

## Electronic Supplementary Information

### ***In situ*-grown Co<sub>3</sub>S<sub>4</sub> sheet-functionalized metal-organic framework via surface engineering as HER catalyst in alkaline media**

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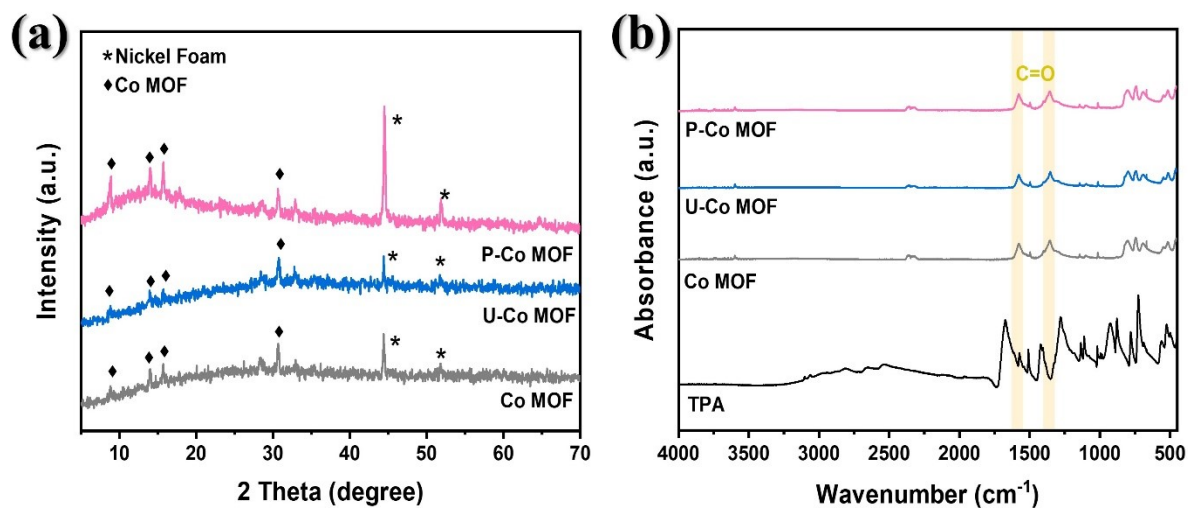
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## 1. Supplementary Results

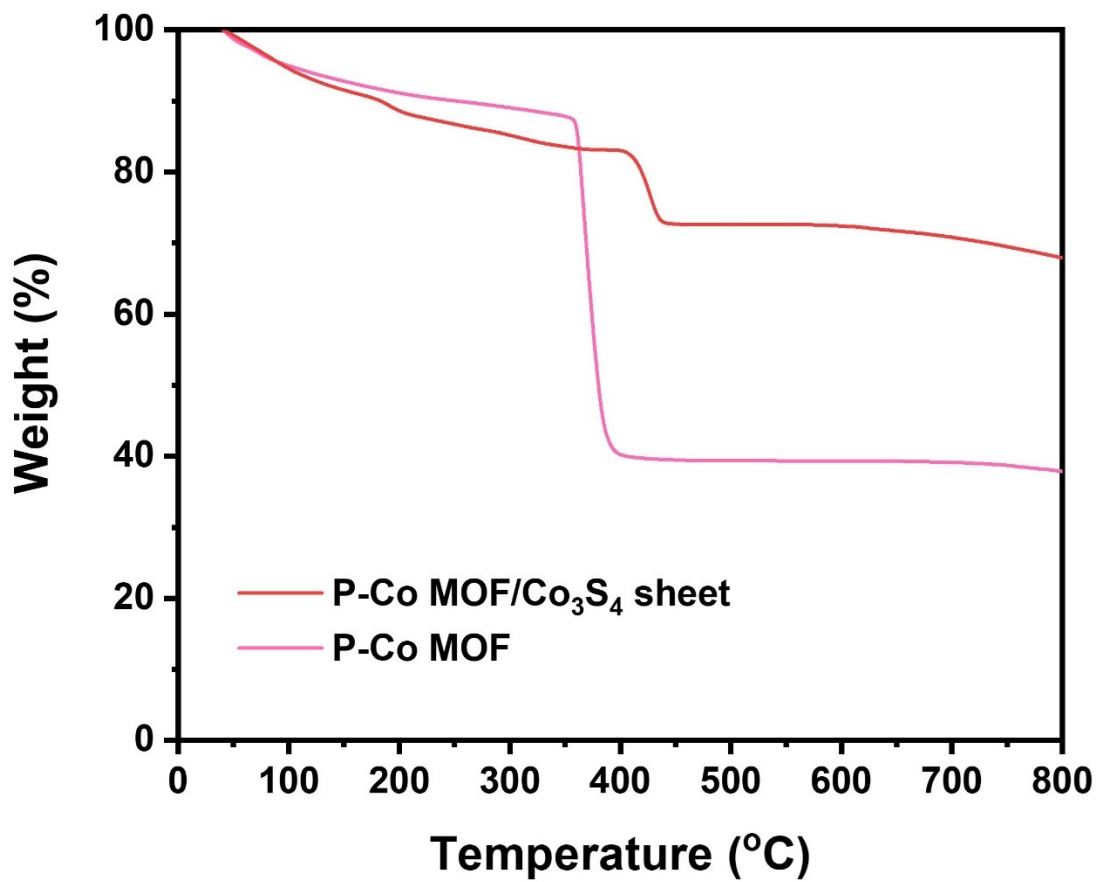
**Table S1.** List of Abbreviations.

