (a), CoP/CC (b) and CoP@Ni/Fe-P/CC (c).
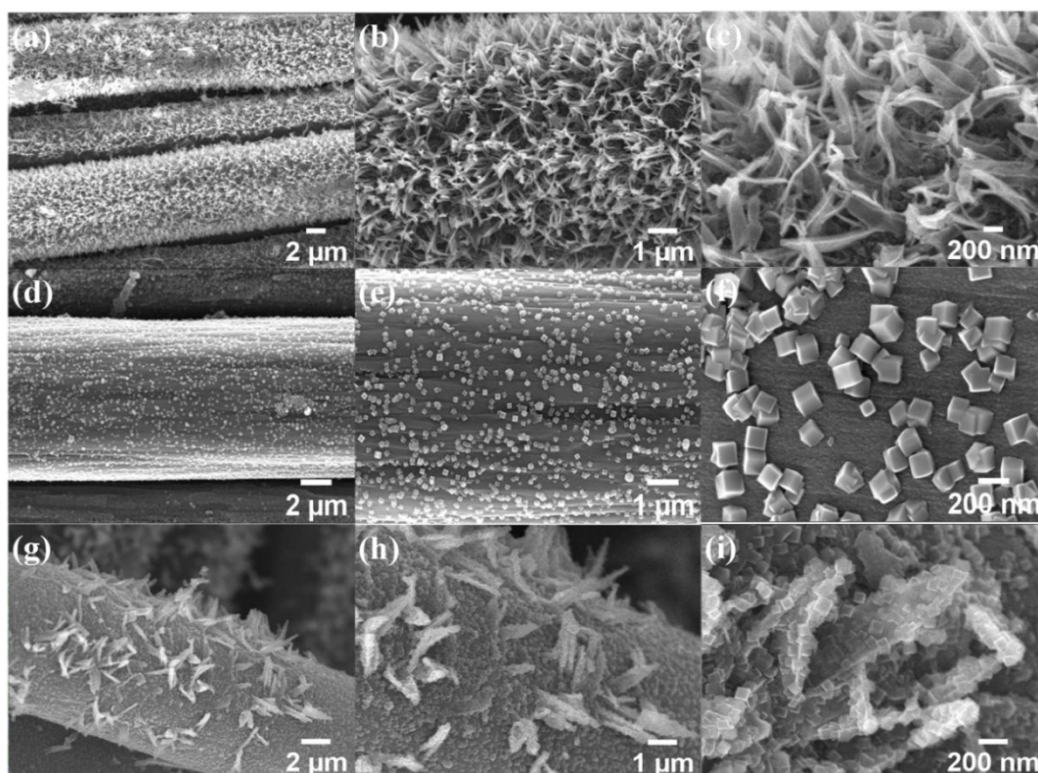
Figure S3. SEM images of Co-MOF/CC precursor.

Figure S4. SEM images with different magnification of Co_3O_4 (a-c), NiFePBA (d-f) and Co_3O_4@NiFePBA (g-i).
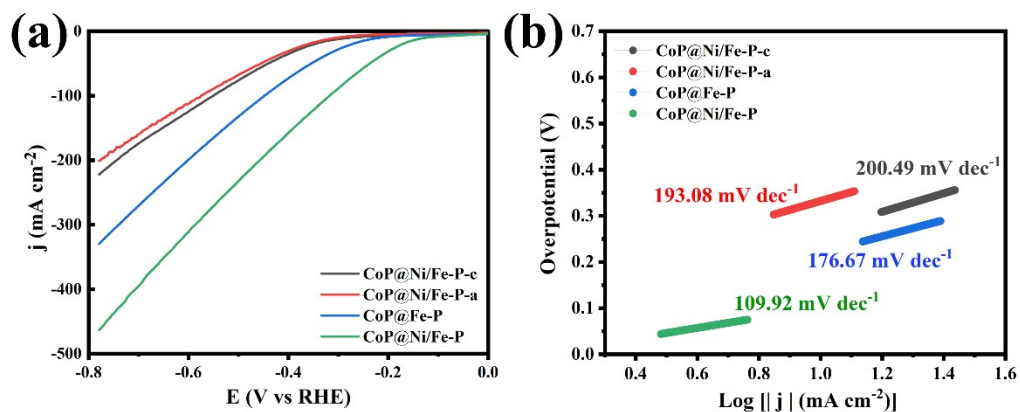
Figure S5. HER polarization curves (a) and the corresponding Tafel slope (b) of CoP@Ni/Fe-P/CC, CoP@Ni/Fe-P-a/CC, CoP@Ni/Fe-P-c/CC and CoP@Fe-P/CC.

