Supporting Information

Multi-interfacial engineering of coil-like NiS-Ni_2P/Ni hybrid to efficiently boost electrocatalytic hydrogen generation in alkaline and neutral electrolyte

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1. Supplementary Figures

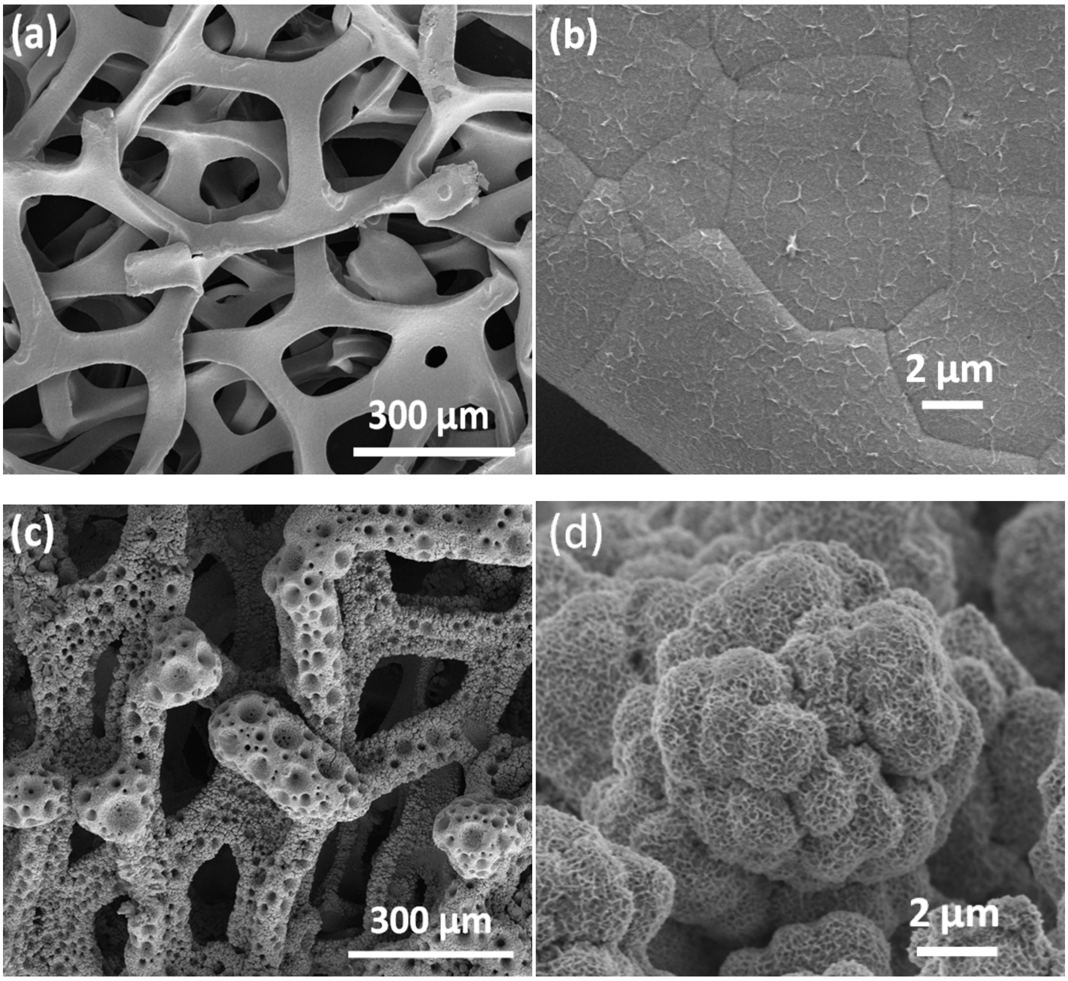

Figure S1. SEM characterization of NF and Ni/NF. (a,b) bare NF and (c,d) electrodeposited Ni/NF.

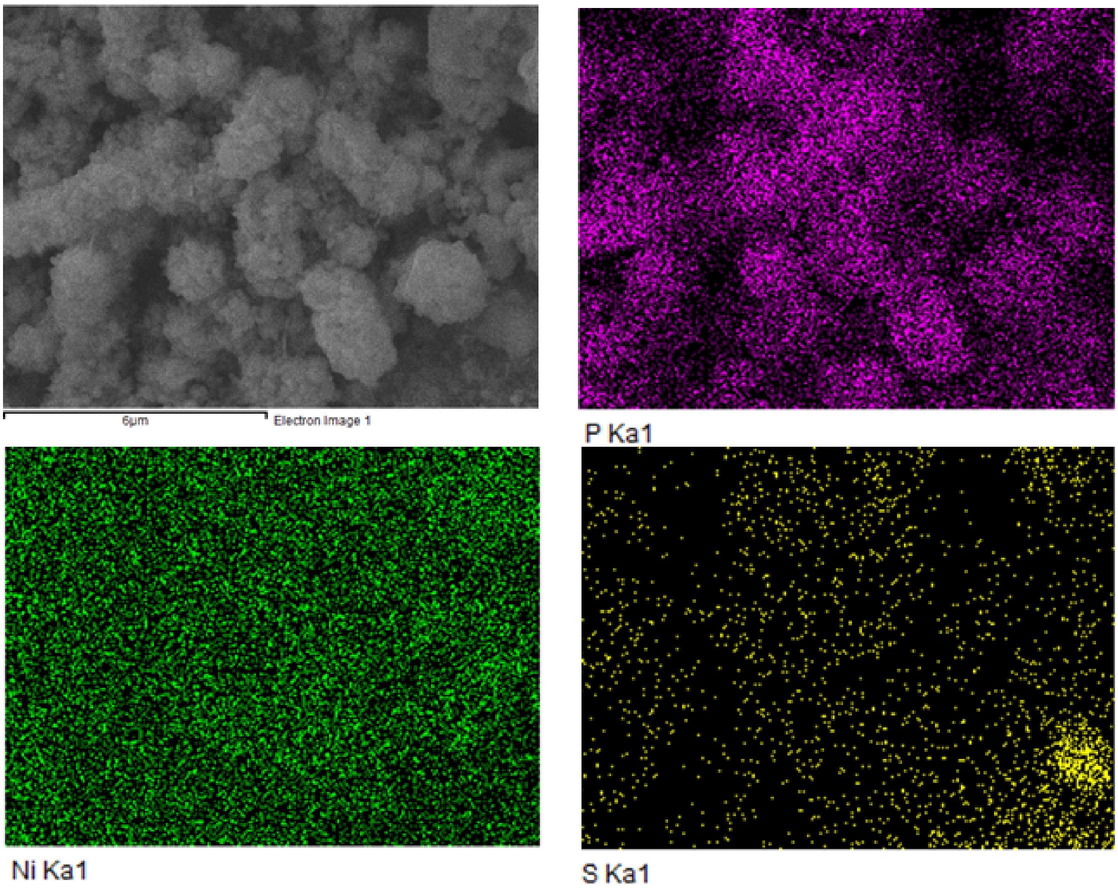

Figure S2. Corresponding elemental mapping images of NiS-Ni_2P/Ni/NF catalyst.

