Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supplementary Information

Phase-engineered nickel sulfide and phosphide (NiS-Ni_2P) heterostructure for enhanced hydrogen evolution performance supported with DFT analysis

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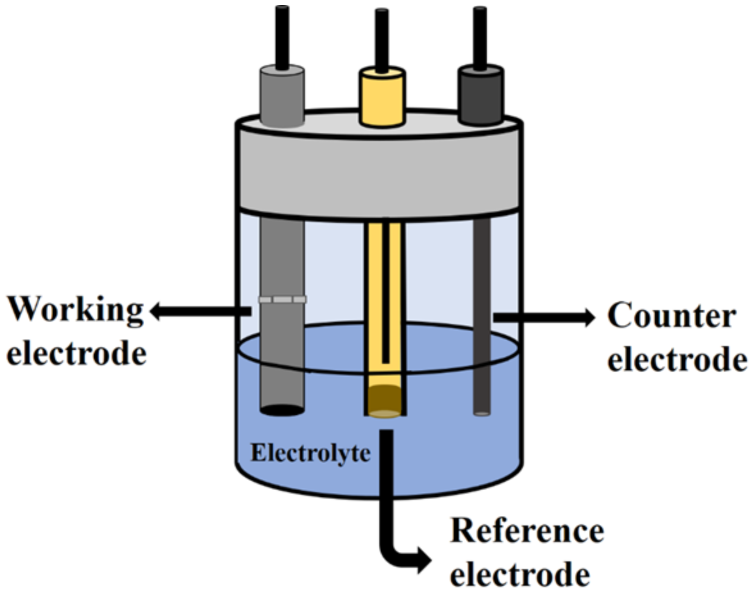


Fig. S1 Schematic representation of electrode setup for the HER studies.

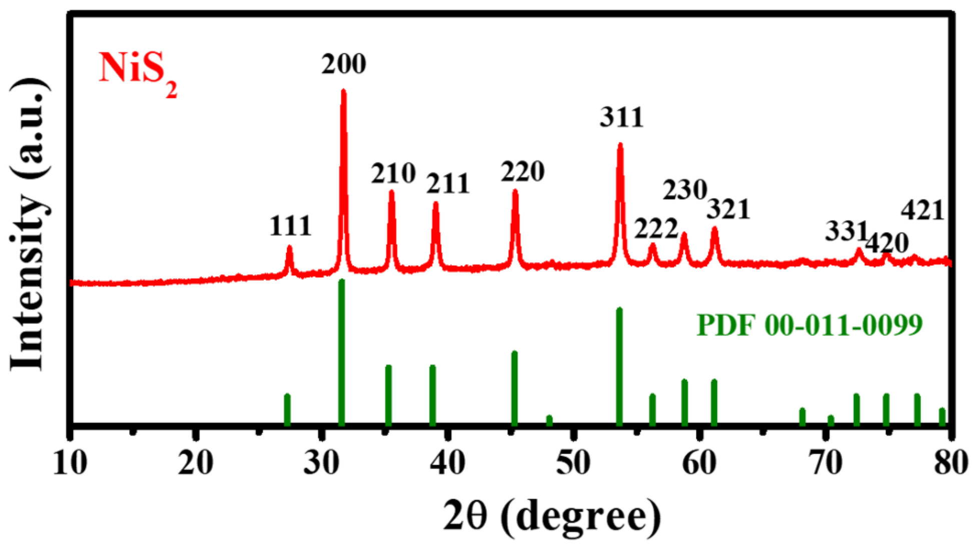


Fig. S2 Powder diffraction pattern of single-phase NiS_2.