Abbreviations	Full form
Co MOF	Cobalt Metal organic framework
U-Co MOF	Urea-Cobalt Metal organic framework
P-Co MOF	PVP-Cobalt Metal organic framework
Co MOF/Co <sub>3</sub> S <sub>4</sub> sheet	Cobalt Metal organic framework derived Co <sub>3</sub> S <sub>4</sub> sheet
U-Co MOF/Co <sub>3</sub> S <sub>4</sub> sheet	Urea-Cobalt Metal organic framework derived Co <sub>3</sub> S <sub>4</sub> sheet
P-Co MOF/Co <sub>3</sub> S <sub>4</sub> sheet	PVP-Cobalt Metal organic framework derived Co <sub>3</sub> S <sub>4</sub> sheet

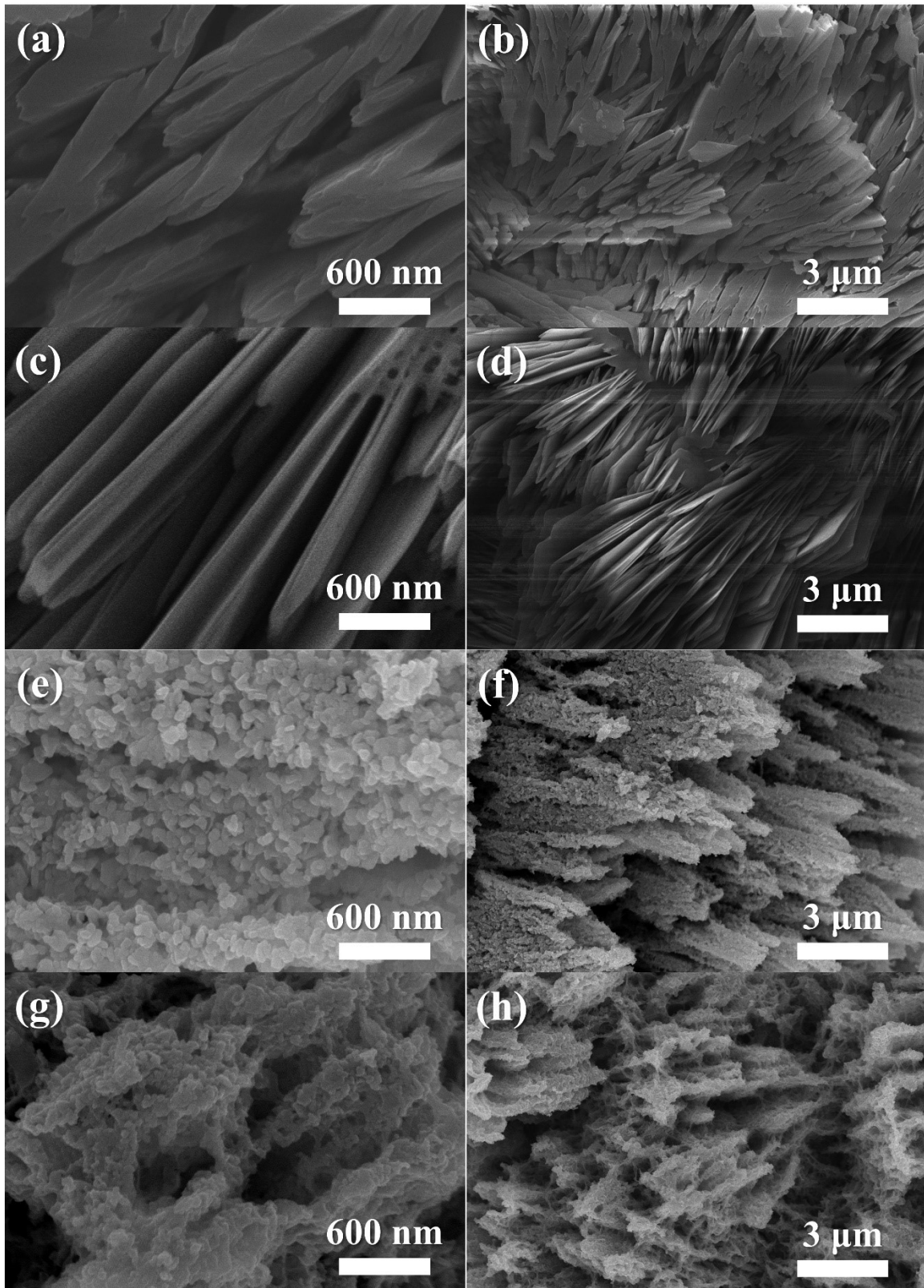
**Figure S1.** (a) XRD patterns and (b) FT-IR spectra of Co MOF, U-MOF, and P-Co MOF.