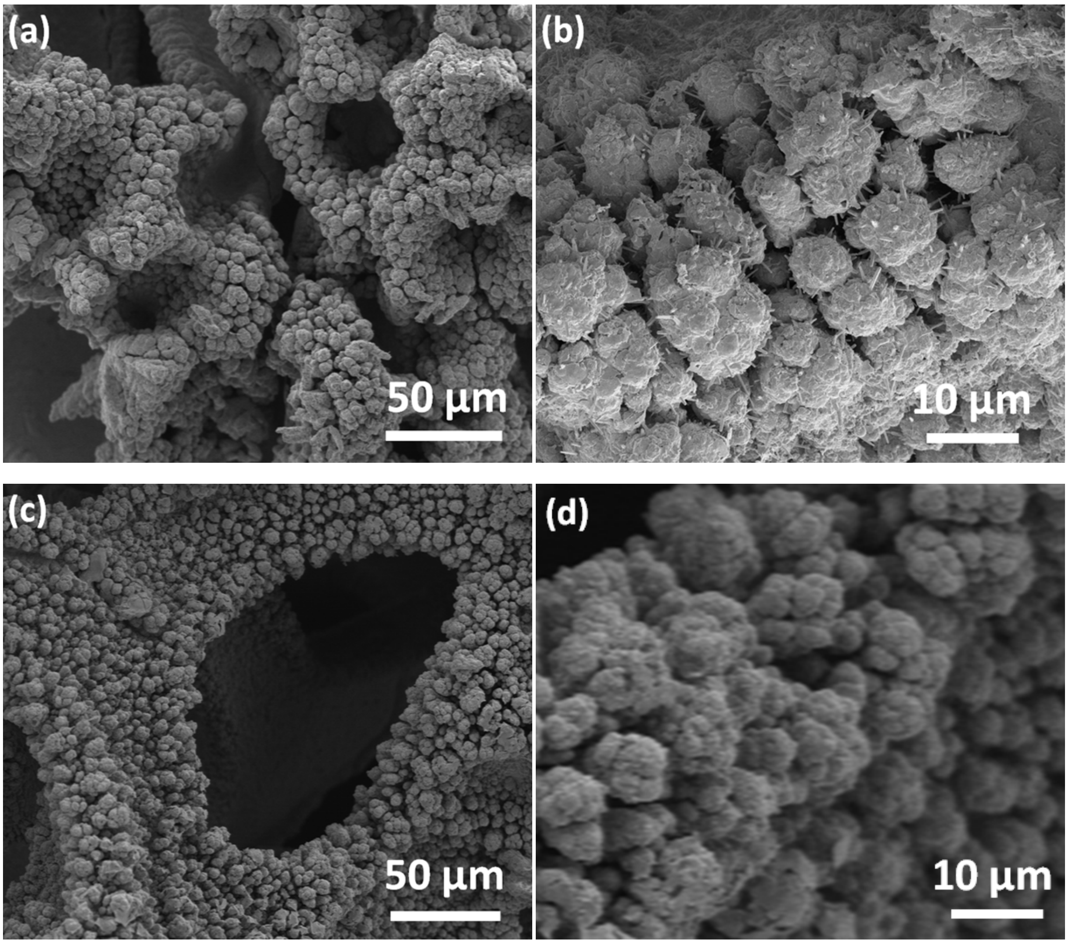

Figure S3. SEM characterization of Ni_2P/Ni/NF and NiS/Ni/NF. (a,b) Ni_2P/Ni/NF and (c,d) NiS/Ni/NF.

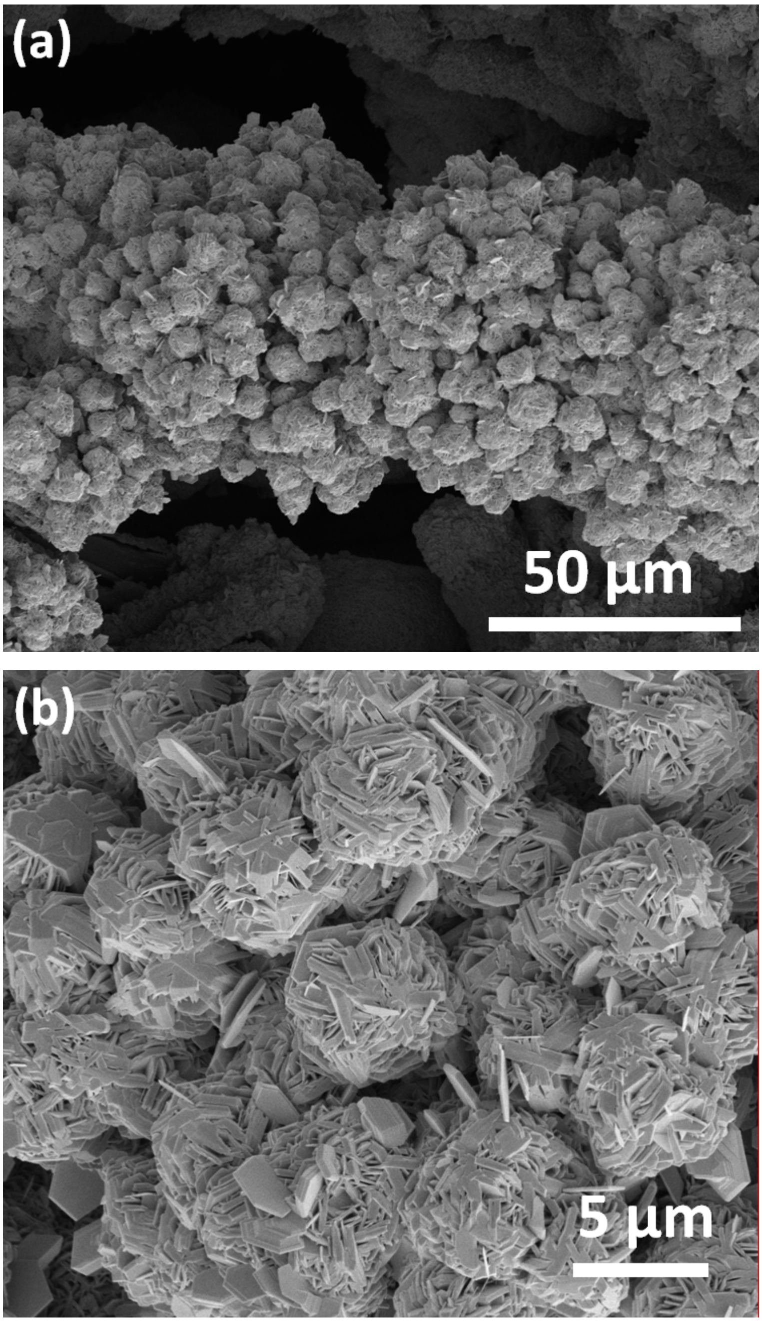

Figure S4. SEM images at different magnifications of the NiS-Ni_2P/Ni/CC with different magnifications.

