

SUPPORTING INFORMATION

Interface engineering of hierarchical P-doped NiSe/2H-MoSe₂ nanorod arrays for efficient hydrogen evolution

Xiaocheng Xu^a, Rui Wang^a, Sijie Chen^a, Alex Trukhanov^b, Yanxue Wu^c, Lianyi Shao

^{a,*}, Le Huang^{a,*}, Zhipeng Sun^{a,*}

^a School of Materials and Energy, Guangdong University of Technology, Guangzhou, 510006, Guangdong, China.

^b Functional Materials Centre, SSPA Scientific and Practical Materials Research Centre of NAS of Belarus, 19 P. Brovki St., 220072, Minsk, Belarus.

^c Analysis and Test Center, Guangdong University of Technology, Guangzhou, 510006, Guangdong, China.

Email: zpsunxj@gdut.edu.cn.

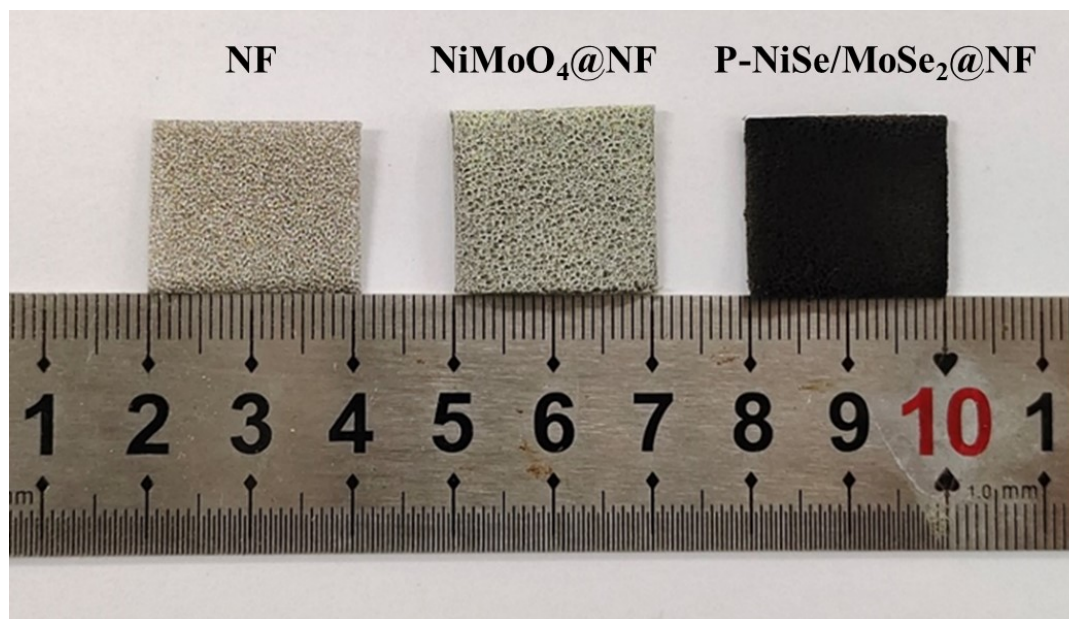


Fig. S1. Digital image of NF, NiMoO₄@NF, and P-NiSe/MoSe₂@NF catalysts.

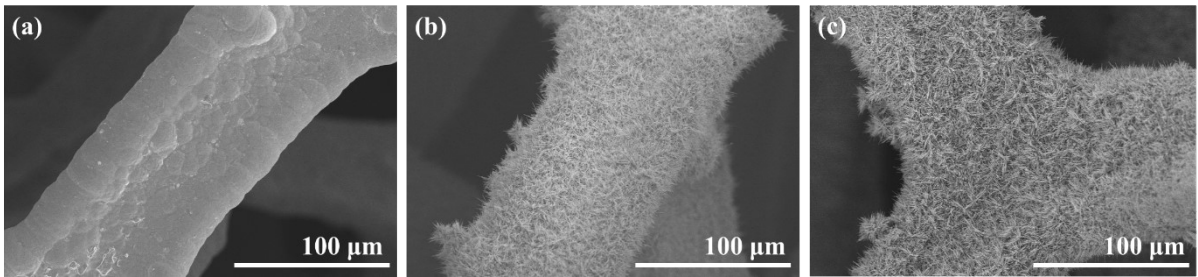


Fig. S2. SEM images of (a) NF, (b) NiMoO₄@NF, and (c) P-NiSe/MoSe₂@NF.