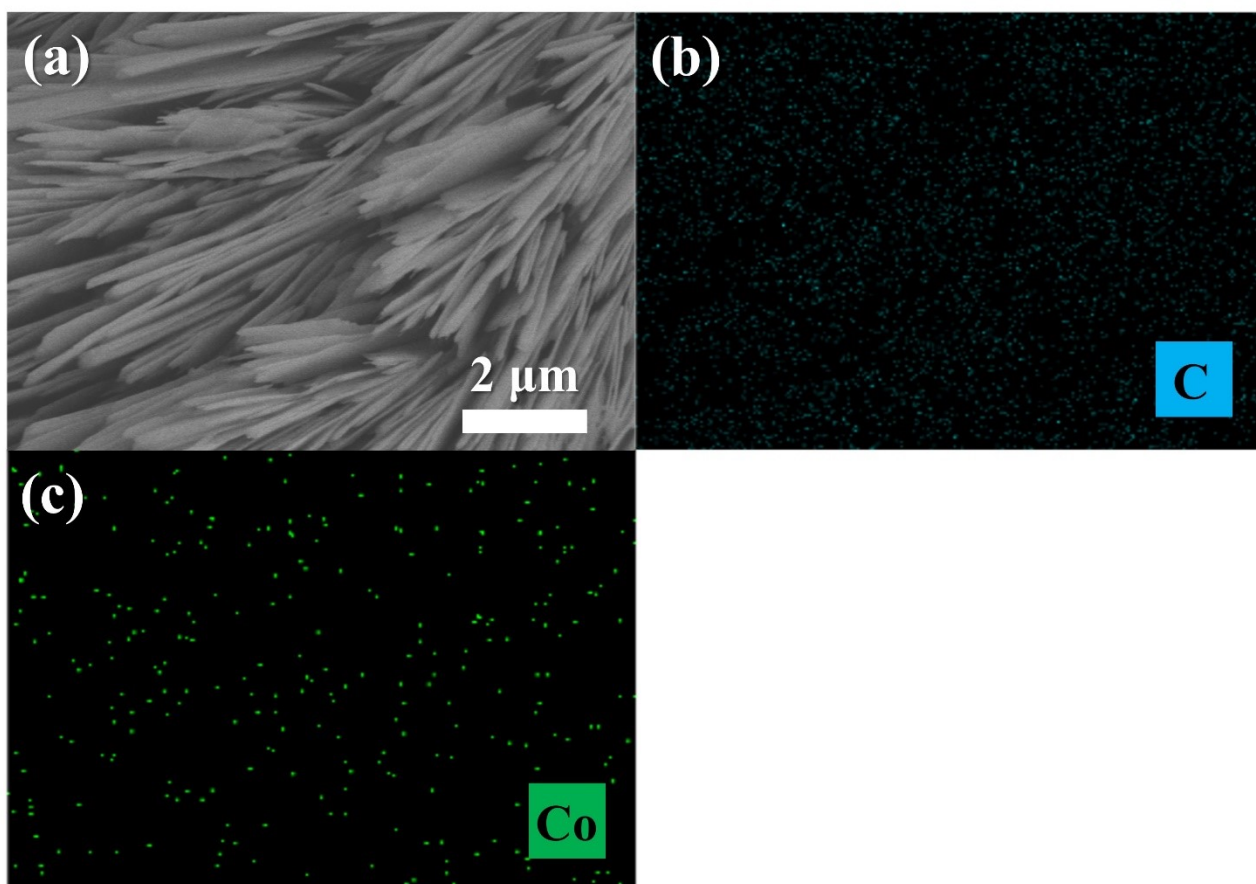
**Figure S2.** TGA curves of P-Co MOF, and P-Co MOF/Co<sub>3</sub>S<sub>4</sub> sheet in N<sub>2</sub> atmosphere.



**Figure S3.** FE-SEM images of the samples: (a, b) high and low magnification images of Co MOF, (c, d) high and low magnification images of U-MOF, (e, f) high and low magnification images of Co MOF/Co<sub>3</sub>S<sub>4</sub> sheet, and (g, h) high and low magnification images of U-Co MOF/Co<sub>3</sub>S<sub>4</sub> sheet.

