Cu_2S/Ni_xS_y multi-interfaces induced Ni (III) for optimizing alkaline hydrogen evolution reaction

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Experiment section

Materials and chemicals

Nickel (II) chloride hexahydrate puratre ($NiCl_2•6H_2O$, ≥98%) was purchased from Beijing Hongxing Co. Ltd. Copper chloride ($CuCl_2•2H_2O$, ≥99%) was got from Tianjin Guangfu technology Co. Ltd. Ethylene glycol ($C_2H_6O_2$, EG, ≥99.5%) was gained from Tianjin Medical Chemistry Co. Ltd. Hydrazine hydrate ($N_2H_4•H_2O$, ≥80%) was obtained from Tianjin Damao technology Co. Ltd. S powder (S, ≥98%) was gained from Tianjin Guangfu technology Co. Ltd. Pt/C (20 wt%) and Nafion (5 wt%) were supplied by Alfa Aesar. In addition, all of regents used in this experiment were analytically pure without purification.

Characterization

The powder X-ray diffraction (XRD) were conducted by using Cu-Kα radiation as the X-ray source in the 2θ range of 20 - 80°. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS Ultra DLD instruments with a monochromatic X-ray source (AL Kα hν =

1486.6) and all elemental peaks were revised by the standard position of C 1s peak. Transmission electron microscope (TEM) images were observed with a Tecnai^{TM} G^{2}F30, FEI operating at 200 KV, equipped with energy dispersive X-ray spectroscopy (EDX, Tecnai G2, USA).

Electrochemical measurement

Generally, 4 mg black catalyst powder was dissolved in a 1 mL solution which was composed of ethanol and ultrapure water in a 1:1 volume ratio. Then, 30 μL Nafion aqueous solution (0.5 wt%) was added into the 1 mL solution mentioned earlier and ultrasonicated it for 0.5 h to form a uniform black solution. Eventually, 5 μl black solution was drop on the 3.0 mm diameter glassy carbon electrode serving as the working electrode (loading 0.286 mg cm^{-2}). In this article, all the electrochemical tests were realized through electrochemical workstation (CHI 660E, Shanghai Chenhua) with three-electrode configuration without *iR* compensation and at room temperature. In the test, a graphite carbon rod was utilized as contrast electrode, while the saturated Ag/AgCl electrode was treated as the reference electrode. All potentials (vs. Ag/AgCl) appearing in the article were transformed into reversible hydrogen electrode (RHE), which were corrected by means of using the Nernst equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.059 pH + 0.198 V.

HER measurement

The HER electrochemical activities were all measured in 1.0 M KOH

electrolyte. Linear sweep voltammetry (LSV) polarization curves were investigated in the range of - 0.8 V - -1.8 V vs. Ag/AgCl with a scan rate of 5 mV s^{-1}. The electrochemical impedance spectroscopy (EIS) measurements were tested at -120 mV *vs.* Ag/AgCl from 10^5 to 0.01 Hz. In order to obtain the electrochemically active surface areas of all the catalysts, cyclic voltammograms (CVs) were investigated between -0.8 V and -0.7 V with the different scan rates (20 - 200 mV s^{-1}). In addition, the HER stability of the catalysts was also performed by Amperometric i-t Curve at -1.20 V vs. RHE for 33 h. All the current density of the catalysts were rectified to the geometrical surface area of the GCE (0.07cm^{-2}).