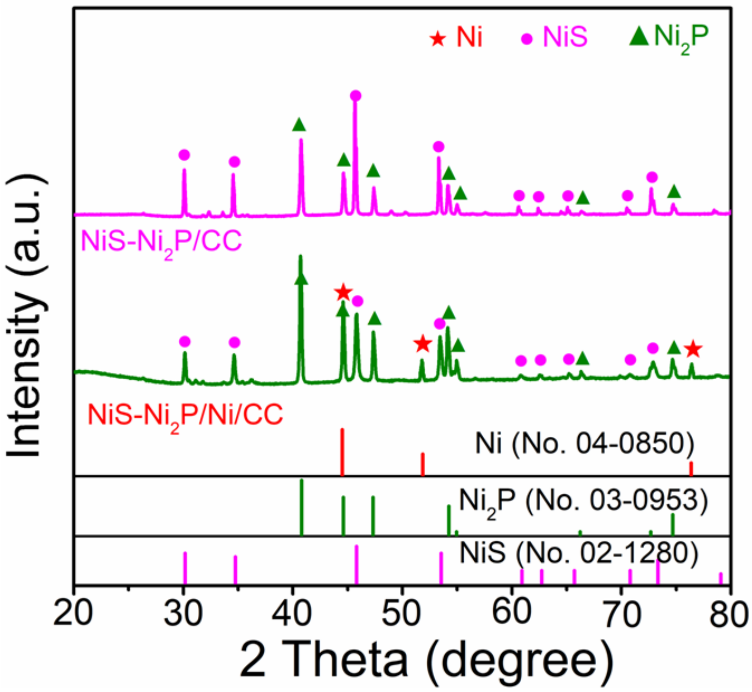

Figure S5. XRD patterns of excessive sulfuration/phosphorization (NiS-Ni_2P/CC) and partial sulfuration/ phosphorization (NiS-Ni_2P/Ni/CC).

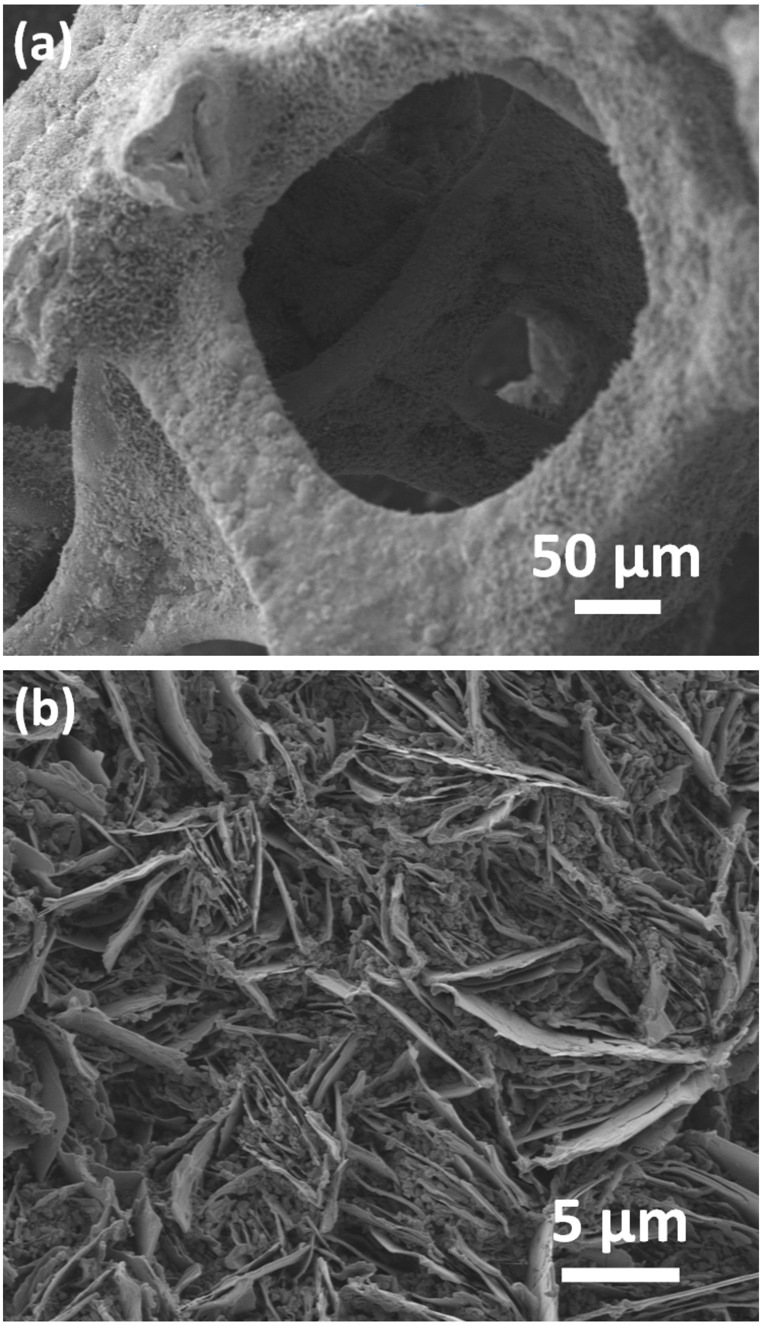

Figure S6. SEM images at different magnifications of the NiS-Ni_2P/NF with different magnifications.