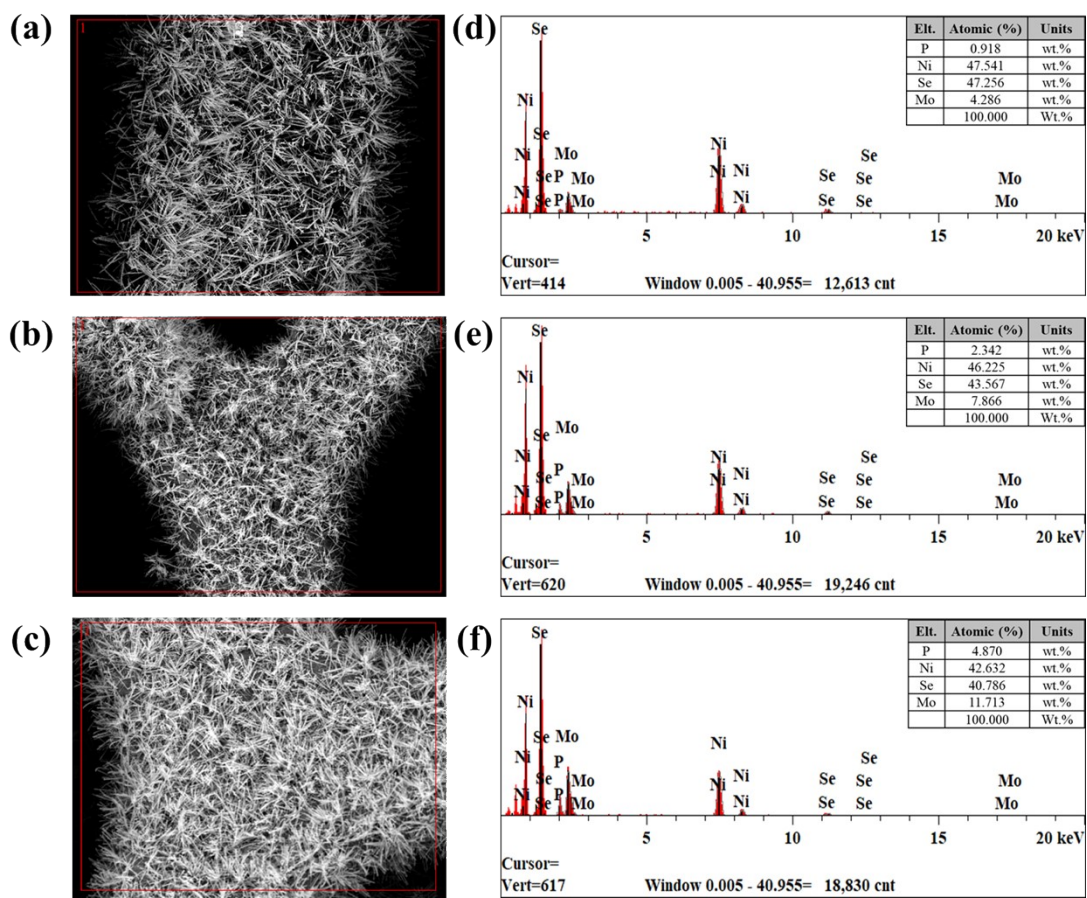


Fig. S3. SEM images and EDS analysis of (a, d) P-NiSe/MoSe₂@NF-1, (b, e) P-NiSe/MoSe₂@NF-2 and (c, f) P-NiSe/MoSe₂@NF-3.