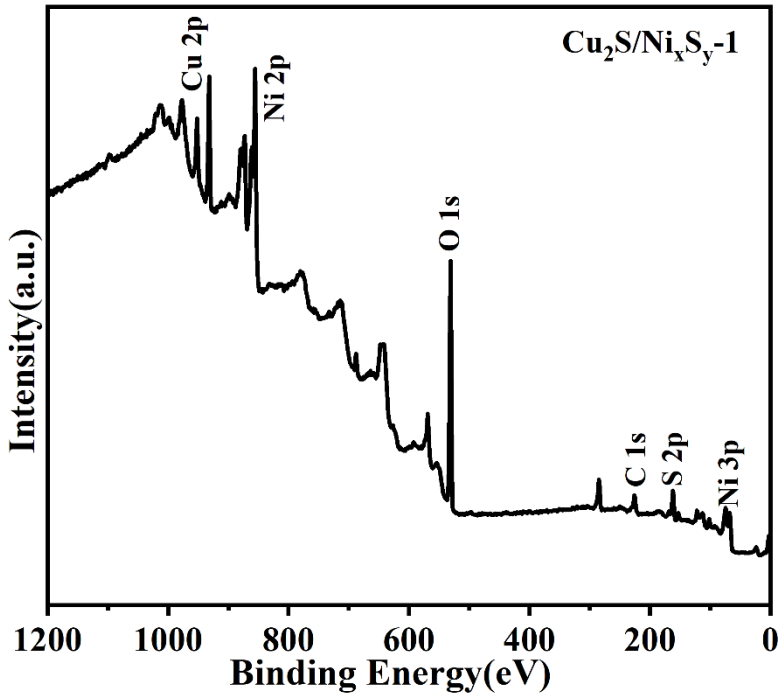

Fig. S1. The full XPS survey spectra of the Cu_2S/Ni_xS_y-1.

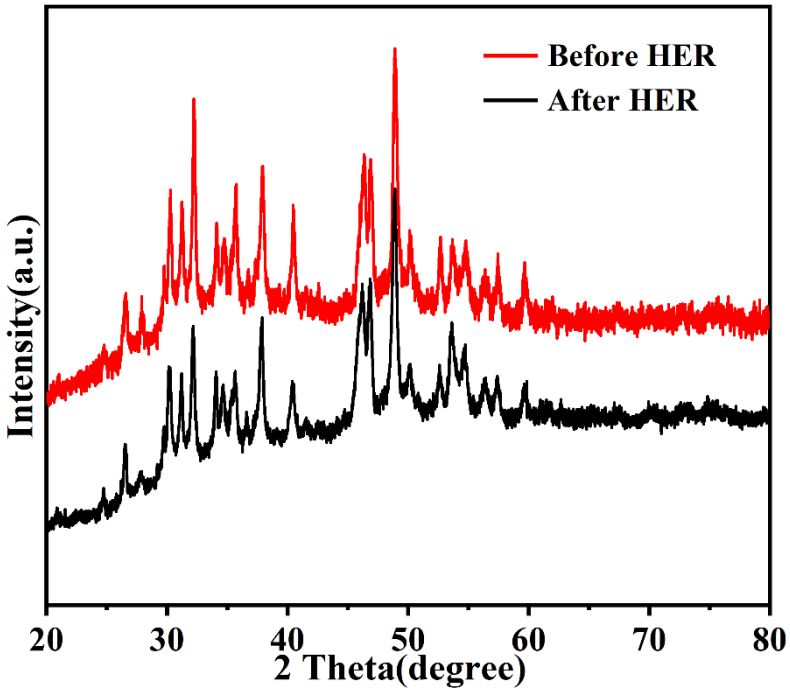

Fig. S2. XRD patterns of Cu_2S/Ni_xS_y-1 after stability test.