Figure S6. The amount of H_2 evolved from the CoP@Ni/Fe-P/CC electrode at a constant current density of 20 mA cm^{-2} and the corresponding FE.

Figure S7. XRD patterns of CoP@Ni/Fe-P/CC after HER stability test.

Figure S8. SEM images of CoP/Ni/Fe-P/CC after HER stability test.

Figure S9. XPS spectrums for different elements after HER stability test.

Figure S10. OER polarization curves (a) and the corresponding Tafel slope (b) of CoP@Ni/Fe-P/CC, CoP@Ni/Fe-P-a/CC, CoP@Ni/Fe-P-c/CC and CoP@Fe-P/CC.
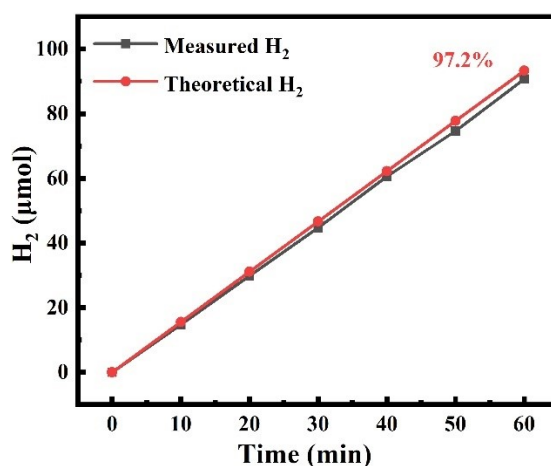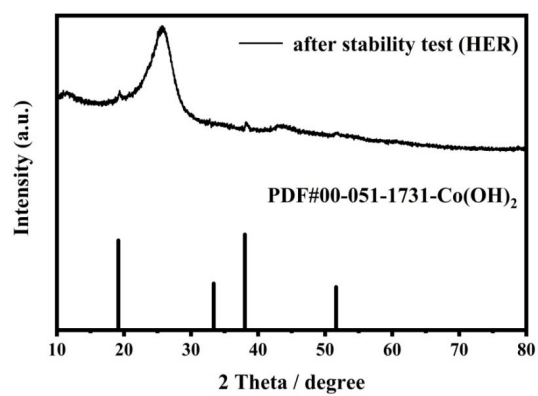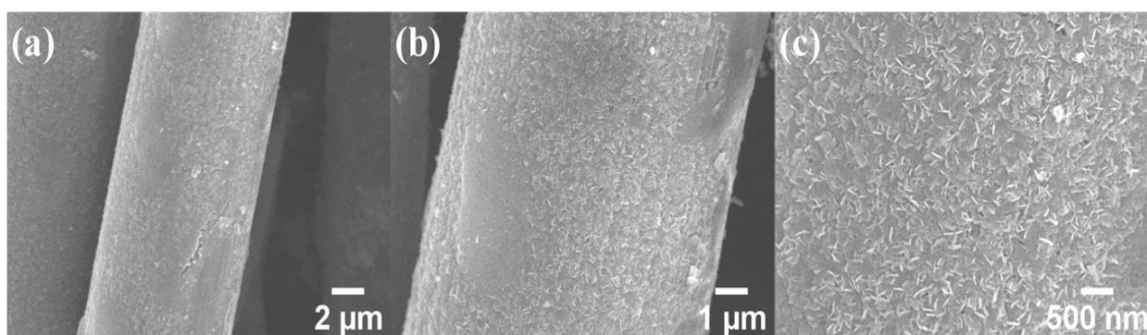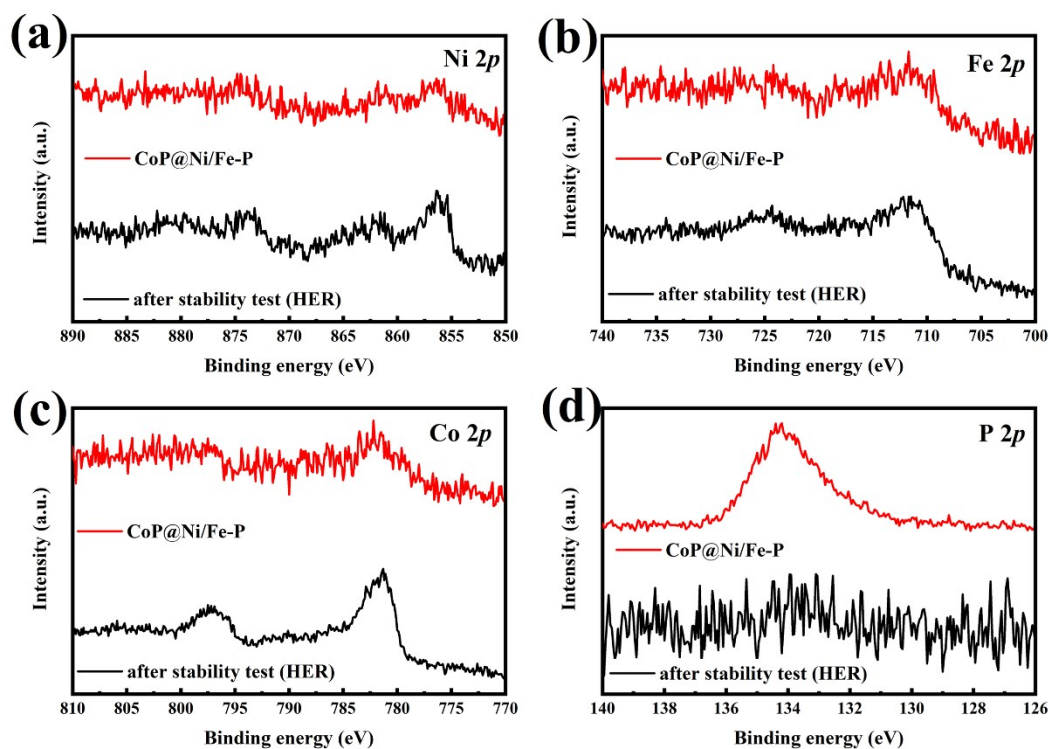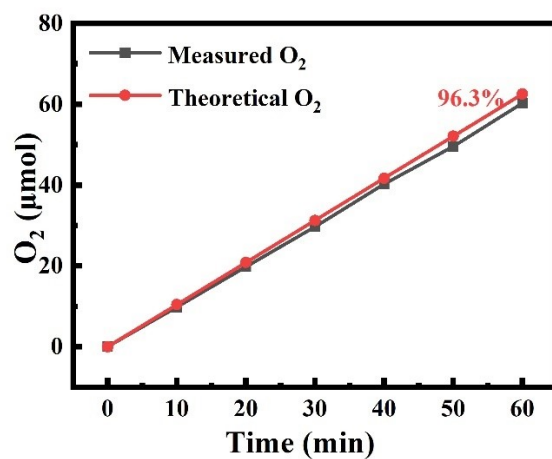
Figure S11. The amount of O$_2$ evolved from the CoP@Ni/Fe-P/CC electrode at a constant current density of 80 mA cm^{-2} and the corresponding FE.