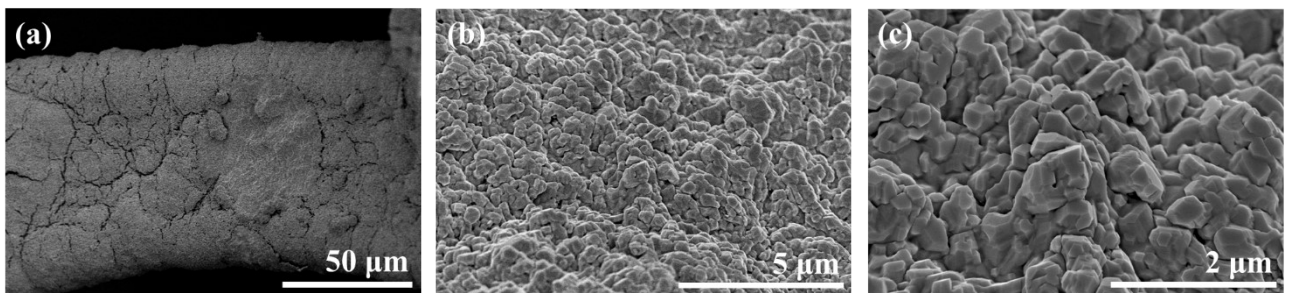


Fig. S4. SEM images of $\text{Ni}_x\text{Se}_y@\text{NF}$ (a-c).

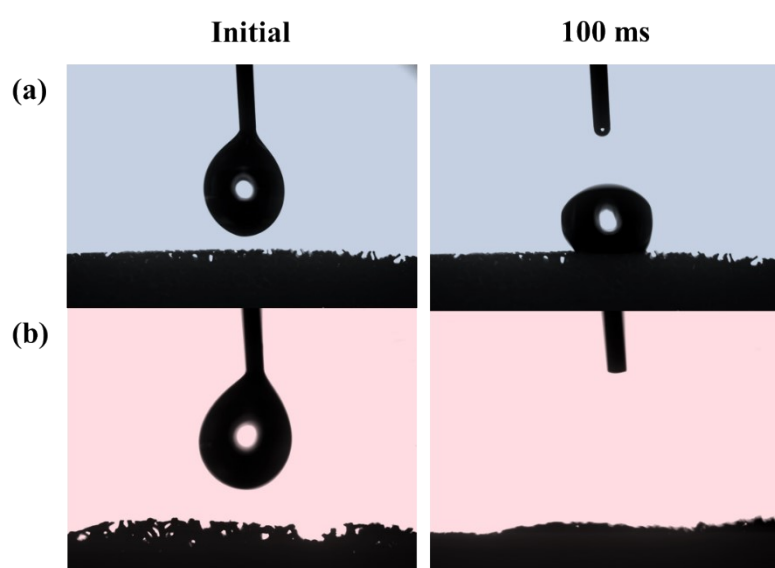


Fig. S5. Wettability test of (a) NF and (b) P-NiSe/MoSe₂@NF electrode.