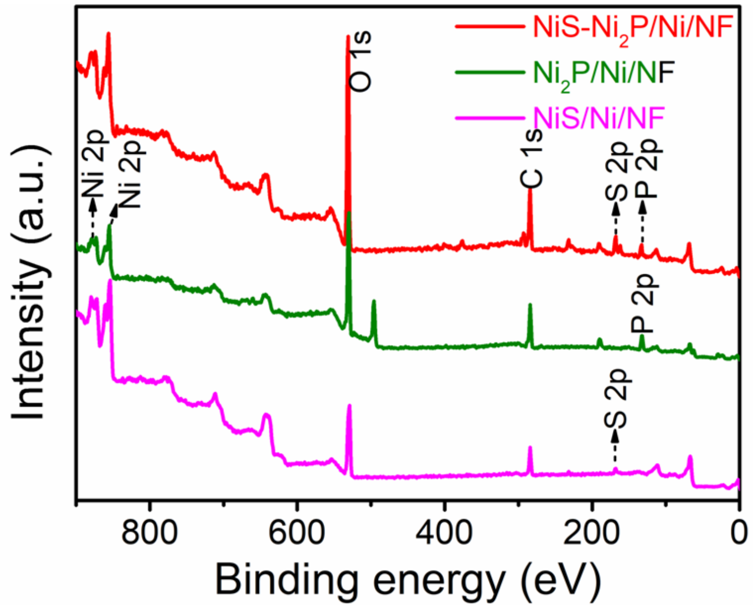

Figure S7. XPS survey spectra of NiS-Ni_2P/Ni/NF, Ni_2P/Ni/NF, and NiS/Ni/NF.

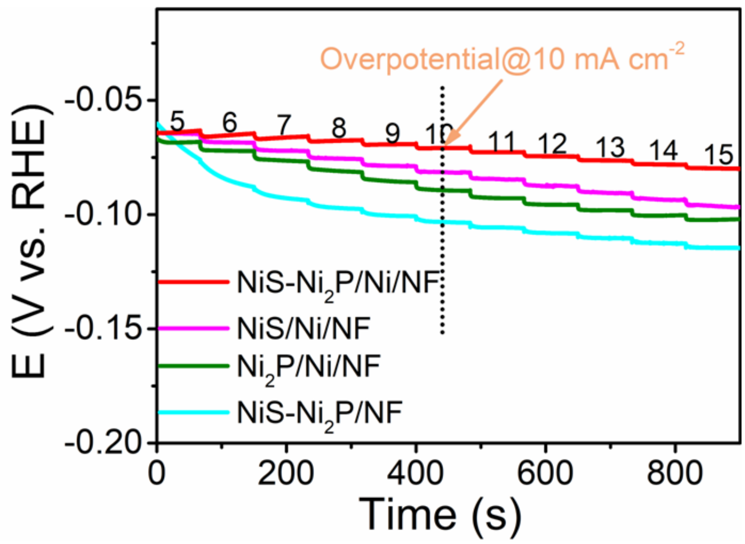

Figure S8. Chronopotentiometric plots of HER of the samples at different current densities in 1 M KOH.

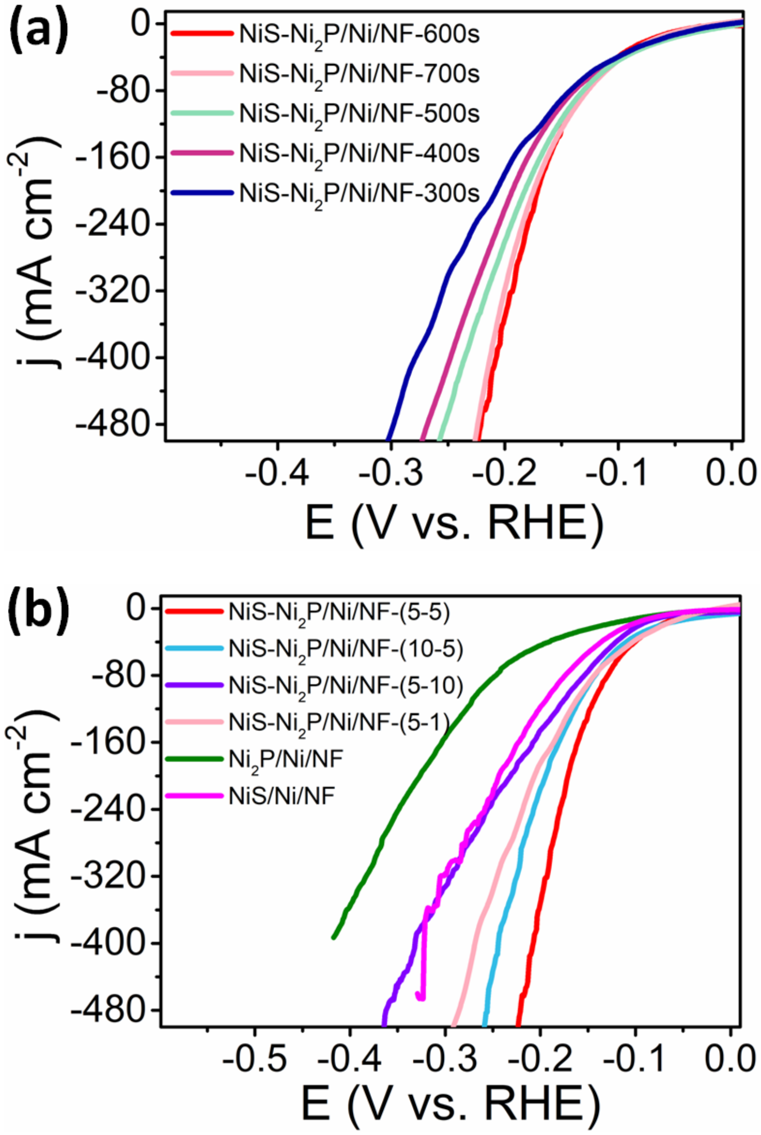

Figure S9. The Polarization curves of (a) different samples of NiS-Ni_2P/Ni/NF-a (a=300, 400, 500, 600, and 700s) obtained by different electrodeposition time, (b) different samples of NiS-Ni_2P/Ni/NF-(x-y) (x is the molar of S and y is the molar of NaH_2PO_2) obtained by different amount of S and P precursor.