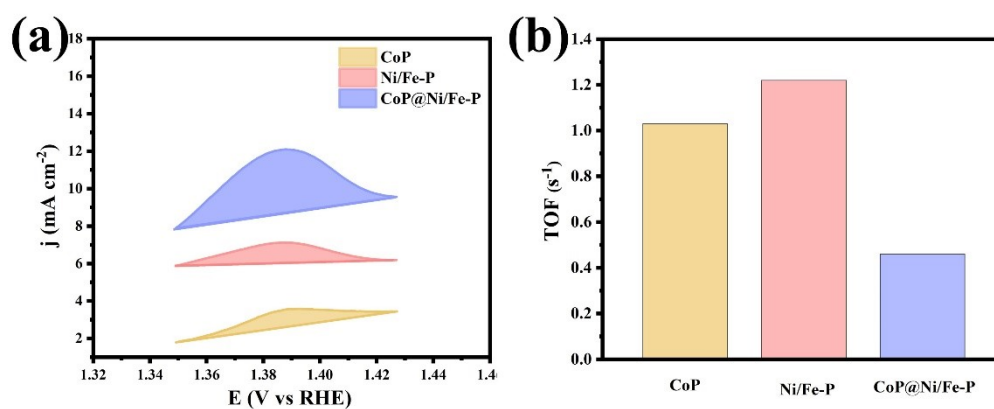
Figure S12. The MOOH formation peak from LSVs used for area integration (a) and TOF value (b) for Ni/Fe-P/CC, CoP/CC and CoP@Ni/Fe-P/CC.
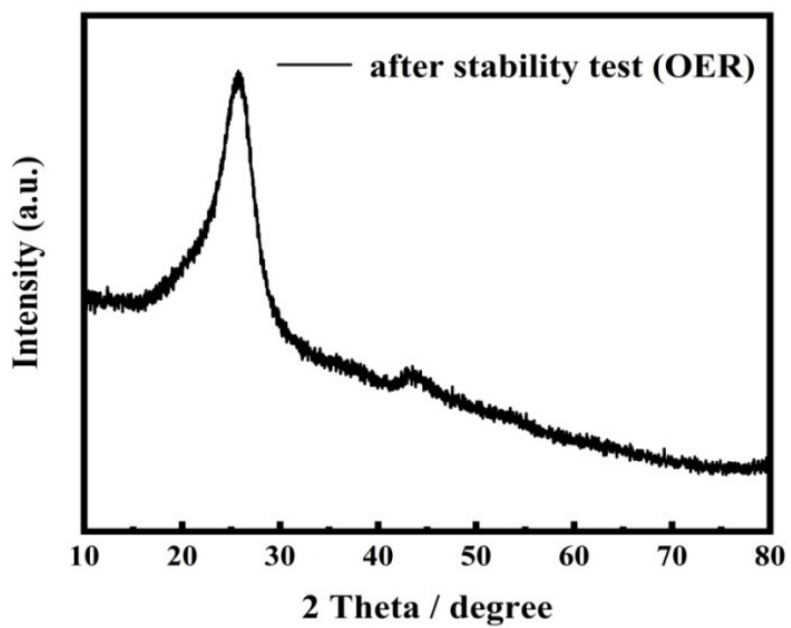
Figure S13. XRD pattern for CoP@Ni/Fe-P/CC after OER stability test.
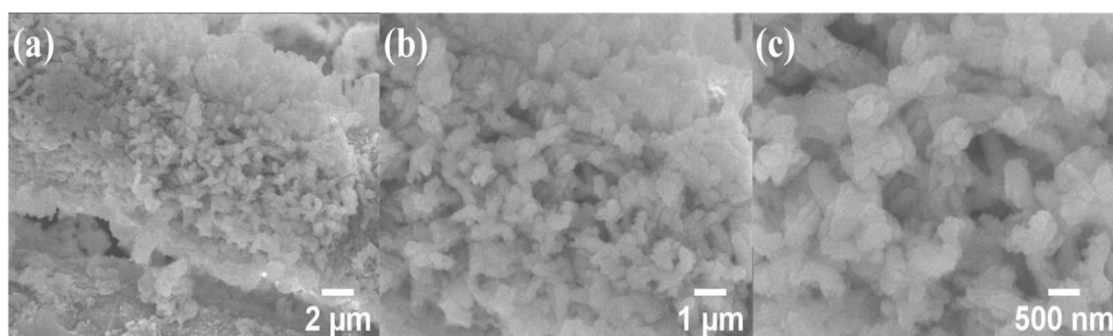
Figure S14. SEM images of CoP@Ni/Fe-P/CC after OER stability test.