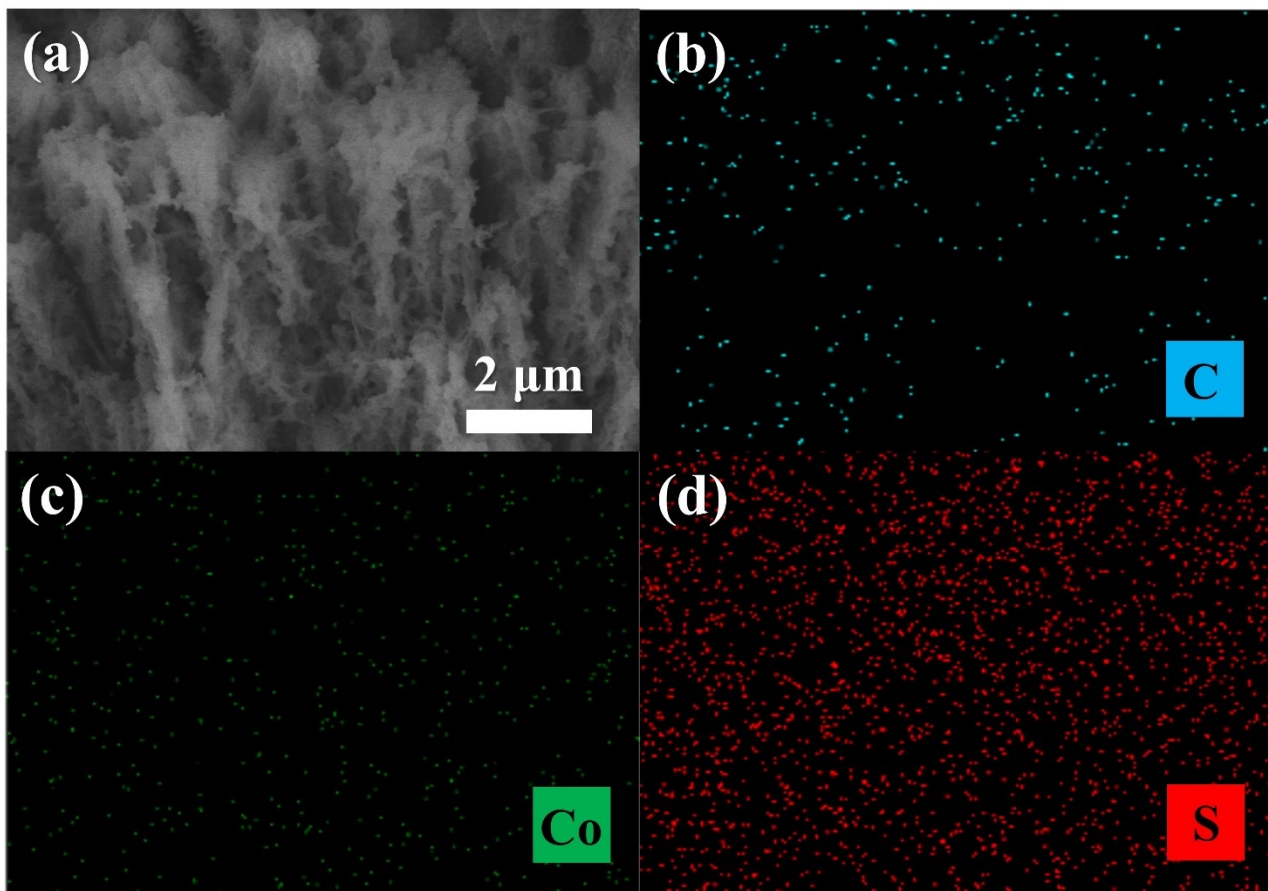


**Figure S4.** (a) SEM-EDS elemental mapping scan area, (b) C, and (c) Co elemental maps of P-Co MOF.





**Figure S5.** (a) SEM-EDS elemental mapping scan area, (b) C, (c) Co, and (d) S elemental maps of P-Co MOF/Co<sub>3</sub>S<sub>4</sub> sheet.



**Figure S6.** Photograph image measuring pH of 1M KOH electrolyte.



**Video S1.** The P-Co MOF/Co<sub>3</sub>S<sub>4</sub> sheet electrode for HER in alkaline media.

Please find attached the video file.

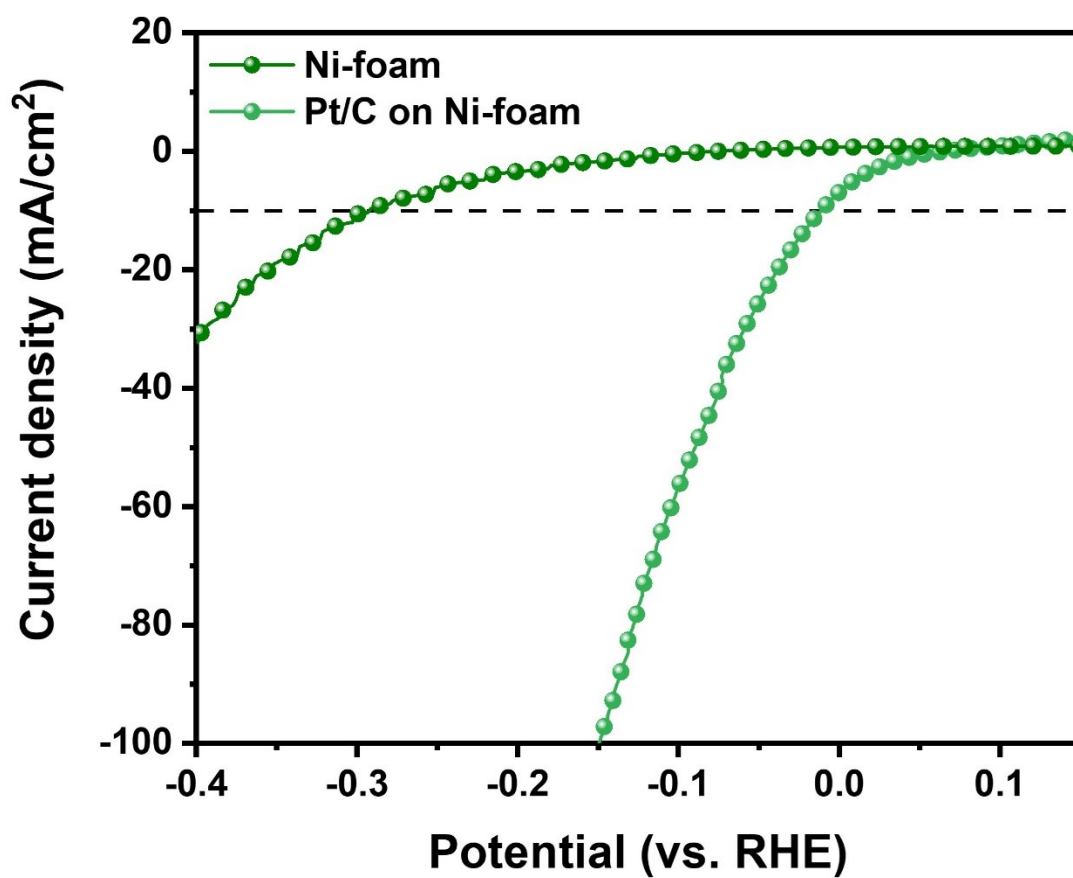
**Table S2.** XPS atomic percentage analysis based on the survey spectra.