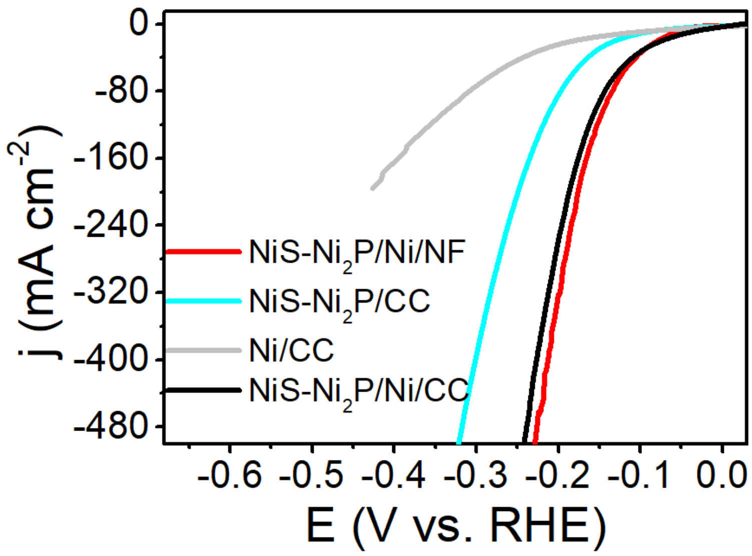

Figure S10. HER polarization curves of NiS-Ni_2P/Ni/NF, NiS-Ni_2P/CC, Ni/CC， and NiS-Ni_2P/Ni/CC in 1 M KOH solution.

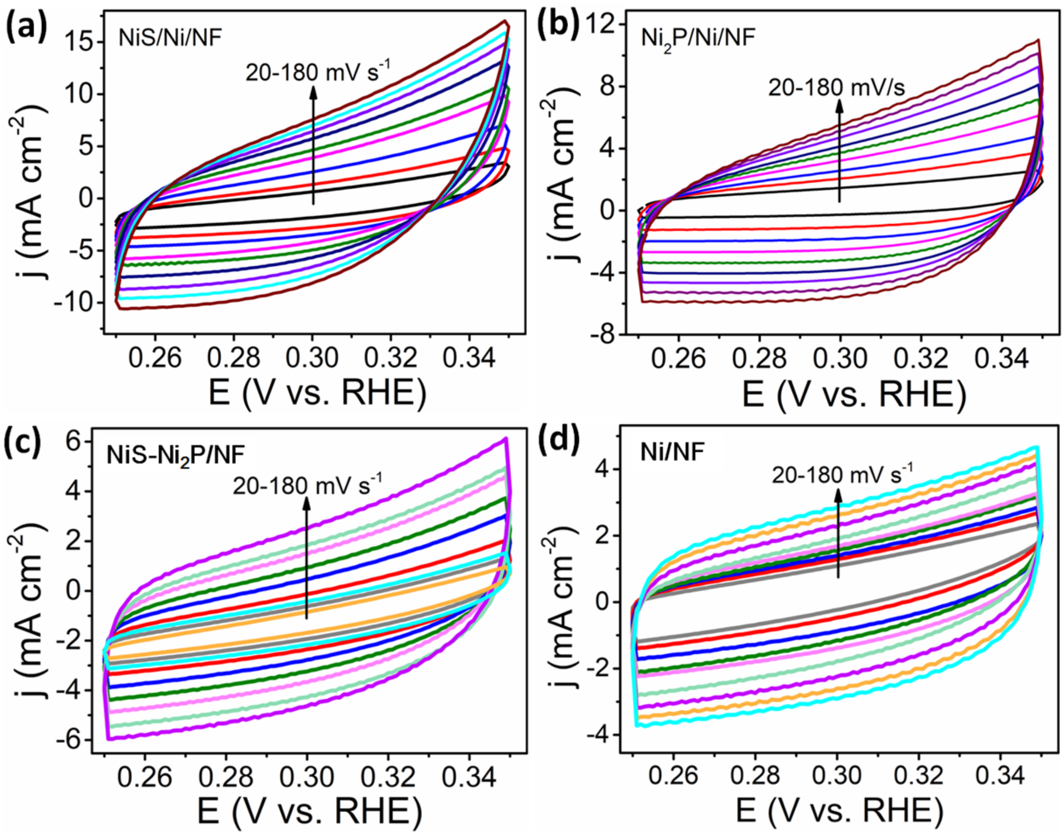

Figure S11. Cyclic voltammograms at various scan rates of 20, 40, 60, 80, 100, 120, 140, 160 and 180 mV s^{-1} at η= 0.25-0.35 V vs RHE for (a) NiS/Ni/NF, (b) Ni_2P /Ni/NF, (c) NiS-Ni_2P/NF, and (d) Ni/NF.

