Supporting Information

Heterostructure Ni_3S_4-MoS_2 with interfacial electron redistribution used for enhancing hydrogen evolution

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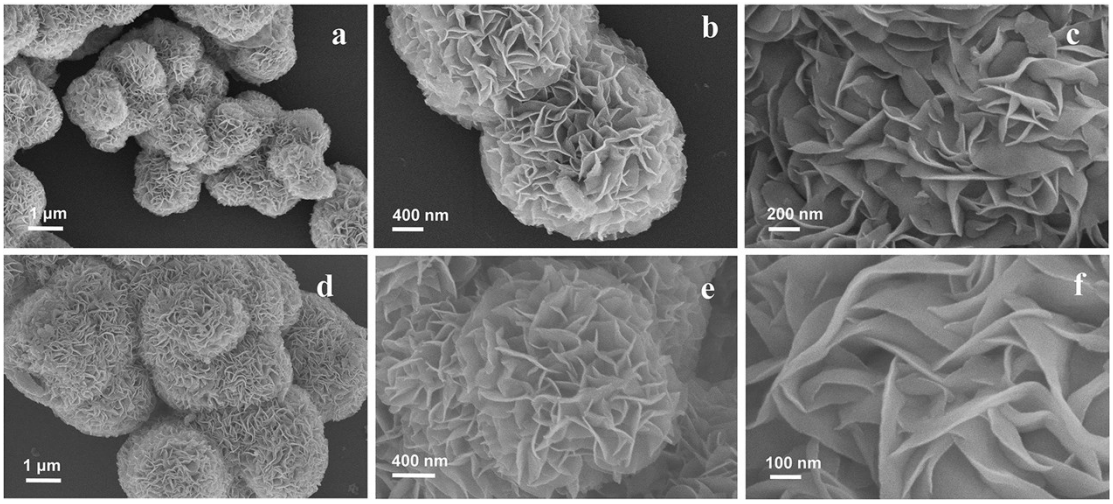

Fig. S1. (a-c) SEM images of pure MoS_2. (d-e) SEM images of Ni_3S_4-MoS_2.

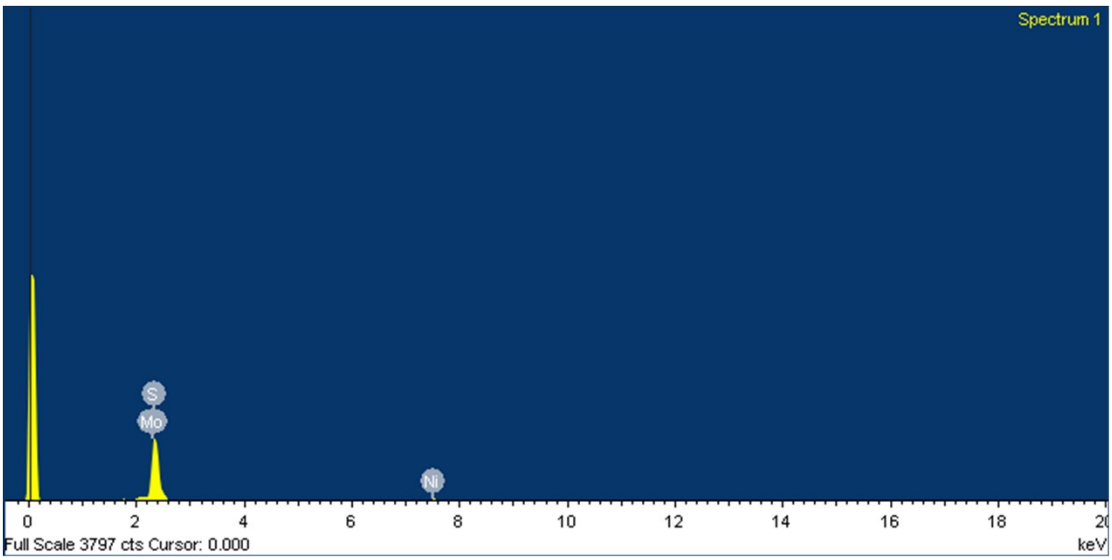

Fig. S2. EDS spectrum of Ni_3S_4-MoS_2.