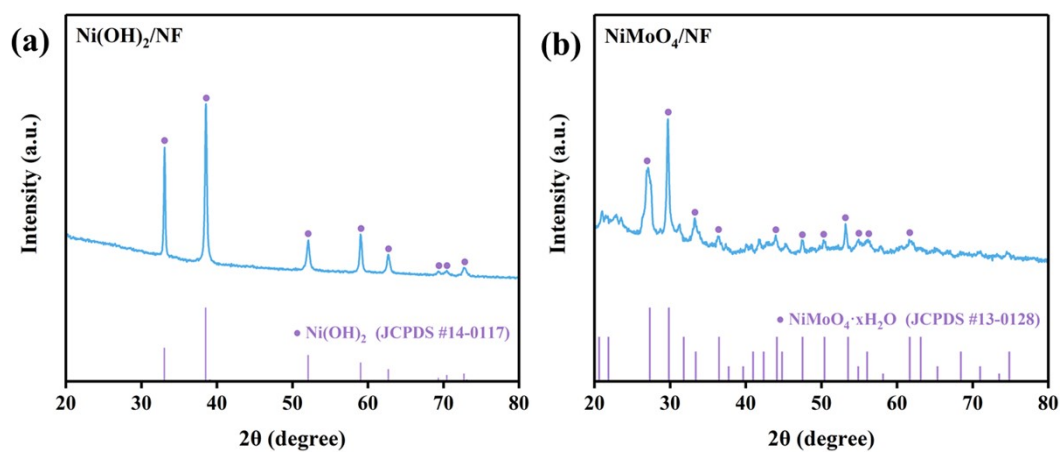


Fig. S6. The typical XRD pattern of (a) Ni(OH)₂@NF and (b) NiMoO₄@NF precursor.

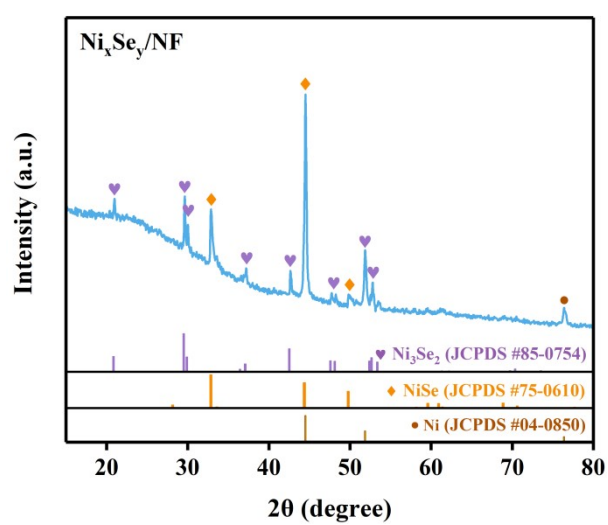


Fig. S7. XRD pattern of $\text{Ni}_x\text{Se}_y/\text{NF}$.

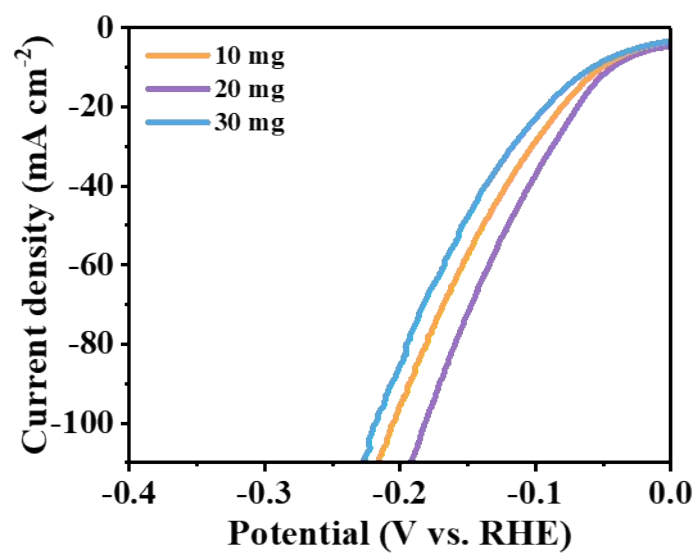


Fig. S8. LSV curves of samples with different doping amounts.