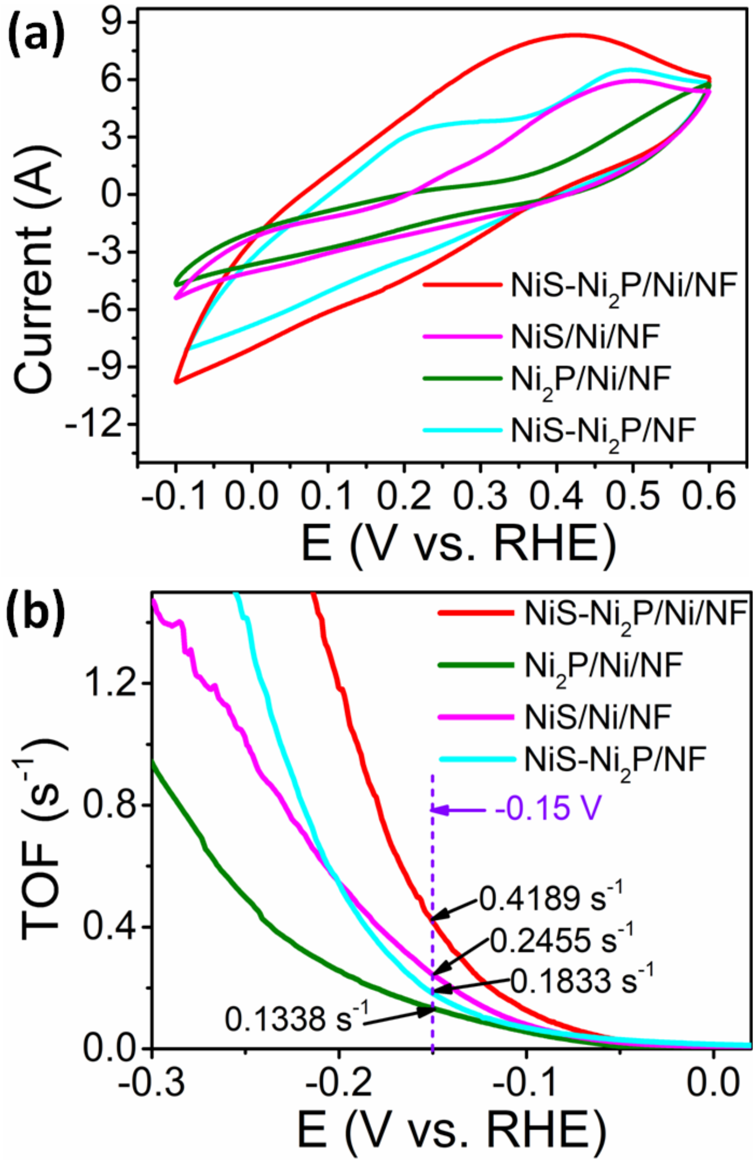

Figure S12. (a) Cyclic voltammograms (−0.1–0.6 V) of NiS-Ni_2P/Ni/NF, NiS/Ni/NF, Ni_2P/Ni/NF, and NiS-Ni_2P/NF recorded at pH = 7 phosphate buffer with a scan rate of 50 mV s^{-1}. (b) TOF curves of the NiS-Ni_2P/Ni/NF, NiS/Ni/NF, Ni_2P/Ni/NF, and NiS-Ni_2P/NF catalysts.

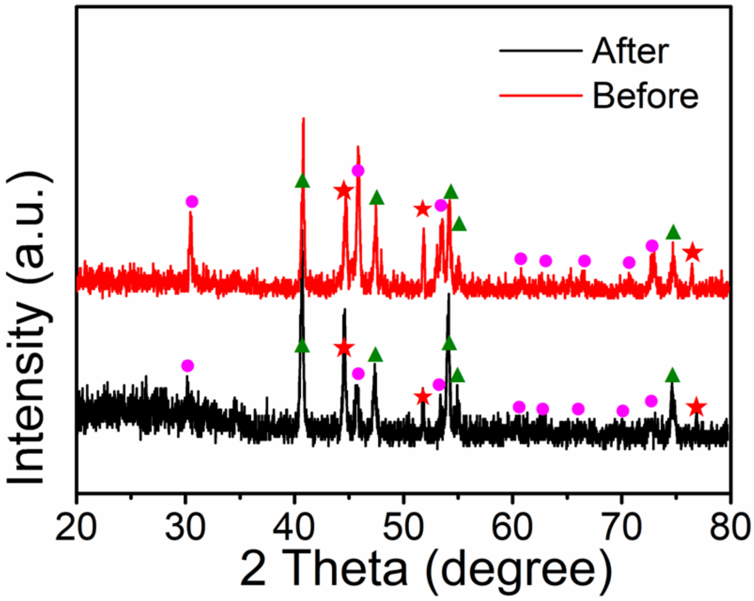

Figure S13. XRD patterns of NiS-Ni_2P/Ni/NF after HER stability test in alkaline solution.

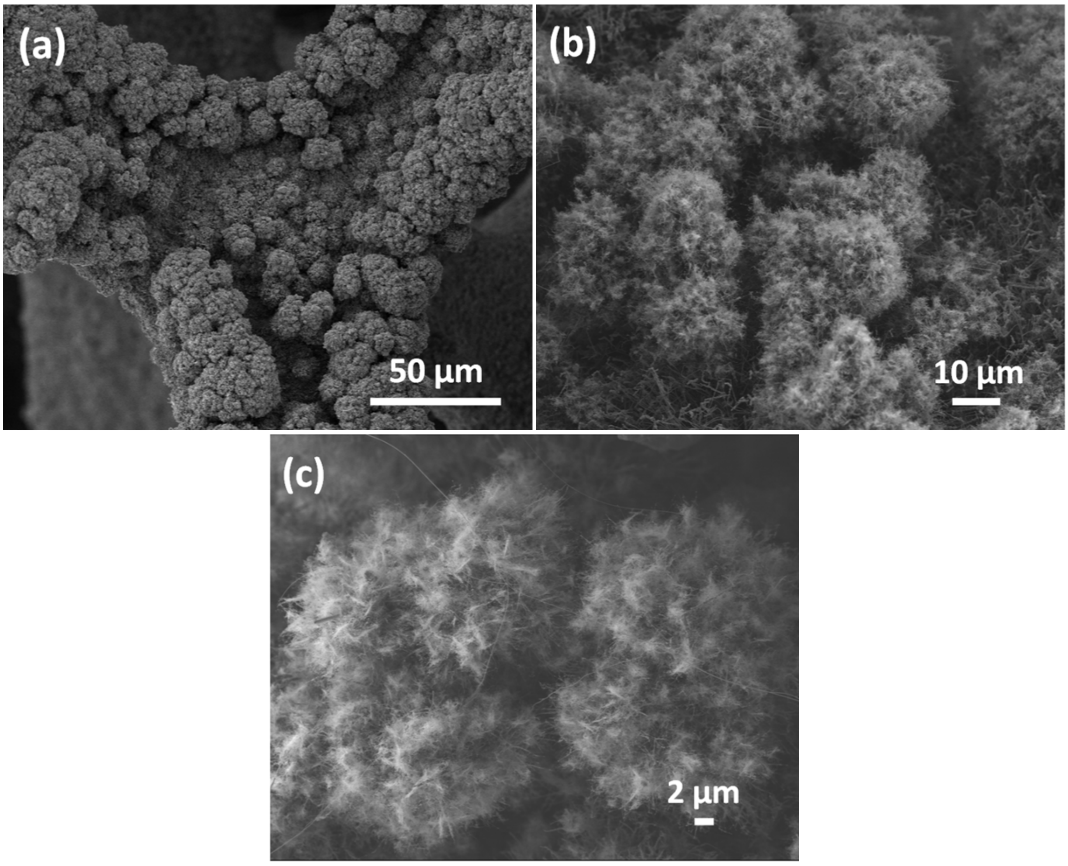

Figure S14. SEM images of $NiS-Ni_2P/Ni/NF$ after HER stability test in alkaline solution.