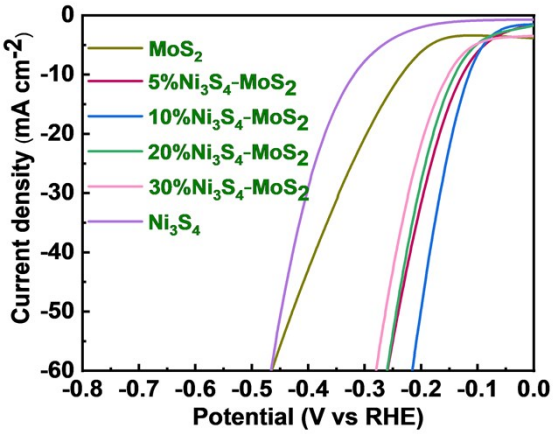

Fig. S3. LSV curves of Ni_3S_4-MoS_2 with different Ni contents in 1M KOH.

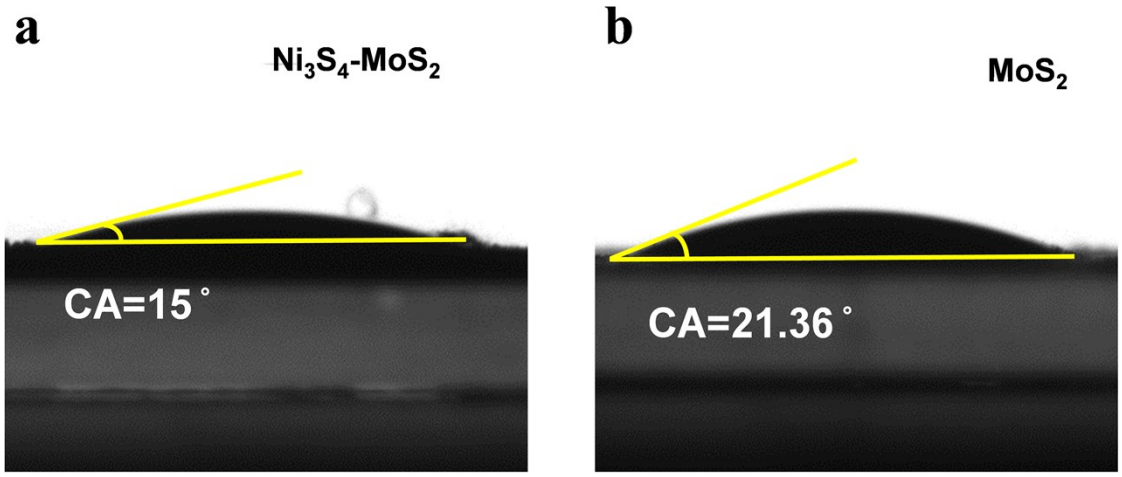

Fig. S4. Contact angles of Ni_3S_4-MoS_2 (a) and MoS_2 (b).

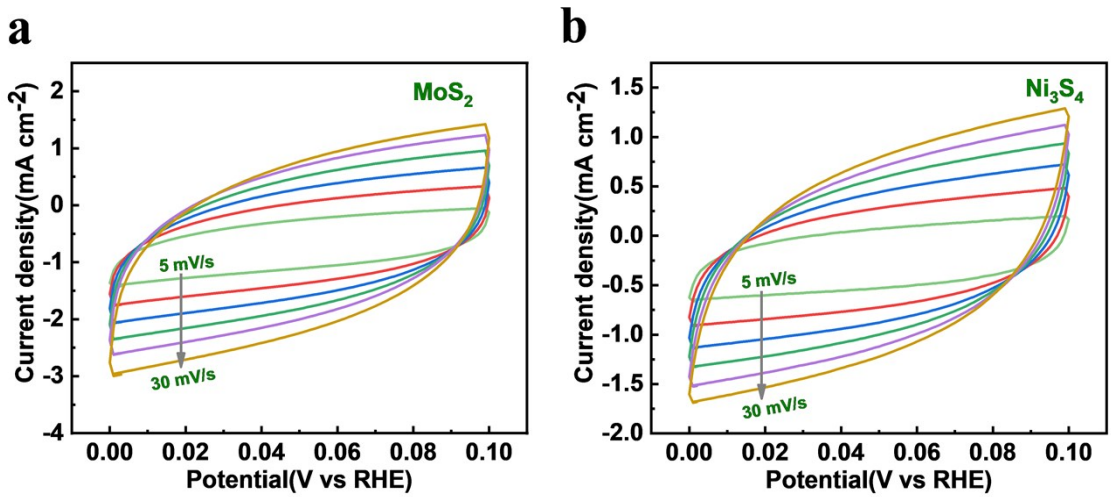

Fig. S5. CV curves of MoS_2 (a) and Ni_3S_4 (b) at the scan rates of 5, 10, 15, 20, 25 and 30 mV s^{-1} in 1.0 M KOH.