Electrocatalyst	C	O	S	Co
P-Co MOF	59.40	33.43	-	7.18
P-Co MOF/Co <sub>3</sub> S <sub>4</sub> sheet	22.02	53.85	7.97	16.15

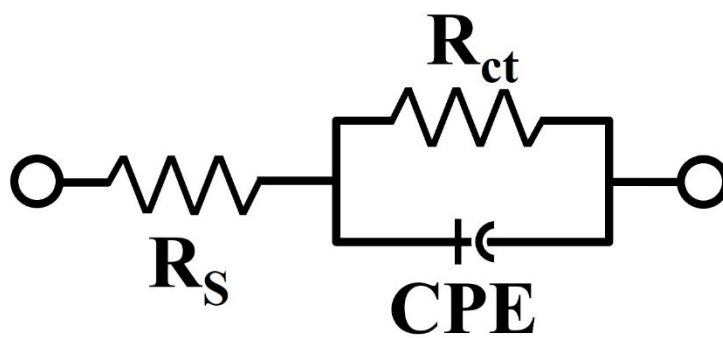
**Table S3.** Electrochemical properties of Co MOF/Co<sub>3</sub>S<sub>4</sub> sheet *via* surface engineering.

Electrocatalyst	$\eta$ , Overpotential@10 mA/cm <sup>2</sup> (mV)	Tafel slope (mV/dec)	C <sub>dl</sub> (mF/cm <sup>2</sup> )
Co MOF	212.8	129	10.22
U-Co MOF	208.4	108	17.04
P-Co MOF	201.6	109	22.96
Co MOF/Co <sub>3</sub> S <sub>4</sub> sheet	154.6	117	45.5
U-Co MOF/Co <sub>3</sub> S <sub>4</sub> sheet	136.2	96	46.4
P-Co MOF/Co <sub>3</sub> S <sub>4</sub> sheet	117.9	96	57.9

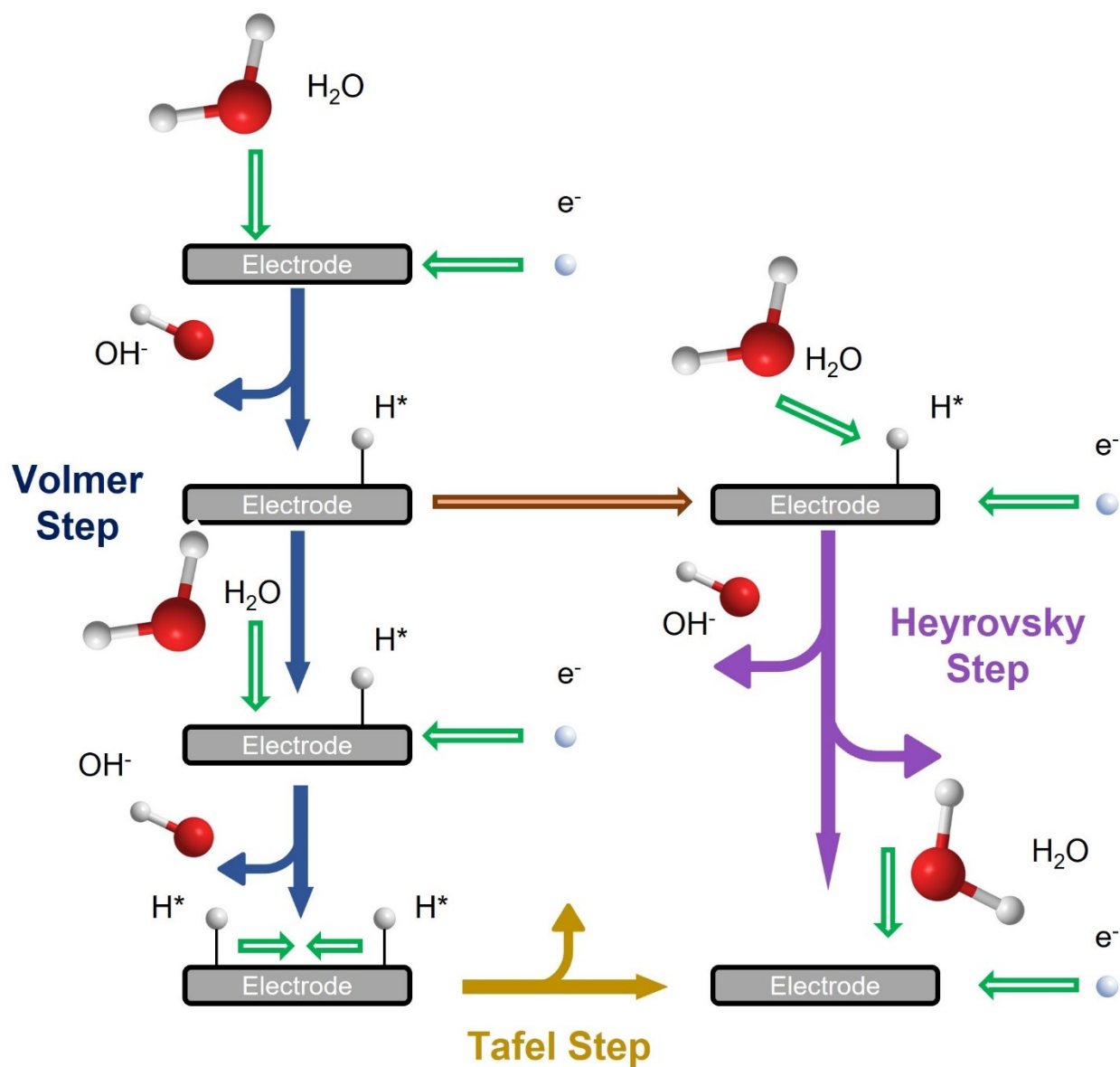
Figure S7. iR-corrected HER polarization curves of Ni-foam and Pt/C on Nickel foam.