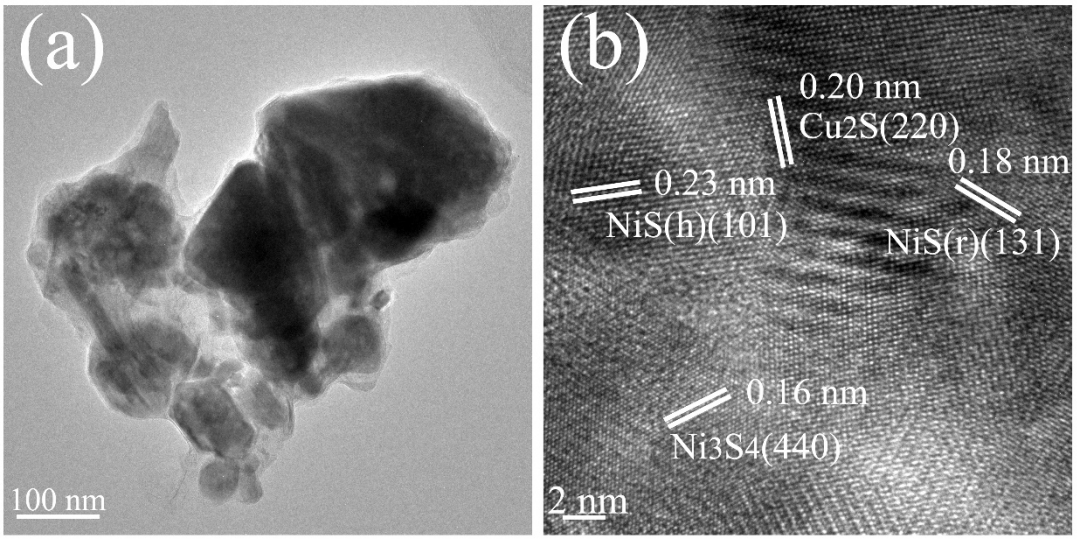

Fig. S3. The TEM and TRTEM of Cu_2S/Ni_xS_y-1 after stability test.

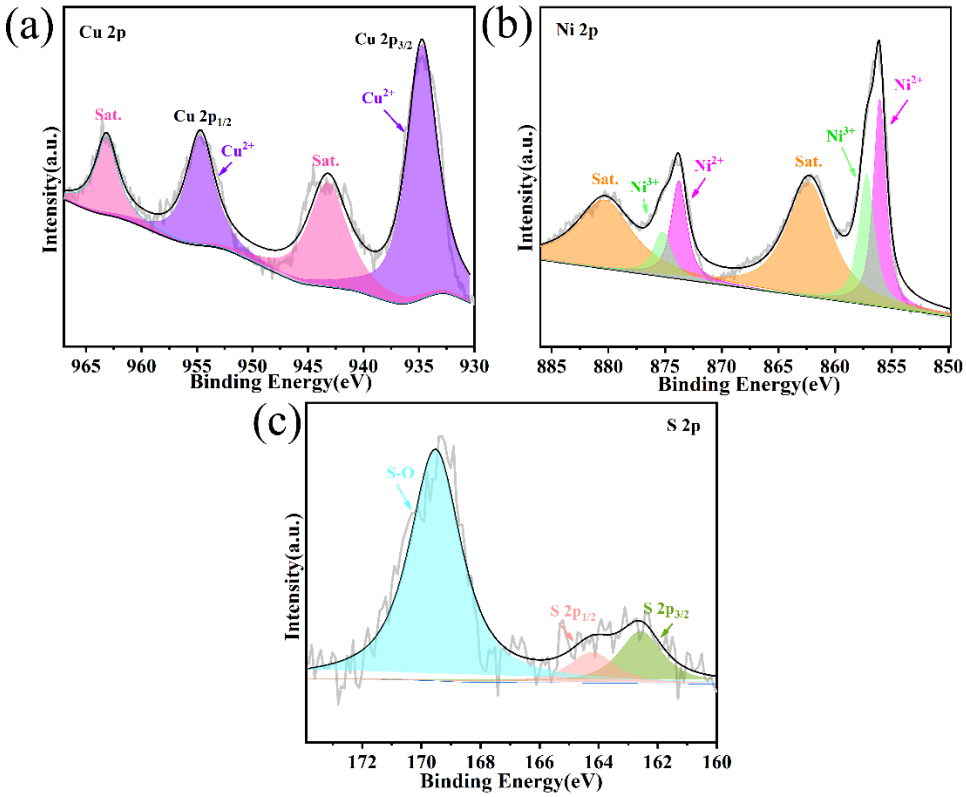

Fig. S4. (a) Cu 2p (b) Ni 2p (c) S 2p spectra of Cu_2S/Ni_xS_y-1 after stability test.