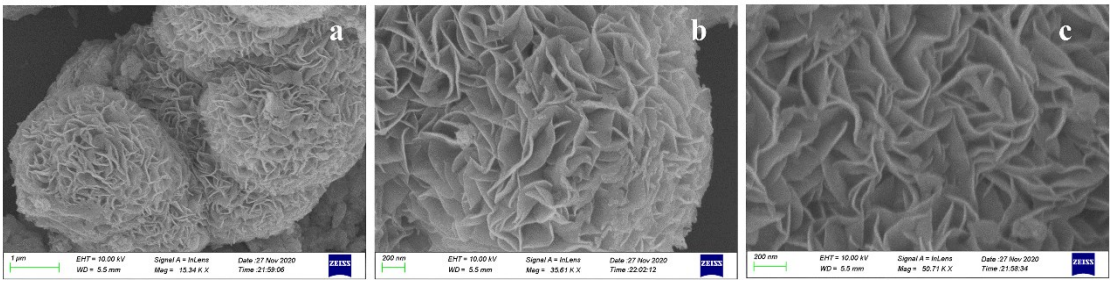

Fig. S6. (a and b) SEM images of Ni_3S_4-MoS_2 after 3000 CV curves. (c) SEM image of Ni_3S_4-MoS_2 after a stability test for 20 h.