**Figure S8.** Equivalent circuit of HER devices.

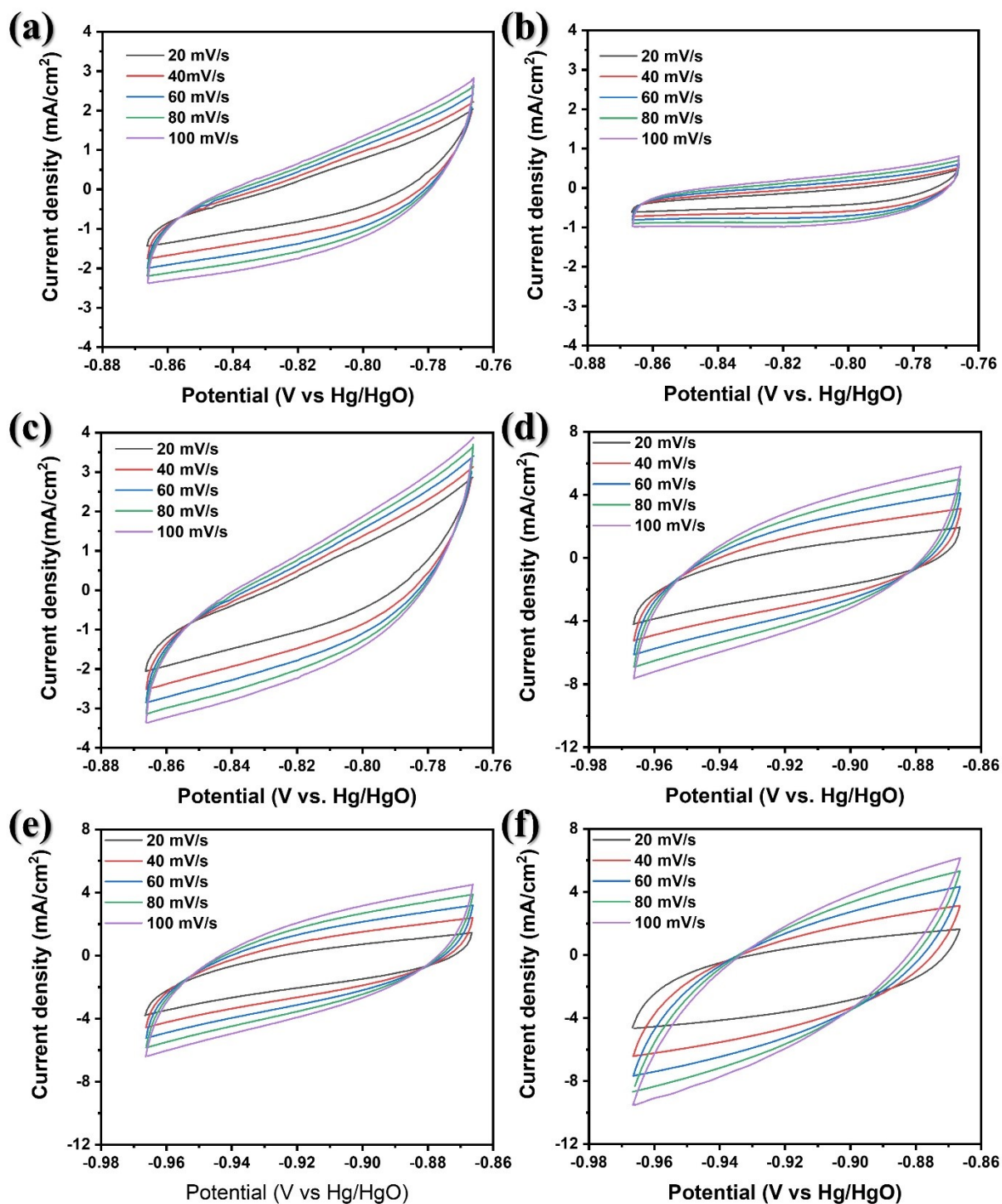


**Figure S9.** Hydrogen evolution reaction (HER) mechanism under alkaline electrolyte.

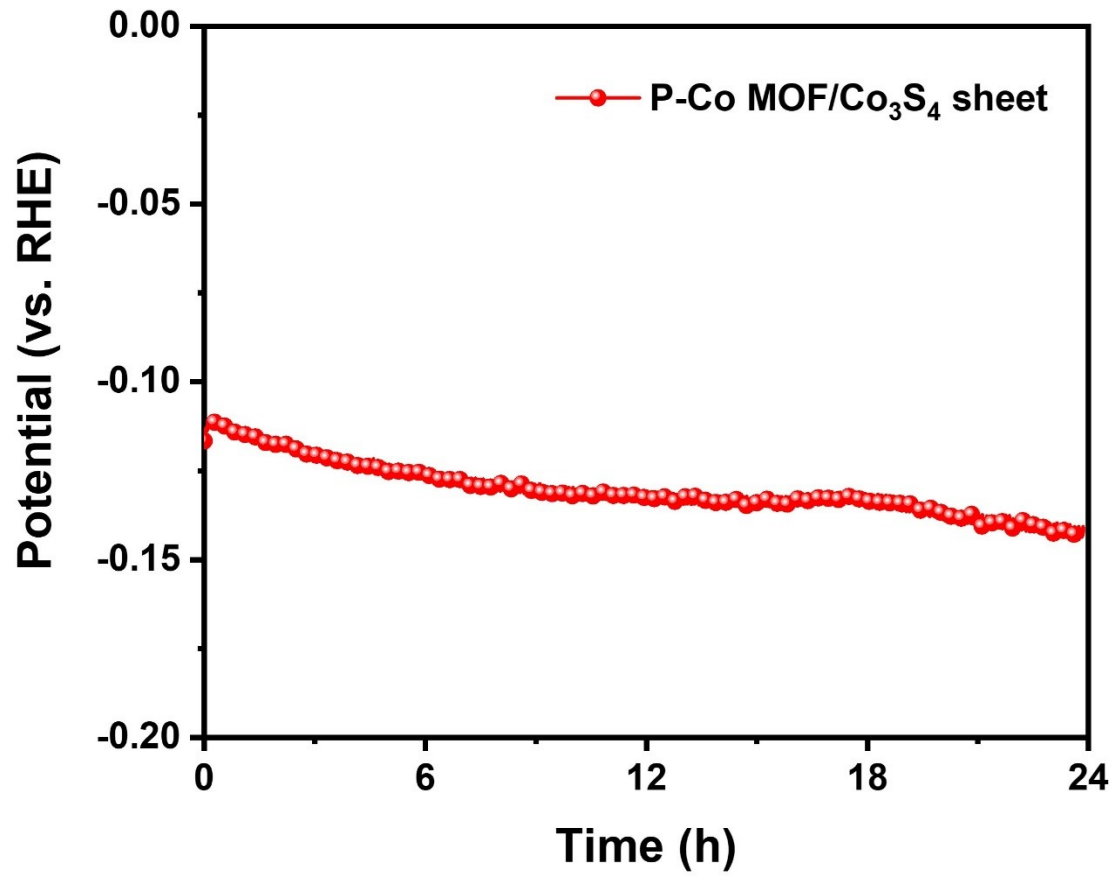




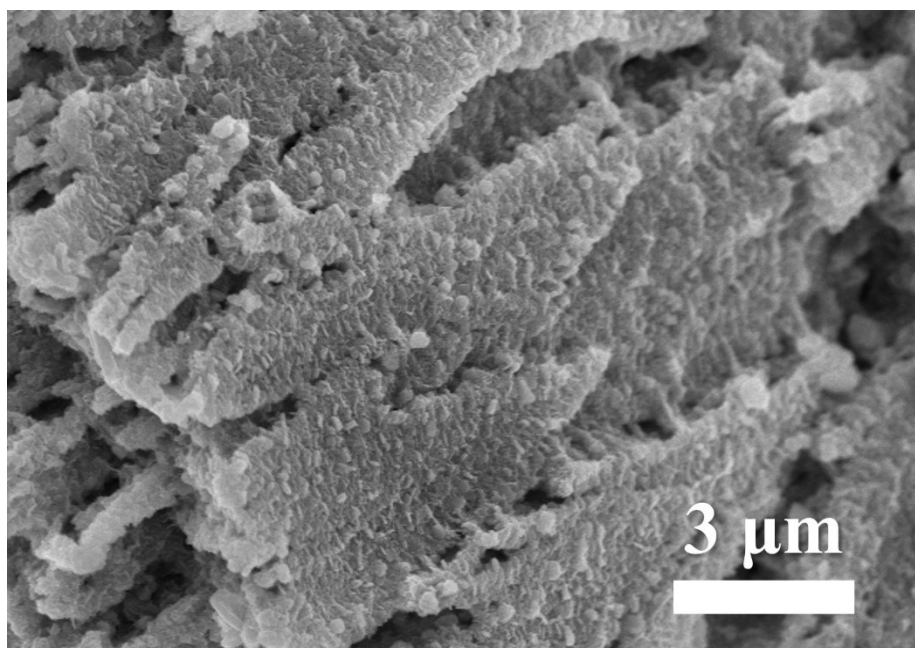
**Figure S10.** Cyclic voltammograms of (a) Co MOF, (b) U-Co MOF, (c) P-Co MOF, (d) Co MOF/Co<sub>3</sub>S<sub>4</sub> sheet, (e) U-Co MOF/Co<sub>3</sub>S<sub>4</sub> sheet, and (f) P-Co MOF/Co<sub>3</sub>S<sub>4</sub> sheet.