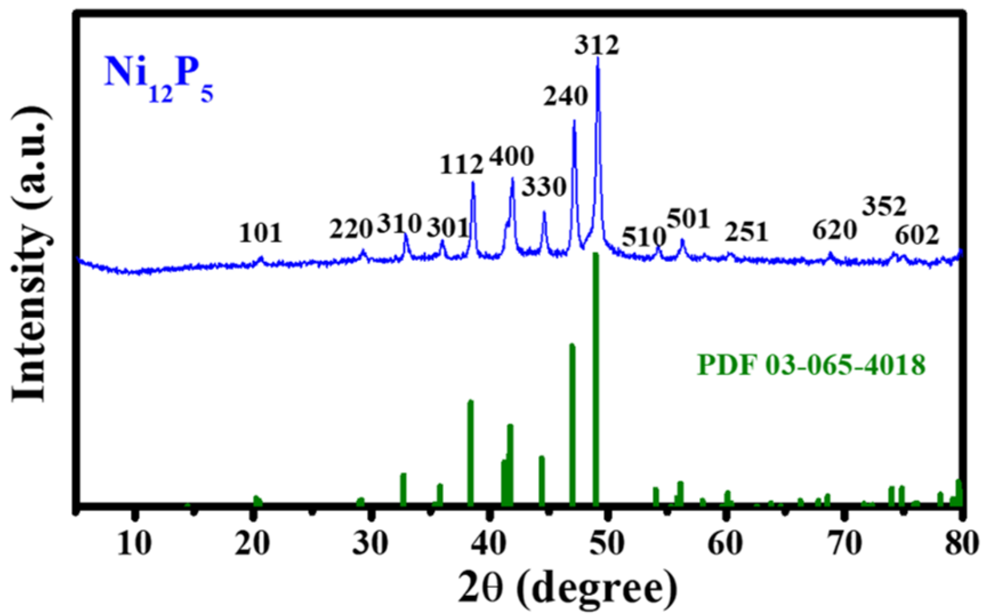


Fig. S3 PXRD pattern of $Ni_{12}P_5$.

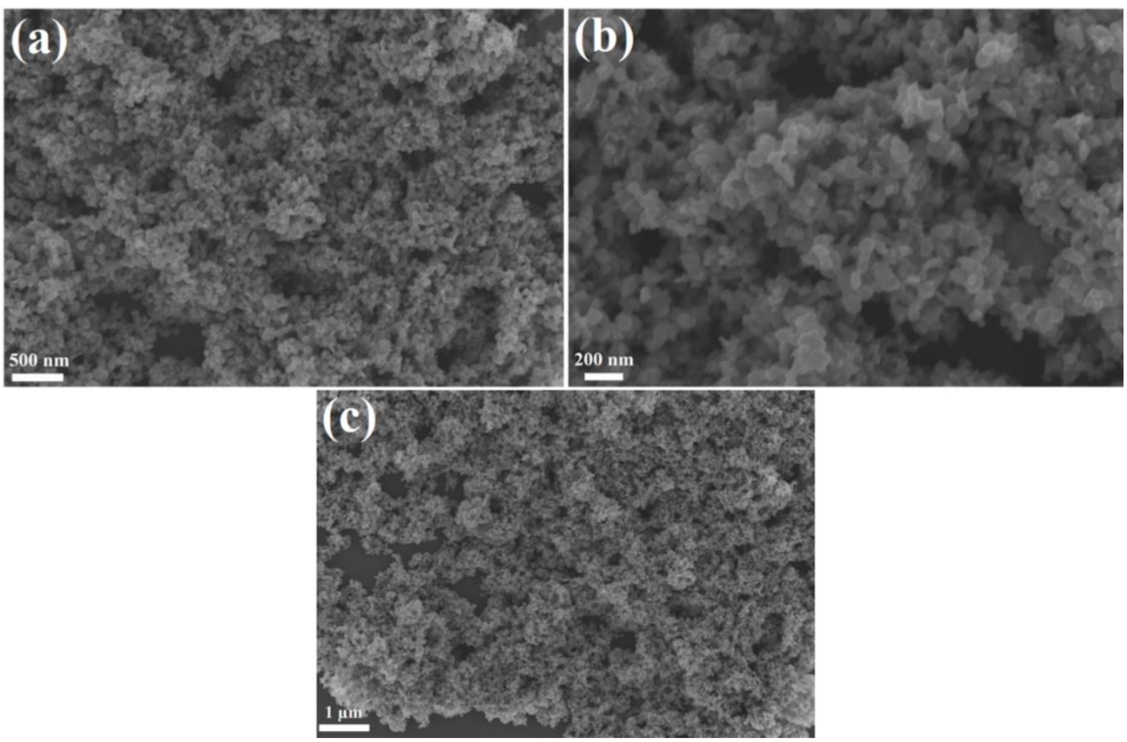


Fig. S4 FESEM pictures of NiS_2.