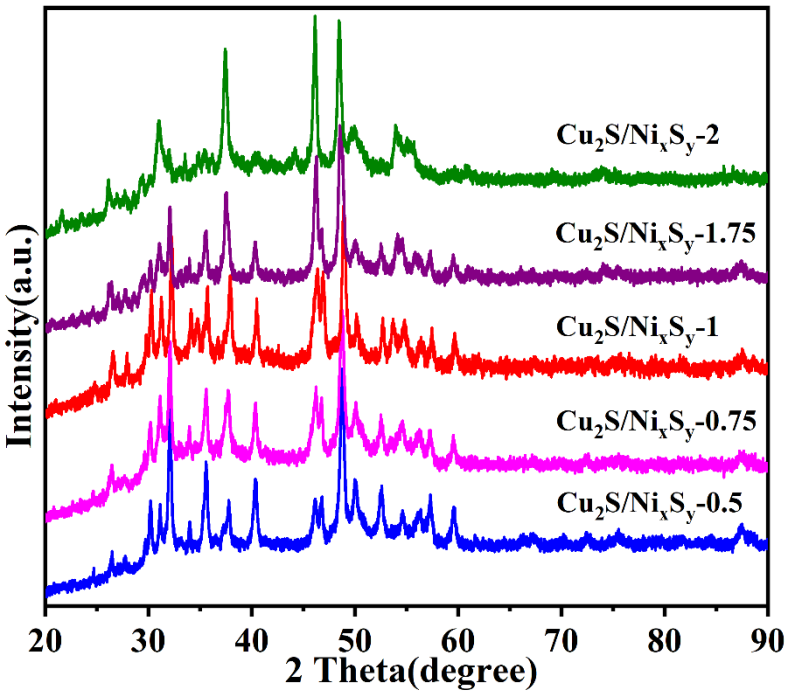

Fig. S5. XRD patterns of Cu_2S/Ni_xS_y-0.5, Cu_2S/Ni_xS_y-0.75, Cu_2S/Ni_xS_y-1, Cu_2S/Ni_xS_y-1.75 and Cu_2S/Ni_xS_y-2.

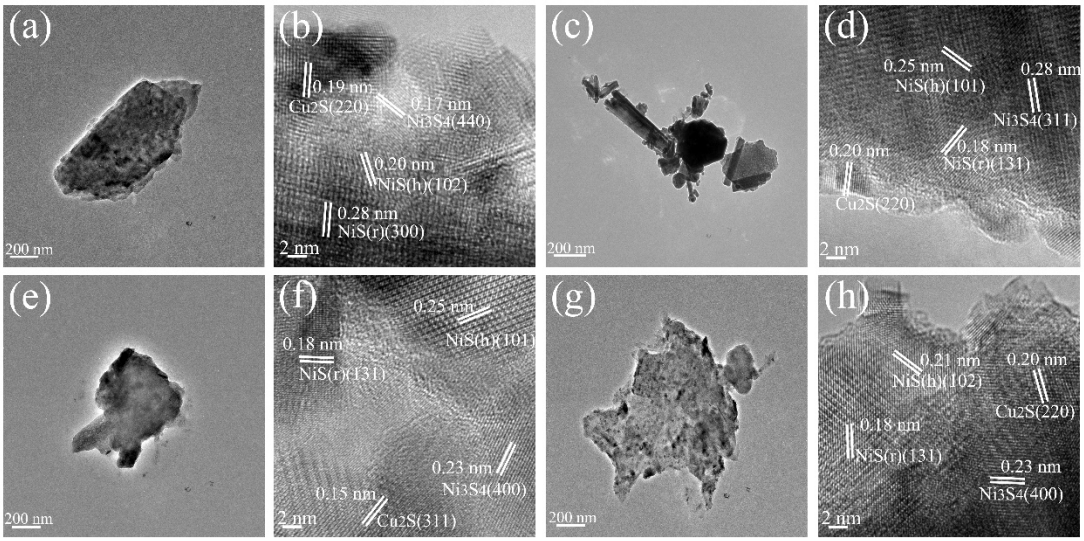

Fig. S6. TEM and TRTEM of (a, b) Cu_2S/Ni_xS_y-0.5 (c, d) Cu_2S/Ni_xS_y-0.75 (e, f) Cu_2S/Ni_xS_y-1.75 and (g, h) Cu_2S/Ni_xS_y-2.

Table S1. Initial dosage mass (mmol) of raw stuff in the prepared Cu_2S/Ni_xS_y-n electrocatalysts.

Sample Cu_2S/Ni_xS_y-n	0.5	0.75	1	1.75	2
$CuCl_2 \cdot 2H_2O$	0.5	0.75	1	1.75	2
$NiCl_2 \cdot 6H_2O$	1	1	1	1	1
S	2	2	2	2	2

Table S2. Content of Cu, Ni and S in the Cu_2S/Ni_xS_y-n electrocatalysts estimated from ICP-OES measurements.