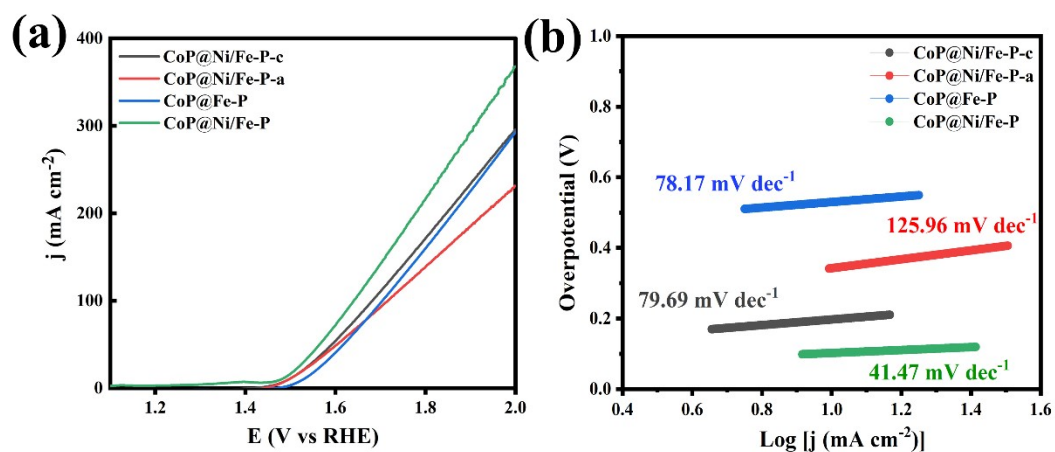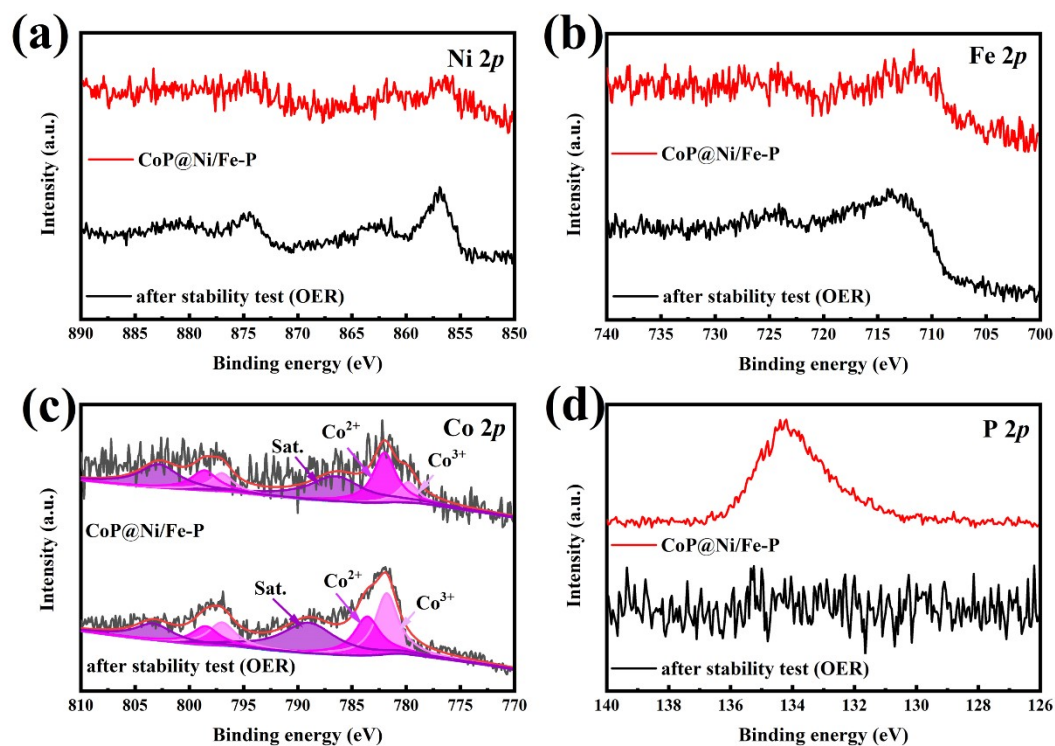
Figure S15. XPS spectrums for different elements of CoP@Ni/Fe-P/CC after OER stability test.
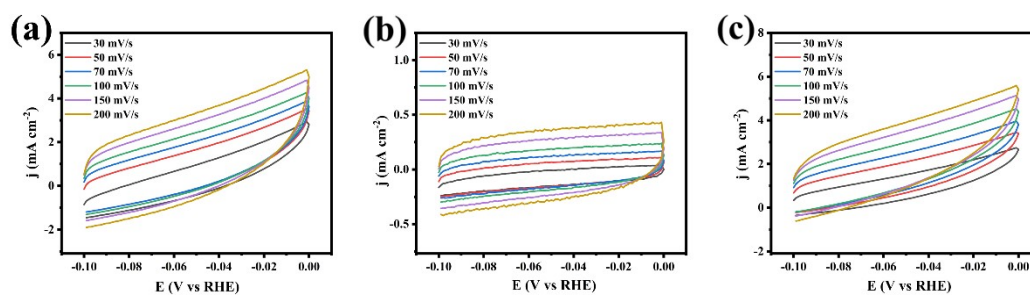
Figure S16. Cyclic voltammetry curves of Ni/Fe-P/CC (a), CoP/CC (b) and CoP@Ni/Fe-P/CC with a different applied scan rate value for obtaining the C_{dl} information.