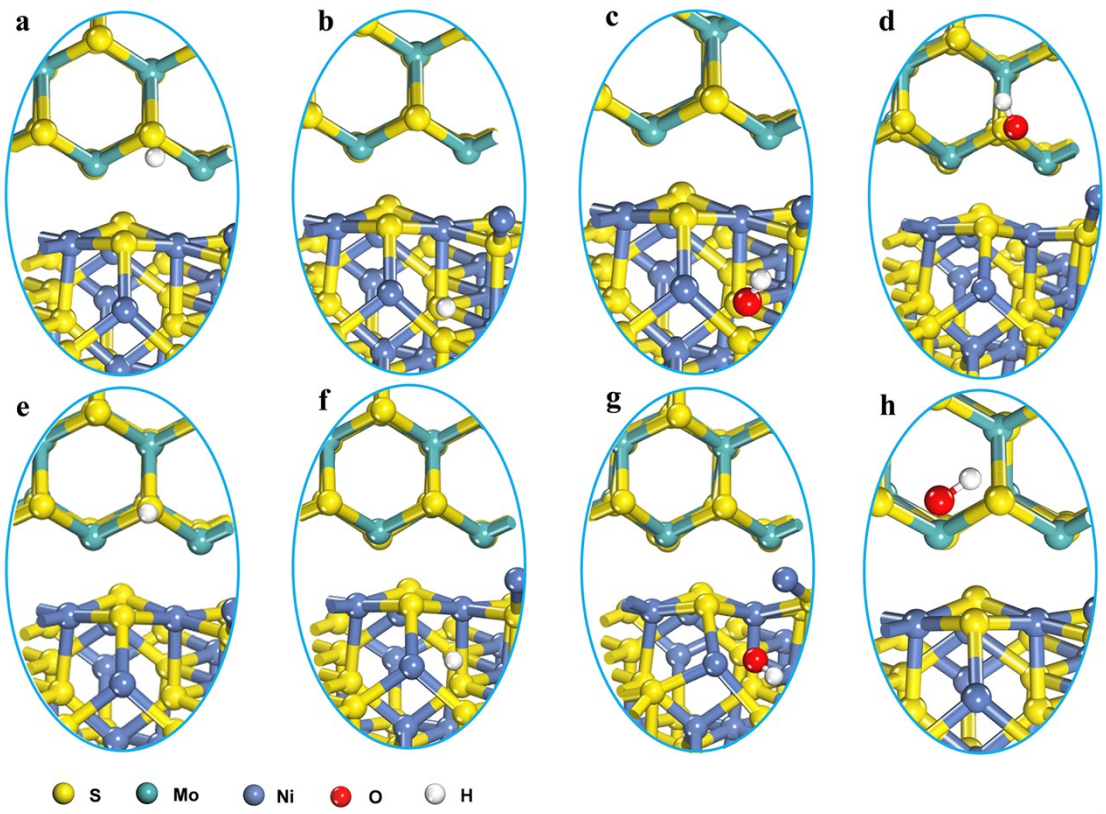

Fig. S7. Top-view of the initial structures for H adsorption on the (002) plane of MoS_2 (a) and the (311) plane of Ni_3S_4 (b), and for OH adsorption on the (311) plane of Ni_3S_4 (c) and the (002) plane of MoS_2 (d) in the heterostructure Ni_3S_4-MoS_2. The optimized structures for H adsorption on the (002) plane of MoS_2 (e) and the (311) plane of Ni_3S_4 (f), and for OH adsorption on the (311) plane of Ni_3S_4 (g) and the (002) plane of MoS_2 (h) in the heterostructure Ni_3S_4-MoS_2.

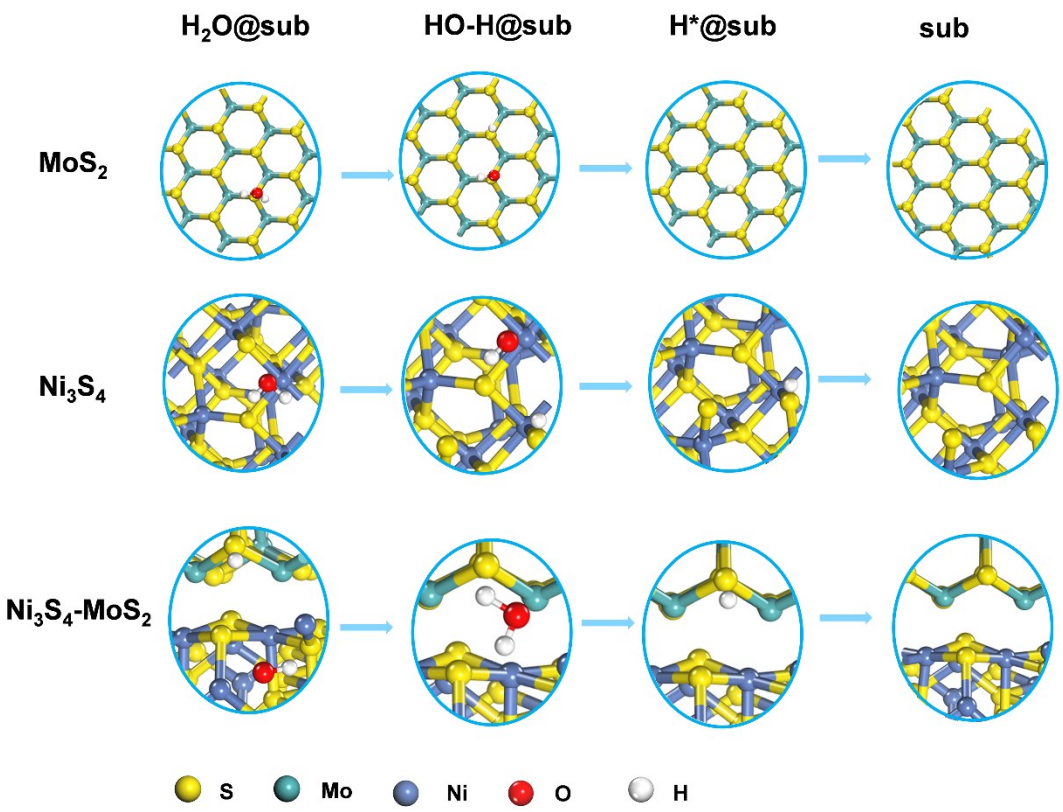

Fig. S8. HER reaction pathways and relevant structures of the most possible intermediate steps on the surface of MoS_2, Ni_3S_4 and Ni_3S_4-MoS_2, respectively.

Table S1 Ni_4S_3-MoS_2 samples with different Ni contents.

