

Supporting Information for
Se-doped Ni₅P₄ nanocatalysts for high-efficiency hydrogen evolution
reaction

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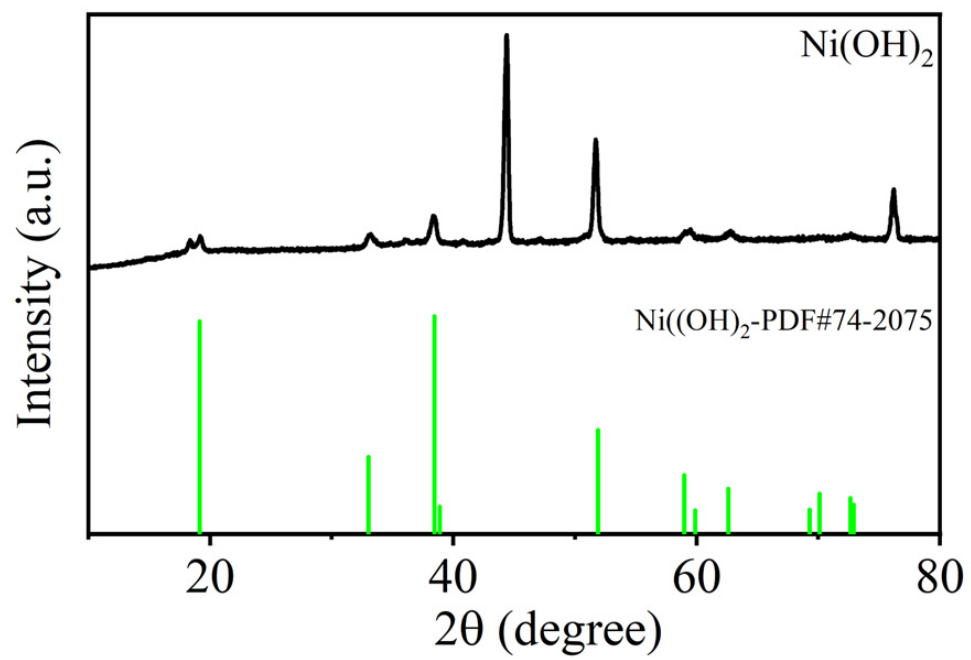


Figure S1 XRD patterns of $\text{Ni}(\text{OH})_2$ precursors.

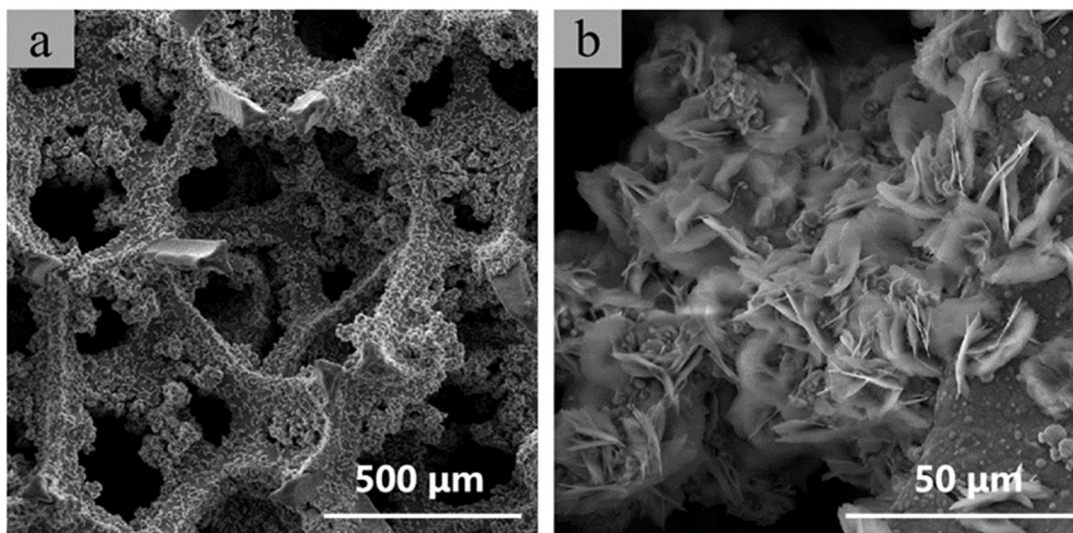


Figure S2 SEM images (a-b) of Ni(OH)_2 precursor.