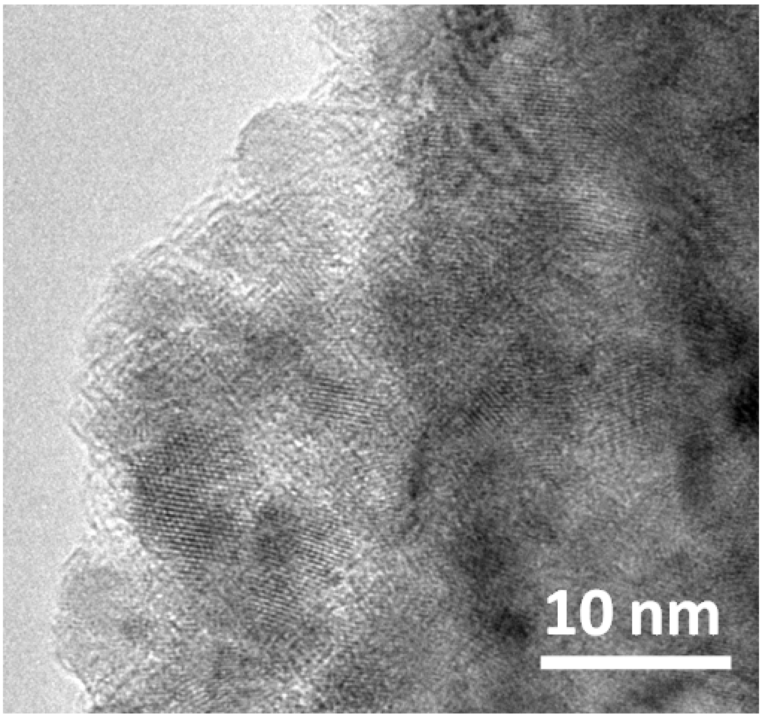

Figure S15. TEM images of NiS-Ni_2P/Ni/NF after stability test in alkaline solution.

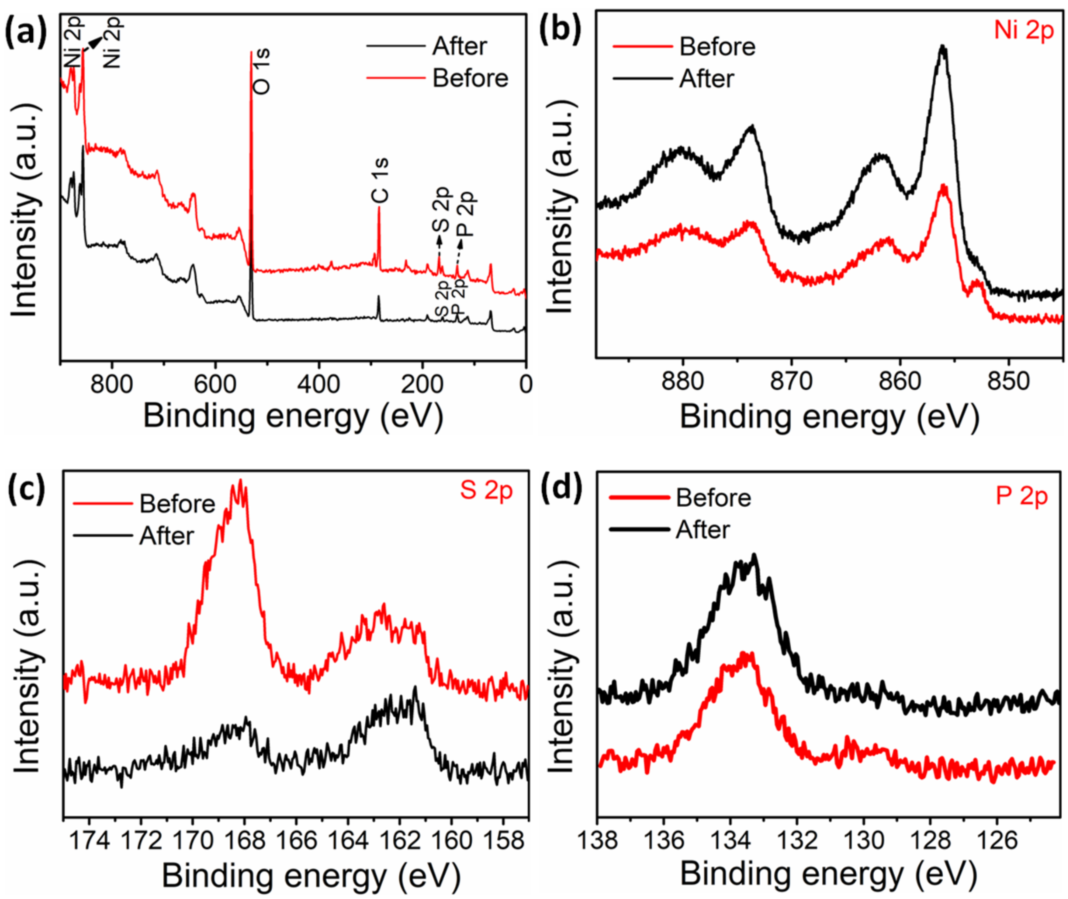

Figure S16. (a) XPS survey and (b-d) High-resolution XPS spectra: (b)Ni 2p, (c) S 2p, and (c) P 2p in NiS-Ni_2P/Ni/NF before and after stability measurement.

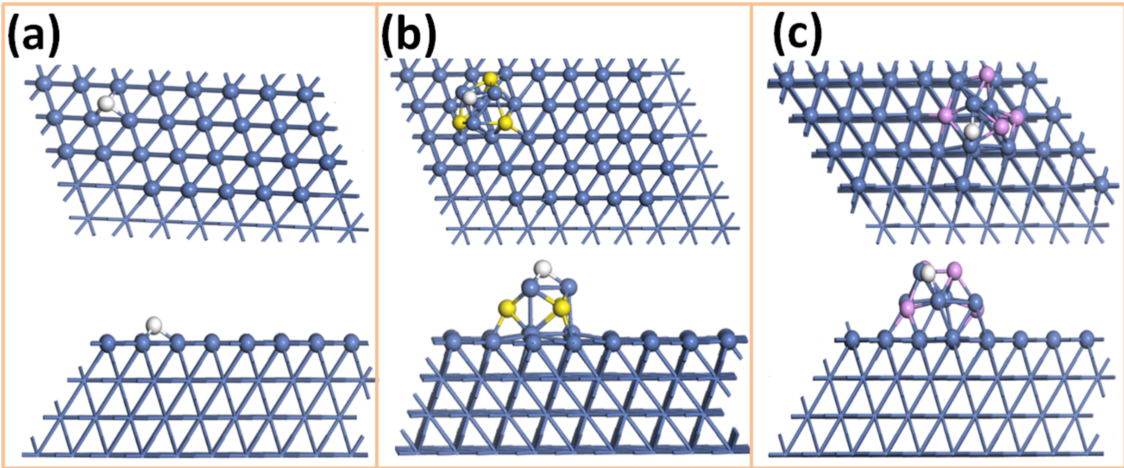

Figure S17. Optimized models for *H intermediate of HER process on site of (a) Ni, (b) NiS/Ni, and (c) Ni_2P/Ni, showing both the top view (top) and side view (bottom) of each structure. Color codes: blue (Ni), pink (P), yellow (S), and white (H).