Sample Cu_2S/Ni_xS_y-n	0.5	0.75	1	1.75	2
Cu (wt.%)	30.62	43.13	50.71	43.15	45.19
Ni (wt.%)	45.48	38.50	32.38	25.95	25.99

S (wt.%)	2.81	2.69	2.66	2.58	2.19
Cu/Ni	0.67	1.12	1.56	1.66	1.74

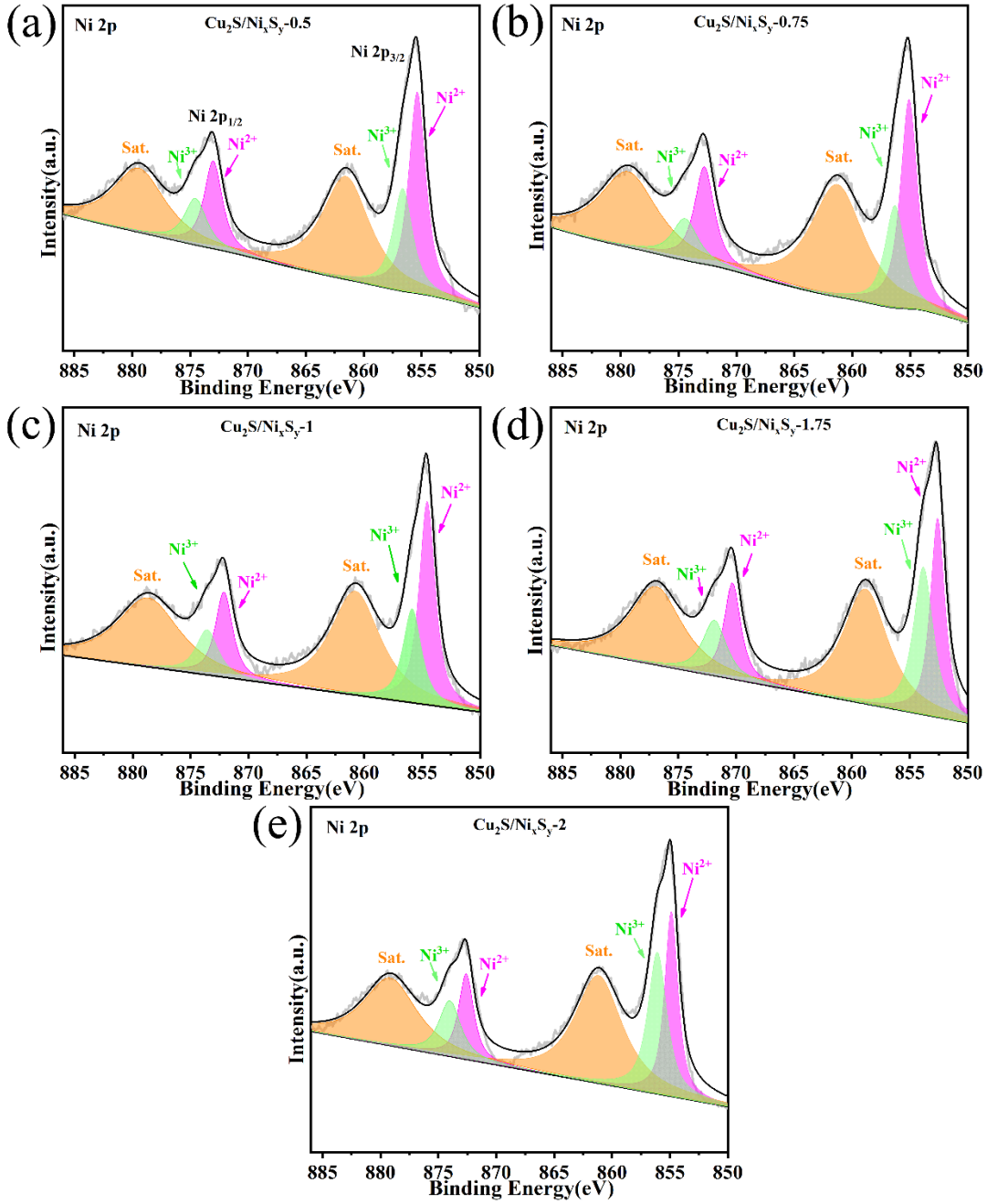

Fig. S7. Ni 2p XPS spectra of (a) Cu_2S-Ni_xS_y-0.5 (b) Cu_2S-Ni_xS_y-0.75 (c) Cu_2S-Ni_xS_y-1 (d) Cu_2S-Ni_xS_y-1.75 (e) Cu_2S-Ni_xS_y-2.