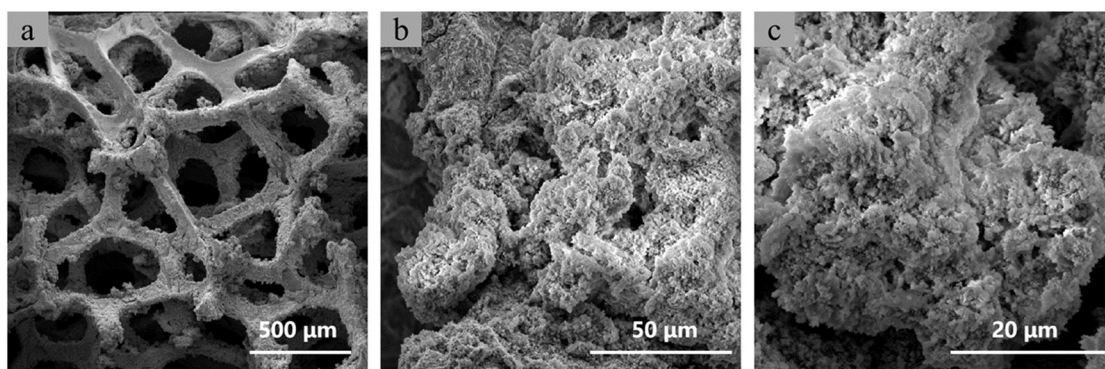


Figure S3 SEM images (a-c) of Ni_5P_4 .

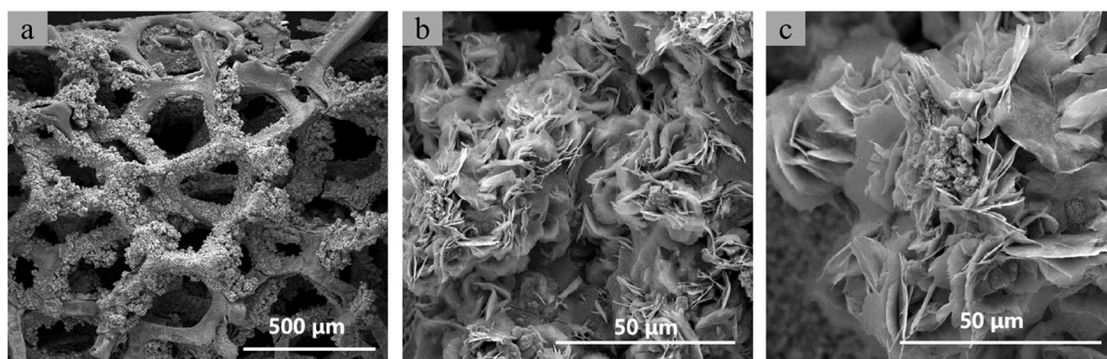


Figure S4 SEM images (a-c) of NiSe₂.