2. Supplementary Tables

Table S1. Average mass loading on Ni foam (NF) current collector.

Samples	Mass loading[a] (mg cm^{-2})
NiS-Ni_2P/Ni/NF	17.1
NiS/Ni/NF	16.8
Ni_2P/Ni/NF	17.0
NiS-Ni_2P/NF	15.6
Ni/NF	15.1
20wt% Pt/C/NF	1.62

Table S2. The Ni, P, and S content of NiS-Ni_2P/Ni/NF electrocatalysts.

Samples	Composition (wt%)		
	Ni[a]	P[a]	S[b]
NiS-Ni_2P/Ni/NF	61.35	8.16	14.74

[a]Ni and P content by ICP-AES. [b]S content by elemental analyzer.

Table S3. The composition of NiS-Ni_2P/Ni/NF, Ni_2P/Ni/NF, and NiS/Ni/NF from XPS.

Catalysts	C (wt.%)	Ni (wt.%)	S (wt.%)	P (wt.%)	O (wt.%)
NiS-Ni_2P/Ni/NF	36.19	19.22	13.5	10.23	20.86
Ni_2P/Ni/NF	40.88	14.79	-	18.51	25.82
NiS/Ni/NF	37.26	15.75	16.84	-	30.15

Table S4. HER performance of the as-prepared samples in 1.0 M KOH solution.

Catalysts	Overpotential at 10 mA cm^{-2} (mV)	Overpotential at 100 mA cm^{-2} (mV)
$NiS\text{-}Ni_2P/Ni/NF$	53	139
NiS/Ni/NF	79	188
$Ni_2P/Ni/NF$	90	265
$NiS\text{-}Ni_2P/NF$	107	218
Ni/NF	121	356
20wt% Pt/C/NF	45	177

Table S5. Comparison of HER performance of the developed NiS-Ni_2P/Ni/NF electrocatalyst in this work with other high-performance catalysts in 1.0 M KOH.

Catalysts	Overpotential	Ref.
NiS-Ni_2P/Ni/NF	**η_{10}=53 mV; η_{100}=139 mV**	**This work**
Ni_2P-Ni_3S_2 HNAs on NF	η_{10}=80 mV	1
$Co_{0.9}S_{0.58}P_{0.42}$	η_{10}=141 mV	2
Ni_3S_4@MoS_2/CC-3	η_{10}=97 mV	3
NiSP/NF	η_{10}=93 mV	4
$N_{i2}P$/Ni_3Se_4-5.0	η_{10}=57 mV	5
V-Ni_3S_2/Ni_xP_y/NF nanosheet	η_{10}=90 mV	6
NiNS	η_{100}=197 mV	7
NiS_2-MoS_2	η_{10}=76 mV	8
O-NiCoP/Ni_2P	η_{10}=58 mV	9
Ni-S-P/NF	η_{10}=120 mV	10
NiS/Ni_2P/CC	η_{20}=111 mV	11
CP/Ni_2P/NiS	η_{10}= 103 mV	12
Ni-P-S nanosheets array	η_{10}= 101.9 mV	13
N-$NiMoO_4$/NiS_2	η_{10}=99 mV	14
Ni_2P@FePOx heterostructure	η_{10}=75 mV	15
Ni_2P/NF	η_{10}=116 mV	16
v-NiS_2/CeO_2 HSs	η_{10}=123 mV	17
NiS-Gr-CC	η_{10}=71 mV	18
NiS/NiS_2/Ni_3S_4	η_{10}=68 mV	19
Mo-NiS/$Ni(OH)_2$	η_{10}=74 mV	20
Ni_2P/Ni@C	η_{10}=149 mV	21
Ni_2P–Cu_3P@NiCuC	η_{10}=78 mV	22
NiCoP/rGO	η_{10}=209 mV	23

Table S6. The C_{dl} and ECSA of the as-prepared samples.

Catalysts	C_{dl} (mF cm^{-2})	ECSA(cm^{-2})
NiS-Ni_2P/Ni/NF	60.99	1524
NiS/Ni/NF	41.90	1047
Ni_2P/Ni/NF	29.45	731
NiS-Ni_2P/NF	19.26	482
Ni/NF	13.10	328
Pt/C/NF	33.31	833

Table S7. HER performance of the as-prepared samples in 1 M PBS.

Catalysts	Overpotential at 10 mA cm^{-2} (mV)	Overpotential at 50 mA cm^{-2} (mV)
NiS-Ni_2P/Ni/NF	115	241
NiS/Ni/NF	129	316
Ni_2P/Ni/NF	175	524
NiS-Ni_2P/NF	148	427
Ni/NF	221	-
20wt% Pt/C/NF	101	247

Table S8. Comparison of HER performance of the as-synthesized NiS-Ni_2P/Ni/NF electrocatalyst in this work with other high-performance catalysts in neutral**.**

Catalysts	Media	Overpotential	Ref.
NiS-Ni_2P/Ni/NF	**1M PBS**	**η_{10}=115 mV; η_{50}=241 mV**	**This work**
$NiCo_2S_4$/N,S-rGO	1M PBS	η_{10}=216 mV	24
Co_9S_8@C	1M PBS	η_{10}=280 mV	25
Ti@$Ni(OH)_2$-NiMoS	1M PBS	η_{10}=198 mV	26
$CoSe_2$/a-CoP,	1M PBS	η_{10}=185 mV	27
$CoNi_2S_4$/WS_2/Co9S8	1M PBS	η_{10}=146 mV	28
$Ni_{12}P_5$-Ni_2P/Ni/NF	0.1M PBS	η_{10}=112 mV	29
W- Ni/$Ni(OH)_2$/Cu foam	1M PBS	η_{100}=310 mV	30
Cu-Ni_3S_2/NF	1M PBS	η_{10}=228 mV	31
MoP-Ru_2P/NPC	1M PBS	η_{10}=126 mV	32
Fe@Fe_xNiO/Ni@Ni_yCoP	1M PBS	η_{100}=386 mV	33
CN/CNL/MoS_2/CP	1M PBS	η_{10}=145 mV	34
PSS-PPy/Ni-Co-P	1M PBS	η_{10}=106 mV	35
Mo-CoP/NC/TF	1M PBS	η_{10}=130 mV	36
FeP NPs@NPC	1M PBS	η_{10}=386 mV	37
$Ni_{0.1}Co_{0.9}P$	1M PBS	η_{10}=125 mV	38
$Cu_{0.075}Co_{0.925}P$/CP	1M PBS	η_{10}=120 mV	39
$Ni(S_{0.5}Se_{0.5})$2	1M PBS	η_{10}=124 mV	40

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