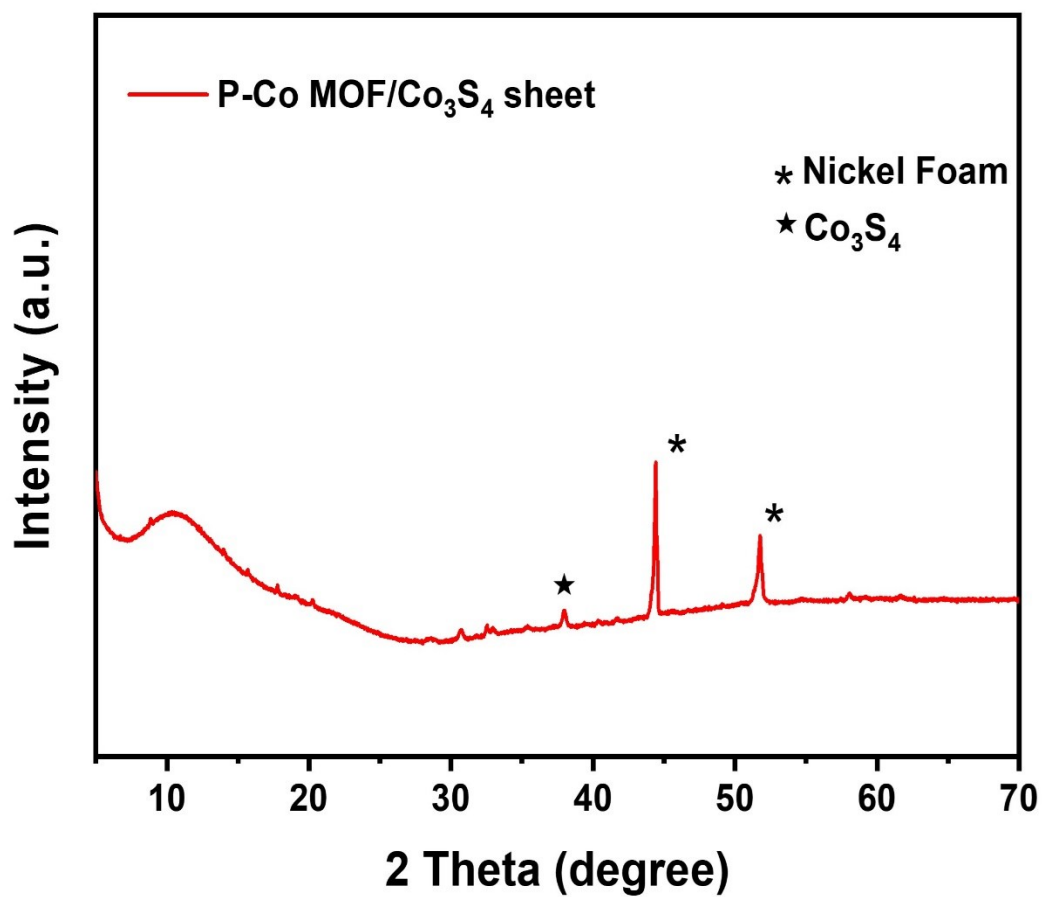
**Figure S11.** Chronopotentiometric curve of the P-Co MOF/Co<sub>3</sub>S<sub>4</sub> sheet with constant current density of -10 mA cm<sup>-2</sup>.



**Figure S12.** SEM image of P-Co MOF/Co<sub>3</sub>S<sub>4</sub> sheet after long-term HER operation.



**Figure S13.** XRD pattern of P-Co MOF/Co<sub>3</sub>S<sub>4</sub> sheet after long-term HER operation.



**Table S4.** Comparison of electrocatalysts for hydrogen evolution reaction reported in the literatures.

Electrocatalyst	Synthesis method	Electrolyte	$\eta$ , Overpotential@- 10 mA/cm <sup>2</sup> (mV)	Tafel slope (mV/dec)	Reference
P-Co MOF/Co <sub>3</sub> S <sub>4</sub> sheet	Hydrothermal	1 M KOH	117.9	96	This work
Co <sub>0.37</sub> S <sub>0.38</sub> P <sub>0.02</sub> NSs	Hydrothermal	1 M KOH	218	103	[61]
Co <sub>3</sub> S <sub>4</sub> /MoS <sub>2</sub> NR	Hydrothermal	1 M KOH	116	59	[62]
Ni-Co sulfide/NF	Hydrothermal	1 M KOH	190	147	[63]
Cu- Ni <sub>3</sub> S <sub>2</sub> /Co <sub>3</sub> S <sub>4</sub> /NF	Hydrothermal	1 M KOH	176	50.4	[64]
Co <sub>3</sub> S <sub>4</sub> @Mo- Co <sub>3</sub> S <sub>4</sub> -Ni <sub>3</sub> S <sub>2</sub> /NF	Hydrothermal	1 M KOH	116	97	[65]
MILN-based Co <sub>3</sub> S <sub>4</sub> /MnS <sub>2</sub>	Hydrothermal	1 M KOH	132	150	[66]
Co <sub>0.5</sub> Mo <sub>0.5</sub> S <sub>x</sub> + XC72R	Hydrothermal	1 M KOH	131	75	[67]
Co <sub>9</sub> S <sub>8</sub> /WS <sub>2</sub> nanobelt	Hydrothermal	1 M KOH	138	80.2	[68]
CoMoS@CNF	Hydrothermal	1 M KOH	105	152.8	[69]
NiS <sub>2</sub> /MoS <sub>2</sub> @GNS	Hydrothermal	1 M KOH	130	40	[70]