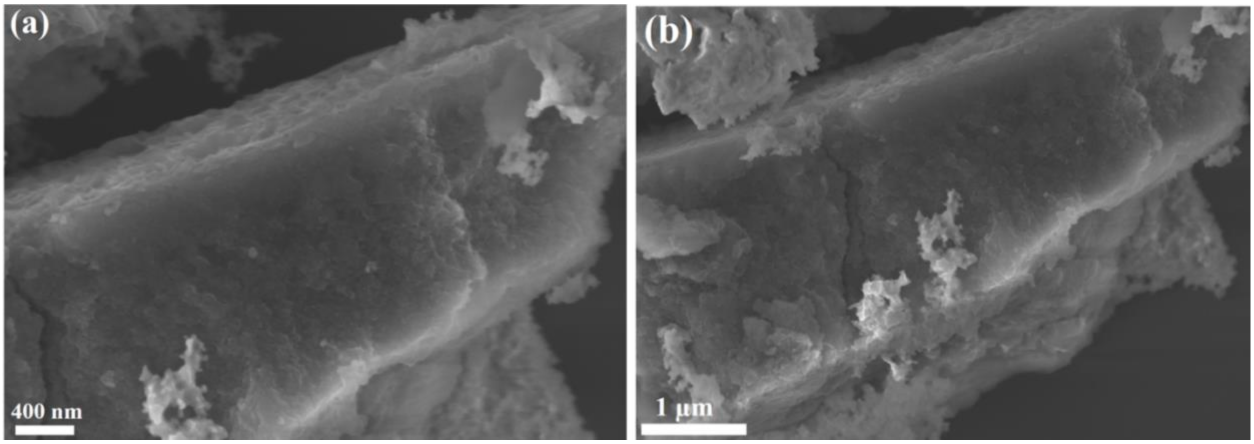


Fig. S5 FESEM analysis of $Ni_{12}P_5$.

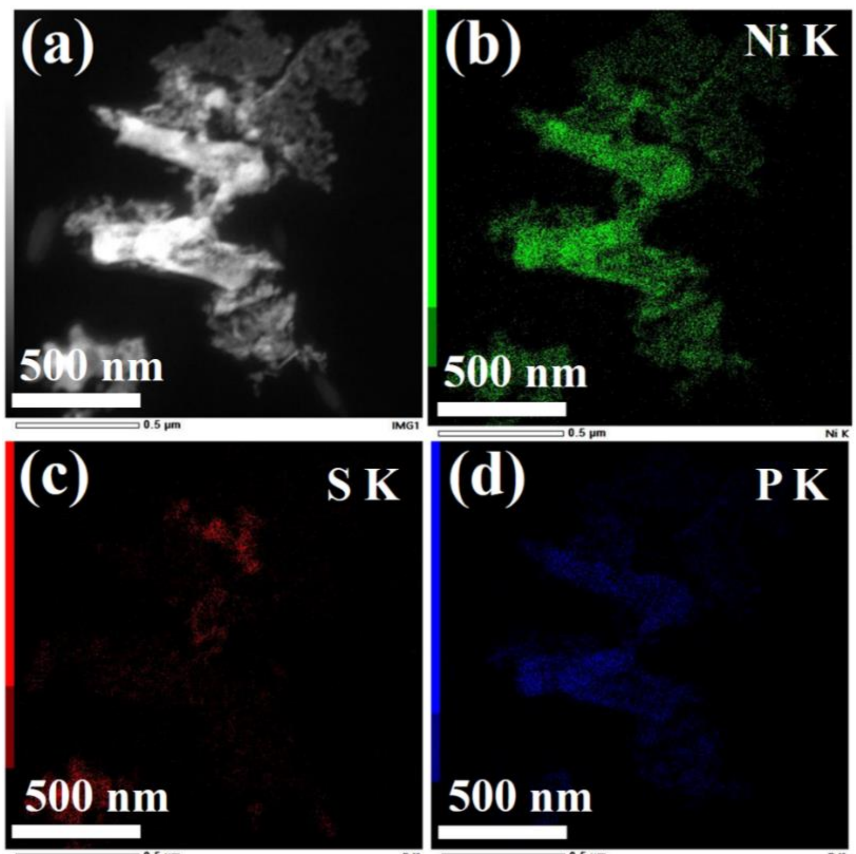
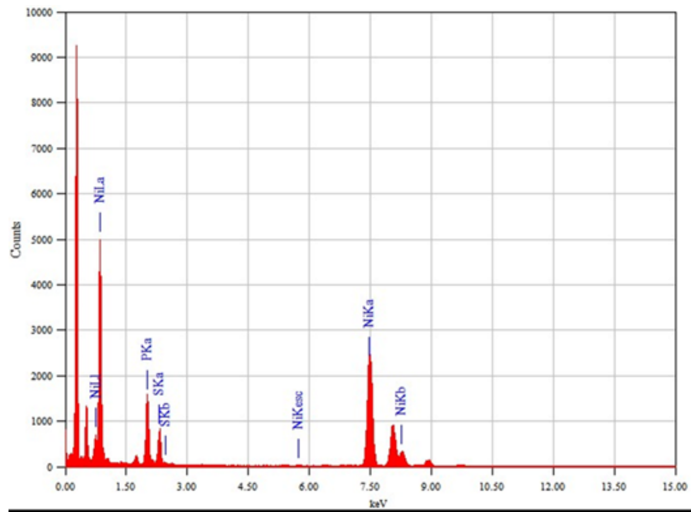