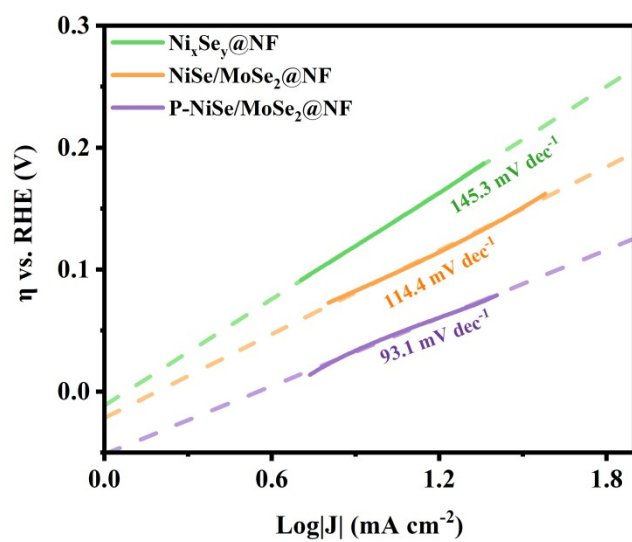


Fig. S9. Tafel plots of $\text{Ni}_x\text{Se}_y@NF$, $\text{NiSe/MoSe}_2@NF$, and $\text{P-NiSe/MoSe}_2@NF$ catalysts to calculate the exchange current density.

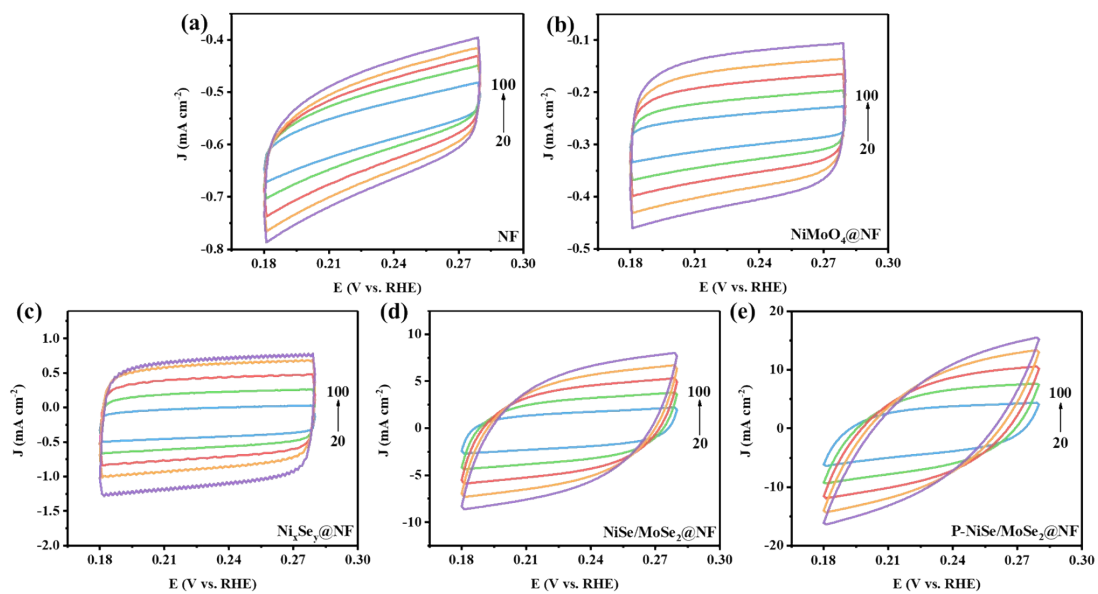


Fig. S10. CV curves within a non-faradaic reaction region of 0.18 ~ 0.28 V versus RHE at different scan rates for (a) NF (b) NiMoO₄@NF, (c) Ni_xSe_y@NF, (d) NiSe/MoSe₂@NF, and (e) P-NiSe/MoSe₂@NF.