Table S3. The properties of the as-prepared electrocatalysts

Sample Cu_2S/Ni_xS_y-n	0.5	0.75	1	1.75	2
Ni^{3+}(wt.%)	19.13	16.76	20.01	24.16	23.98

The Ni_3S_4, NiS (r) and NiS (h) of the samples were quantitatively analyzed by XRD peak intensity comparison. In Fig. 1a, according to the standard XRD diffraction peaks of Ni_3S_4 (JCPDS Card No. 76-1813), NiS (r) (JCPDS Card No. 12-41) and NiS (h) (JCPDS Card No. 65-830), we can see that the peaks corresponding to (311), (300) and (220) are diffraction peaks with strong relative intensity of Ni_3S_4, NiS (r) and NiS (h), respectively. The specific strength and ratio are shown in the Table S1.

Table S4. The intensity of XRD peaks (cm) corresponding to Ni_3S_4, NiS (r) and NiS (h), and the proportion of Ni_3S_4 in the total Ni.

Sample Cu_2S/NixSy-n	0.5	0.75	1	1.75	2
Ni_3S_4 (311)	0.69	0.88	0.81	0.67	0.91
NiS (r) (300)	1.89	1.49	1.64	1.07	0.44
NiS (h) (220)	0.66	0.93	1.20	1.55	2.13
sum	3.24	3.30	3.65	3.31	3.48
Ni_3S_4 (wt.%)	21.29	26.66	22.19	20.24	26.14

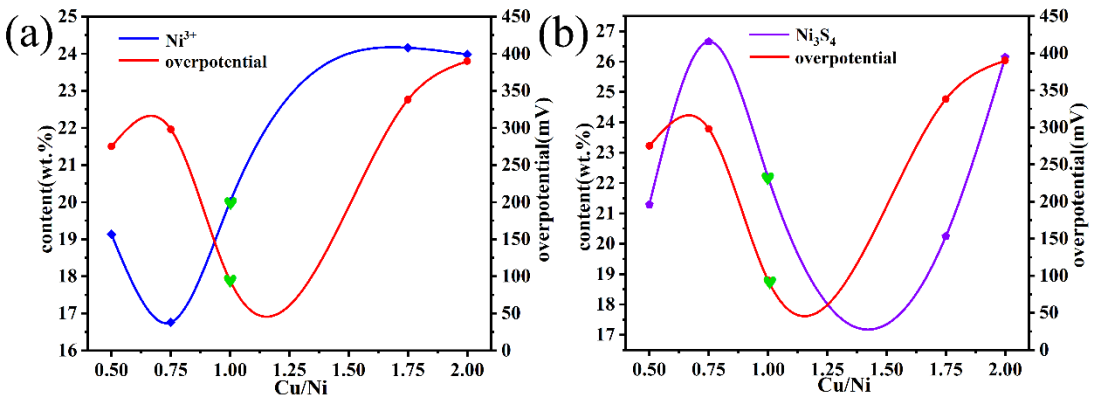

Fig. S8. (a) relationship between Ni^{3+} and overpotential at different ratios of Cu and Ni (b) relationship between Ni_3S_4 and overpotential at different ratios of Cu and Ni.

Table S5. Comparison of the nickel sulfide compound catalysts HER activity in alkaline electrolyte.

catalyst	Tafel slope (mV dec^{-1})	Overpotential (mV)	Ref.
Ni/NiS/P, N, S–rGO	135.00	155	1
Zn–NiS-3	113.00	208	2
NiS@C	89.00	232	3
NiS film	143.30	290	4
Ni_3S_2@NiS-250/NF	75.50	129	5
NiS/VS	116.10	158	6
Ni-M@C-130	50.80	123	7
NiS film	125.00	169	8

Cu_2S/Ni_xS_y-1	97.69	94	This work

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