Fig. S6 Elemental mapping images of NiS-Ni_2P show the presence of Ni (K), S (K), and P (K).



Element	Mass %	Atom %
Ni K	71.75	57.54
P K	19.22	29.21
S K	9.02	13.25
Total	100.00	100.00

Fig. S7 EDAX spectrum with the elemental composition of NiS-Ni_2P heterostructure.

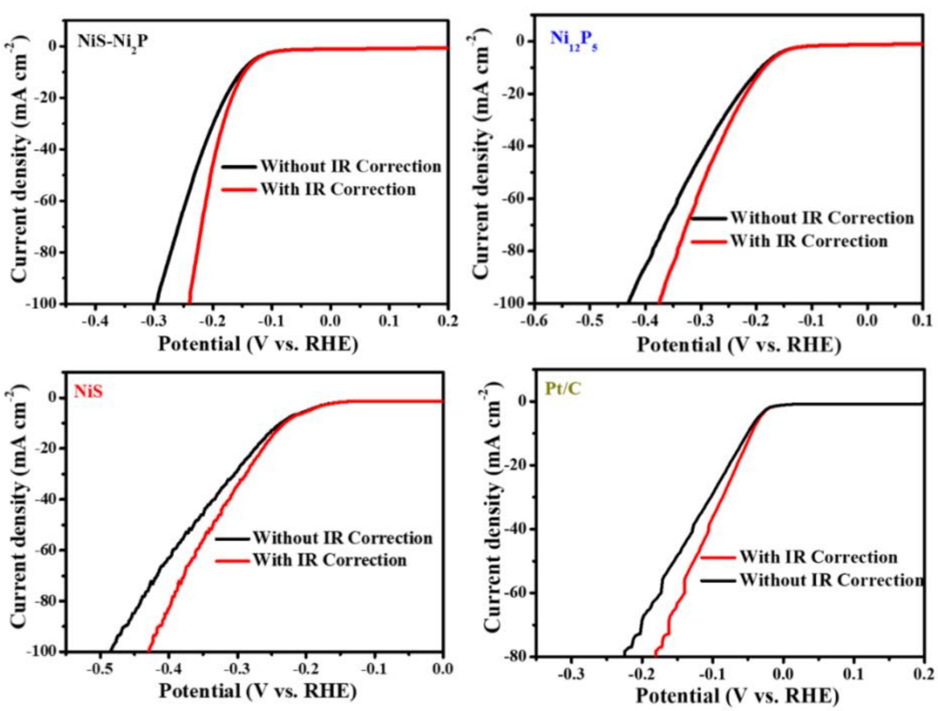


Fig. S8 LSVs for NiS-Ni_2P, NiS_2, $Ni_{12}P_5$, and Pt/C before and after an *iR* correction in 0.5 M H_2SO_4.