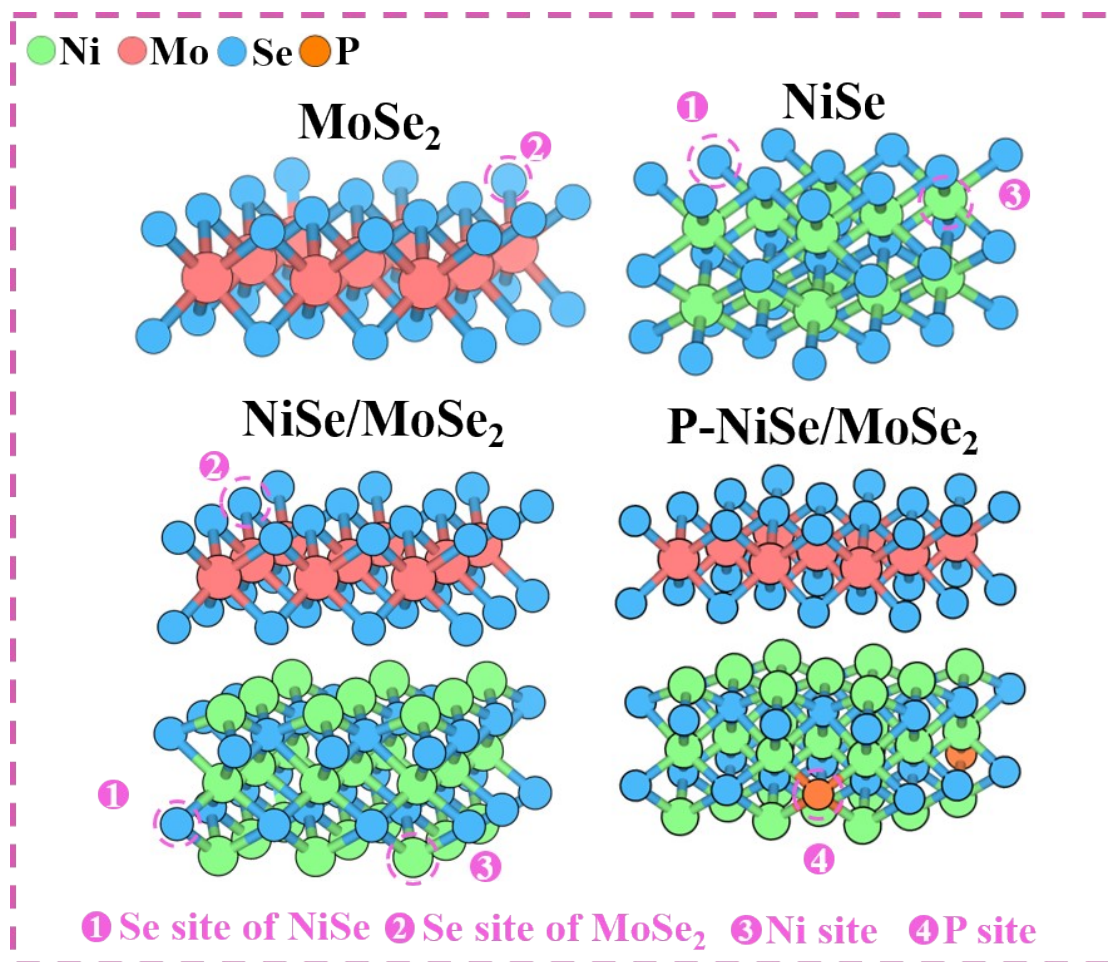


Fig. S11. Optimized geometric models of MoSe₂, NiSe, NiSe/MoSe₂ and P-NiSe/MoSe₂ with possible H* adsorption sites.