Crystalline	ICP-OES test results
5%Ni_4S_3-MoS_2	Ni 4.37 wt.%
10%Ni_4S_3-MoS_2	Ni 7.7 wt.%
20%Ni_4S_3-MoS_2	Ni 14.2 wt.%
30%Ni_4S_3-MoS_2	Ni 20.7 wt.%

Table S2 The EDS quantitative analysis results of Ni_3S_4-MoS_2.

Element	Weight%	Atomic%
S	55.75	77.26
Ni	7.63	5.77
Mo	36.63	16.96
Totals	100.00	

Table S3 Bader charge analysis of Ni_3S_4-MoS_2.

Element	Bader Charge /|e|
Mo-10	0.05
Mo-20	0.02
Ni-5	-0.13
Ni-8	-0.27
Ni-11	-0.14
Ni-17	-0.06
Ni-22	-0.05
S-15	0.21
S-35	0.19
S-41	0.16
S-45	0.15

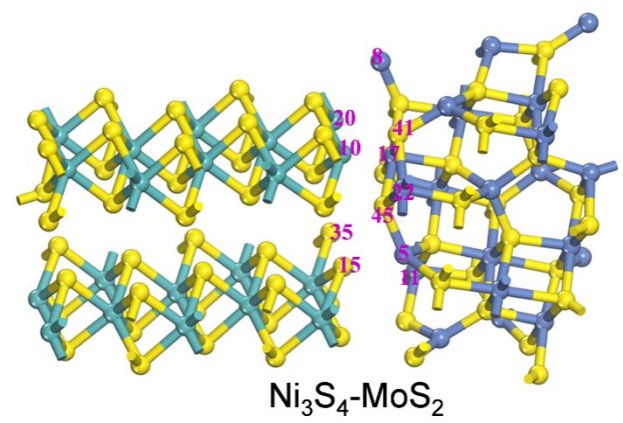

Table S4 The adsorption free energy (ΔE) and Gibbs free energy (ΔG) of hydrogen generations and water dissociation during HER on the surface of MoS_2, Ni_3S_4 and Ni_3S_4-MoS_2.

	ΔE(H*)/eV	ΔG(H*)/eV	ΔE (H_2O)/eV	ΔG (H_2O)/eV
MoS_2	1.69	1.93	3.73	4.18
Ni_3S_4	-0.90	-0.66	3.84	4.29
Ni_3S_4-MoS_2	-0.60	-0.36	-0.55	-0.10

Table S5 Summary of several representative recently reported HER electrocatalysts employed in acidic and alkaline electrolytes.

Catalyst	Electrolyte	η_{10} (mV)	Tafel slope (mV dec^{-1})	Reference
NiS_2/MoS_2	1M KOH	235	58	[1]
MoO_3-MoS_2	0.5 M H_2SO_4	200	74	[2]
MoP/MoS_2	1M KOH	92	59.8	[3]
Ni_2P/MoS_2/N:CNT	1M KOH 0.5 M H_2SO_4	149 39.5	60.22 57.8	[4]
Mo_2N–Mo_2C/HGr	0.5 M H_2SO_4 1M KOH	154 157	55 68	[5]
MoSSe@rGO	0.5 M H_2SO_4	135(η_5)	51	[6]
$(CoMo)S_2$/graphene	0.5 M H_2SO_4	100	60.8	[7]
Fe-MoS_2/Ni_3S_2/NF	1M KOH	130.6	112.7	[8]
Co_3O_4/MoS_2	1M KOH	205	98	[9]
MoS_2/Ni_3S_2	1M KOH	110	83.1	[10]
MoS_2-Ni_3S_2	1M KOH	98	61	[11]
$Ni(OH)_2/MoS_2$	1M KOH	156	56.4	[12]
MoS_2|NiS|MoO_3	1M KOH	95	54.5	[13]
Ni-MoS_2/CC	1M NaOH	107	162	[14]

Ni–MoS_2/NCNTs	0.5 M H_2SO_4 1M KOH	158 179	69.3 62.3	[15]
MoS_2/rGO	0.5 M H_2SO_4	160	52	[16]
MoS_2/g-CN	0.5 M H_2SO_4	141	57	[17]
NC@MoS_2/Ni-NC	1M KOH	96.3	81.1	[18]
CoS_2-MoS_2	1M KOH	130	66.8	[19]
Ni_3S_4-MoS_2	1M KOH	116	81	***This work***

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