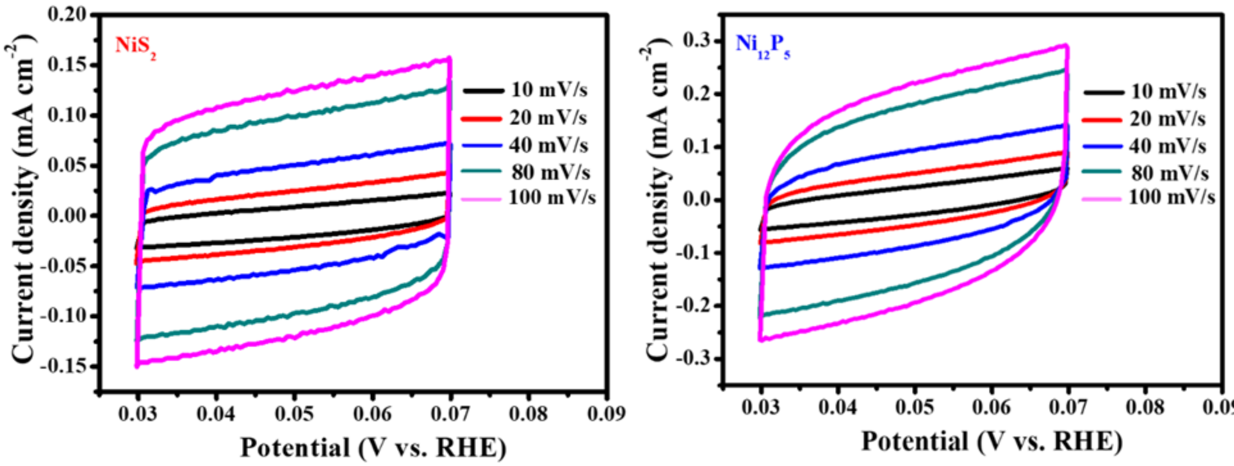


Fig. S9 (a, b) Cyclic voltammetry curve recorded in 0.5 M H_2SO_4 at scan rates of 10-100 mV/s for NiS_2 and $Ni_{12}P_5$.