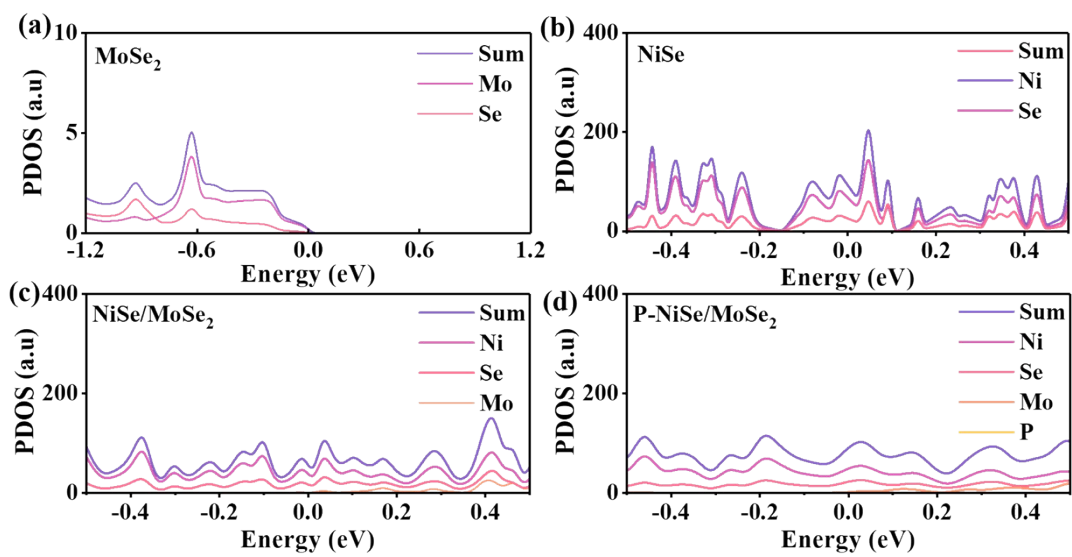


Fig. S12. Projected electronic density of states (PDOS) of (a) MoSe₂, (b) NiSe, (c) NiSe/MoSe₂ and (d) P-NiSe/MoSe₂.

Table S1. Amount of NaH_2PO_2 used and phosphorus doping for different samples.

Sample	Dosage of NaH_2PO_2 (mg)	P atomic ratio (%)
P-NiSe/MoSe2-1	10 mg	0.918
P-NiSe/MoSe2-2	20 mg	2.342
P-NiSe/MoSe2-3	30 mg	4.870

Table S2. Comparison of HER catalytic performance of recently reported catalysts.

Catalyst	Electrolyte	η_{10} vs. RHE (mV)	η_{100} vs. RHE (mV)	Ref
P-NiSe/MoSe₂@NF	1.0 M KOH	43	182	This work
NiMoSe/NF-2	1.0 M KOH	91	223	1
NiMoO ₄ @MoSe ₂ /Ni _x Se _y /NF	1.0 M KOH	69	/	2
P-NiSe ₂ /MoSe ₂ @CC	1.0 M KOH	175	/	3
	0.5 M H ₂ SO ₄	93	/	
1T-MoSe ₂ /NiSe	1.0 M KOH	120	200 mV @ 50 mA cm ⁻²	4
MoSe ₂ @Ni _{0.85} Se	1.0 M KOH	117	204	5
	0.5 M H ₂ SO ₄	154	/	
MoSe ₂ -NiSe@C	1.0 M KOH	180	/	6
MoSe ₂ /NiSe ₂ @CFP	0.5 M H ₂ SO ₄	193	249	7
NiMoSe	0.5 H ₂ SO ₄	197	/	8
SC-NiSe/MoSe ₂ @CFP	1.0 M KOH	71	129	9
Mo, S-codoped NiSe/NF	1.0 M KOH	88	/	10
NiMoSe@Ni _{0.33} Mo _{0.67} O ₄	1.0 M KOH	82.1	/	11
MoSe ₂ /NiSe-2	1.0 M KOH	87	/	12

Table S3. The calculated adsorption energies (eV) of the hydrogen atom.

	Ni site	Se site	P site
MoSe ₂	--	2.10	--
NiSe	0.23	0.22	--
NiSe/MoSe ₂ -NiSe	0.88	0.17	--
NiSe/MoSe ₂ -MoSe ₂	--	1.60	--
P-NiSe/MoSe ₂	--	--	0.16