Table S1. The elements content for different electrocatalysts.

| Sample	Ni	Fe	Co	P	C	O	N
CoP	/	/	6.80	19.25	27.50	40.79	5.66
Ni/Fe-P	1.16	1.65	/	7.05	65.89	19.53	4.73
CoP@Ni/Fe-P	2.24	2.68	4.69	13.93	45.97	25.81	4.68
NiFePBA/Co$_3$O$_4$	2.88	3.01	3.74	/	60.07	13.40	16.90
after I-t test (HER)	1.97	2.25	8.43	4.63	45.94	32.70	4.08
after I-t test (OER)	1.57	2.82	5.31	2.78	45.60	37.80	4.12

Table S2. Electrocatalytic parameters for HER performance of the CoP@ Ni/Fe-P and as-prepared contrast electrocatalysts in 1 M KOH electrolyte.

Catalyst	Current density [mA cm^{-2}]	Overpotential [mV]	Tafel slope [mV dec^{-1}]
CoP	10/50/100	137/265/375	150.27
Ni/Fe-P	10/50/100	240/430/535	257.35
CoP@Ni/Fe-P	10/50/100	125/237/318	109.92
Pt/C	10/50/100	33/146/262	44.28
CoP@Fe-P	10/50/100	218/355/448	176.67
CoP@Ni/Fe-P-c	10/50/100	277/441/551	200.49
CoP@Ni/Fe-P-a	10/50/100	303/456/575	193.08

Table S3. Electrocatalytic parameters for HER performance of the CoP@ Ni/Fe-P and previously reported electrocatalysts in 1 M KOH electrolyte.

Catalyst	Substrate	Current density j (mA cm^{-2})	Overpotential at corresponding E (mV)	Tafel slope (mV dec^{-1})	Ref.
CoP@Ni/Fe-P	CC	10	125	109.92	This work
Ti@Ni(OH)$_2$-NiMoS	Ti mesh	10	180	81	2
Cu-(a-NiSe$_x$/c-NiSe$_2$)/TiO$_2$	CC	10	156.9	51.2	3
MoS$_x$-20@rGO/CNTs	/	10	179	78.1	4
A-RuS$_2$	CFP	10	141	65.6	5
EDTA-CoCoPBA-1	/	10	173	69.5	6

Table S4. Electrocatalytic parameters for OER performance of the CoP@Ni/Fe-P and as-prepared contrast electrocatalysts in 1 M KOH electrolyte.

Catalyst	Current density [mA cm^{-2}]	Overpotential [mV]	Tafel slope [mV dec^{-1}]
CoP	10/50/100	315/439/548	156.26
Ni/Fe-P	10/50/100	284/373/463	80.06
CoP@Ni/Fe-P	10/50/100	250/335/411	41.47
RuO$_2$	10/50/100	320/404/482	62.88
CoP@Fe-P	10/50/100	267/363/453	78.17
CoP@Ni/Fe-P-c	10/50/100	267/375/487	79.69
CoP@Ni/Fe-P-a	10/50/100	299/389/475	125.96

Table S5. Electrocatalytic parameters for OER performance of the CoP@ Ni/Fe-P and previously reported electrocatalysts in 1 M KOH electrolyte.

Catalyst	Substrate	Current density j (mA cm^{-2})	Overpotential at corresponding E (mV)	Tafel slope (mV dec^{-1})	Ref.
CoP@Ni/Fe-P	CC	10	250	35.33	This work
Cu-(a-NiSe$_x$/c-NiSe$_2$)/TiO$_2$	CC	10	339	54.2	3
F-Co$_2$B	CC	10	320	32	7
Ru-H$_2$O/CC-350	CC	10	270	63	8
FePB/NiFeP	NF	10	182	43.9	9
Ni-B$_i$/meso-Ir	/	10	250	54.8	10

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