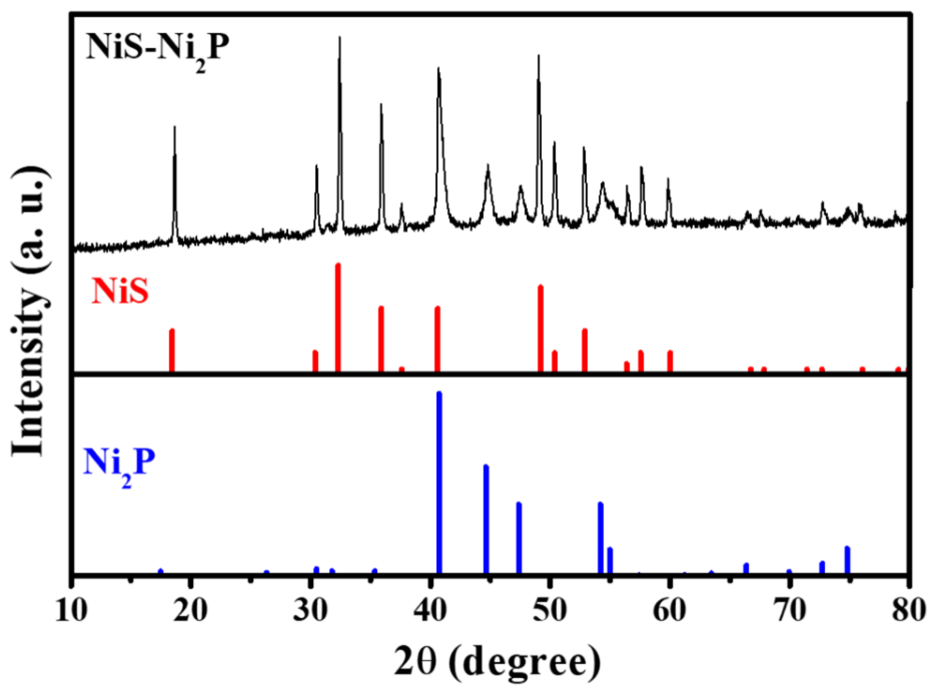


Fig. S10 PXRD pattern for NiS-Ni_2P heterostructure after the 23 h of durability test at 10 mA/cm^2.

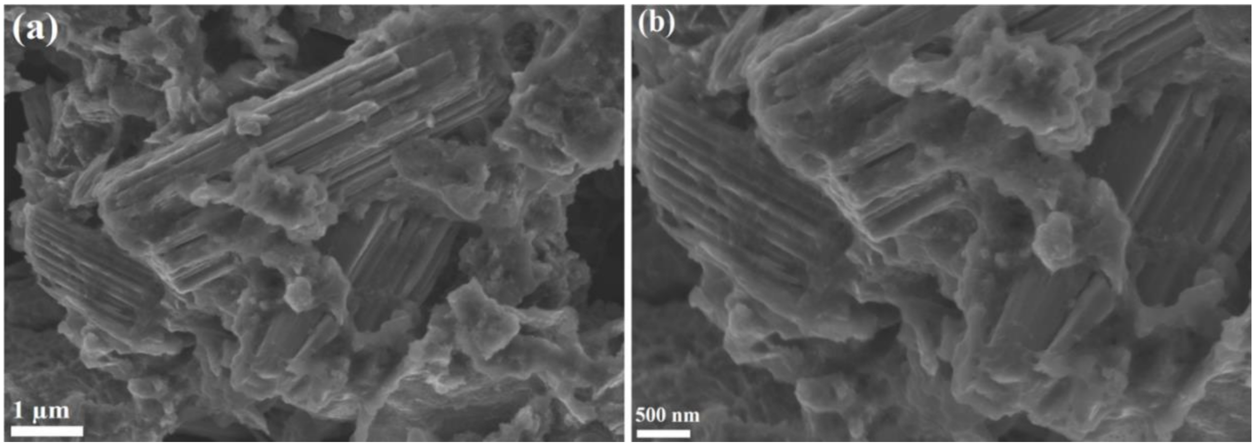


Fig. S11 (a, b) FESEM analysis of the active material NiS-Ni_2P after the chronopotentiometry test at the current density of 10 mA/cm^2.