Reference

- 1 W. Feng, M. Bu, S. Kan, X. Gao, A. Guo, H. Liu, L. Deng, W. Chen, Interfacial hetero-phase construction in nickel/molybdenum selenide hybrids to promote the water splitting performance, *Applied Materials Today*, 2021, **25**, 101175.
- 2 Z. Zhang, S. Ye, J. Ji, Z. Li, F. Wang, Core/shell -structured NiMoO₄@MoSe₂/Ni_xSe_y Nanorod on Ni Foam as a Bifunctional Electrocatalyst for Efficient Overall Water Splitting, *Colloids Surf. A*, 2020, **599**, 124888.
- 3 M. Zhu, Q. Yan, Y. Xue, Y. Yan, K. Zhu, K. Ye, J. Yan, D. Cao, H. Xie, G. Wang, Free-Standing P-Doped NiSe₂/MoSe₂ Catalyst for Efficient Hydrogen Evolution in Acidic and Alkaline Media, *ACS Sustain. Chem. Eng.*, 2022, **10**, 279–287.
- 4 X. Zhang, Y.-Y. Zhang, Y. Zhang, W.-J. Jiang, Q.-H. Zhang, Y.-G. Yang, L. Gu, J.-S. Hu, L.-J. Wan, Phase-Controlled Synthesis of 1T-MoSe₂/NiSe Heterostructure Nanowire Arrays via Electronic Injection for Synergistically Enhanced Hydrogen Evolution, *Small Methods*, 2019, **3**, 1800317.
- 5 C. Wang, P. Zhang, J. Lei, W. Dong, J. Wang, Integrated 3D MoSe₂@Ni_{0.85}Se Nanowire Network with Synergistic Cooperation as Highly Efficient Electrocatalysts for Hydrogen Evolution Reaction in Alkaline Medium, *Electrochim. Acta*, 2017, **246**, 712–719.
- 6 C. Liu, K. Wang, X. Zheng, X. Liu, Q. Liang, Z. Chen, Rational design of MoSe₂-NiSe@carbon heteronanostructures for efficient electrocatalytic hydrogen evolution in both acidic and alkaline media, *Carbon*, 2018, **139**, 1–9.
- 7 L. Zhang, T. Wang, L. Sun, Y. Sun, T. Hu, K. Xu, F. Ma, Hydrothermal synthesis of 3D hierarchical MoSe₂/NiSe₂ composite nanowires on carbon fiber paper and their enhanced electrocatalytic activity for the hydrogen evolution reaction, *J. Mater. Chem. A*, 2017, **5**, 19752–19759.
- 8 K. Premnath, P. Arunachalam, M.S. Amer, J. Madhavan, A.M. Al-Mayouf, Hydrothermally synthesized nickel molybdenum selenide composites as cost-effective and efficient trifunctional electrocatalysts for water splitting reactions, *Int. J. Hydrog. Energy*, 2019, **44**, 22796–22805.
- 9 H. Ding, Q. Jiao, H. Lv, K. Xu, Q. Xing, M. Chen, W. Chu, X. Wu, Y. Guo, Promoting the water reduction reaction of transition metal dichalcogenides in a basic electrolyte by interface engineering, *J. Mater. Chem. A*, 2018, **6**, 17488–17494.
- 10 S. Zhang, X. Zhang, J. Li, E. Wang, Morphological and electronic modulation of NiSe nanosheet assemblies by Mo, S-codoping for an efficient hydrogen evolution reaction, *J. Mater. Chem. A*, 2017, **5**, 20588–20593.
- 11 T. He, Y. He, H. Li, X. Yin, L. Zhou, H. Shi, J. Ma, L. Chen, Core/shell NiMoSe@NiMoO₄ micro-cuboids anchored on Nickel foam as self-supported

electrode towards efficient and stable hydrogen generation, *J. Electroanal. Chem.*, 2022, **904**, 115829.

12 J.-Y. Xue, F.-L. Li, B. Chen, H. Geng, W. Zhang, W.-Y. Xu, H. Gu, P. Braunstein, J.-P. Lang, Engineering multiphase MoSe₂/NiSe heterostructure interfaces for superior hydrogen production electrocatalysis, *Appl. Catal. B*, 2022, **312**, 121434.