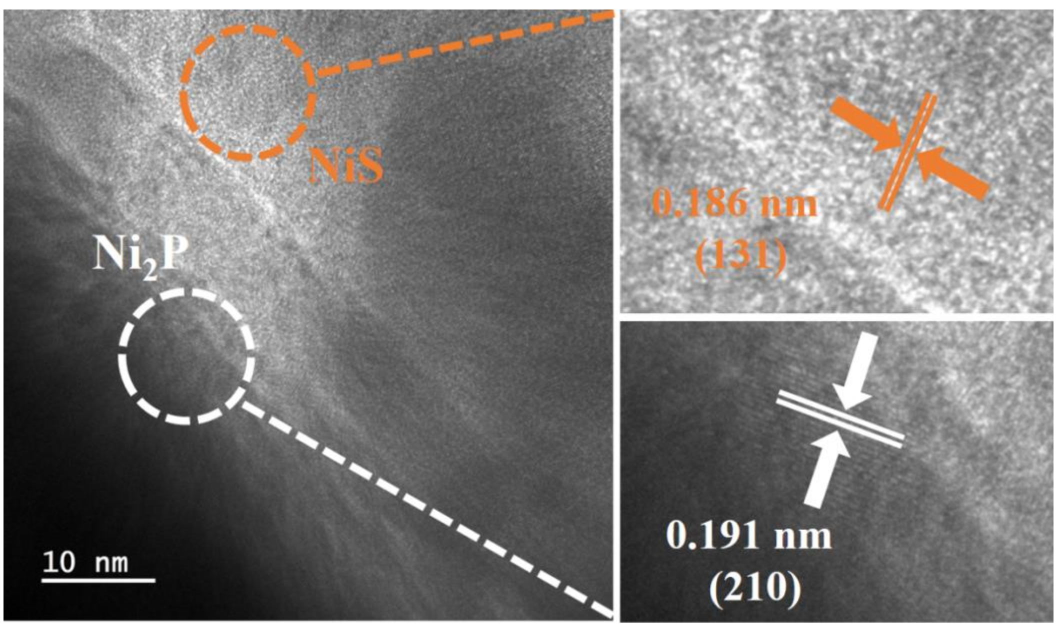


Fig. S12 HRTEM analysis of NiS-Ni_2P heterostructures after the stability test.

Table S1. The comparison of HER performance in 0.5 M H_2SO_4 with reported nickel phosphides and sulfides electrode materials.

Electrocatalyst used	Overpotential at 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Electrolyte	References
Ni_2P	295	115	0.5 M H_2SO_4	ChemElectroChem, 2017, 4(2), 340–344
$Ni_{12}P_5$	182	63	0.5 M H_2SO_4	Chem.–Eur. J., 2018, 24(45), 11748–11754
Ni_8P_3	152	86	0.5 M H_2SO_4	ACS Appl. Mater. Interfaces, 2016, 8(41), 27850–27858
NiS	250	51.2	0.5 M H_2SO_4	RSC Adv., 2015, 5(127), 104740–104749
NiP_2	172	62	0.5 M H_2SO_4	RSC Adv., 2015, 5(14), 10290–10295
NiS_2	249	55	0.5 M H_2SO_4	J. Mater. Chem. A, 2017, 5, 10173–10181
Fe-doped NiS_2	198	42	0.5 M H_2SO_4	J. Mater. Chem. A, 2019, 7, 4971–4976
Ni_2P	224	82	0.5 M H_2SO_4	ACS Appl. Energy Mater. 2020, 3, 6525−6535
NiS-Ni_2P Heterostructure	**147**	**68**	**0.5 M H_2SO_4**	**This Work**

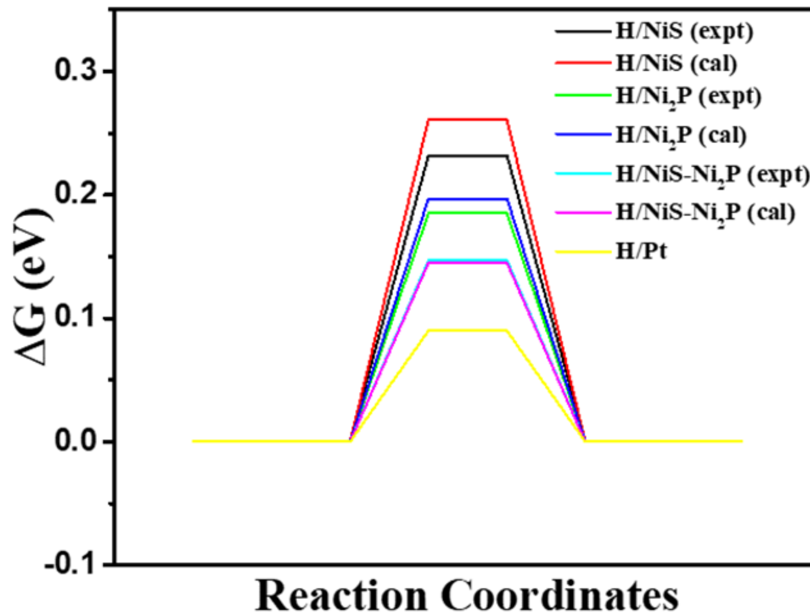


Figure S13 Comparison of variation of change in Gibb's free energy with the reaction coordinates for all electrode materials, along with the value for the best catalyst Pt also included.

Table S2. Comparison of overpotential for HER between experimental and simulations.

System	**HER(Expt.) mV**	**HER(Cal.) mV**
NiS	232	261
Ni_2P	185	197
$NiS-Ni_2P$	147	145