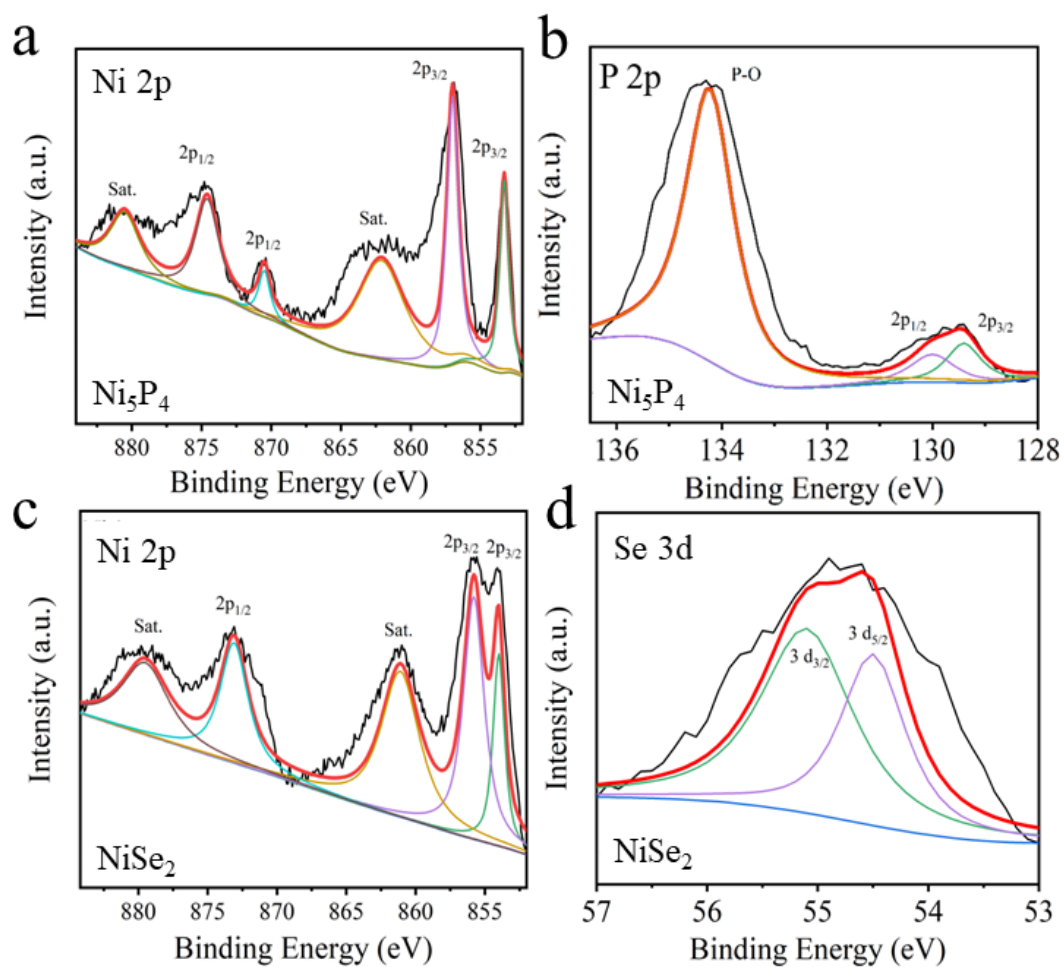


Figure S5 High-resolution XPS spectra of Ni_5P_4 and NiSe_2 , (a) Ni 2p in pure Ni_5P_4 , (b) P 2p in pure Ni_5P_4 , (c) Ni 2p in NiSe_2 , (d) Se 3d in NiSe_2

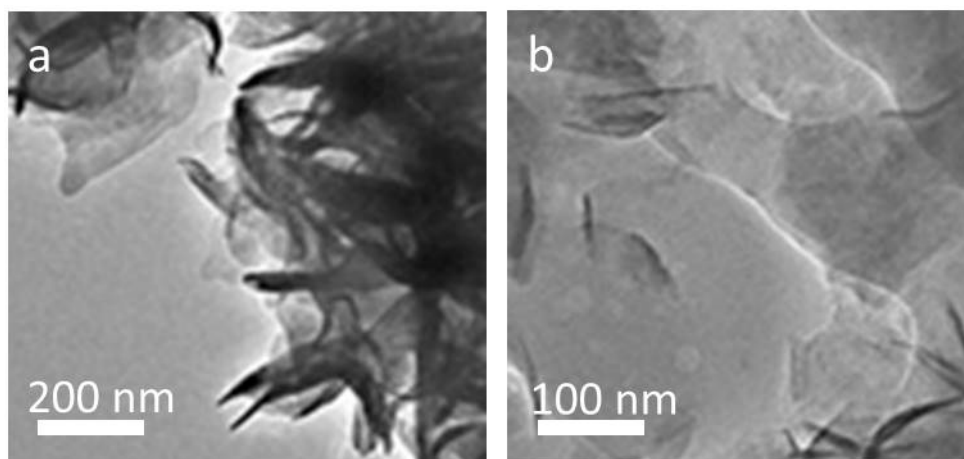


Figure S6 TEM images (a-b) of $\text{Ni}_5\text{P}_4\text{-Se}$ composites.

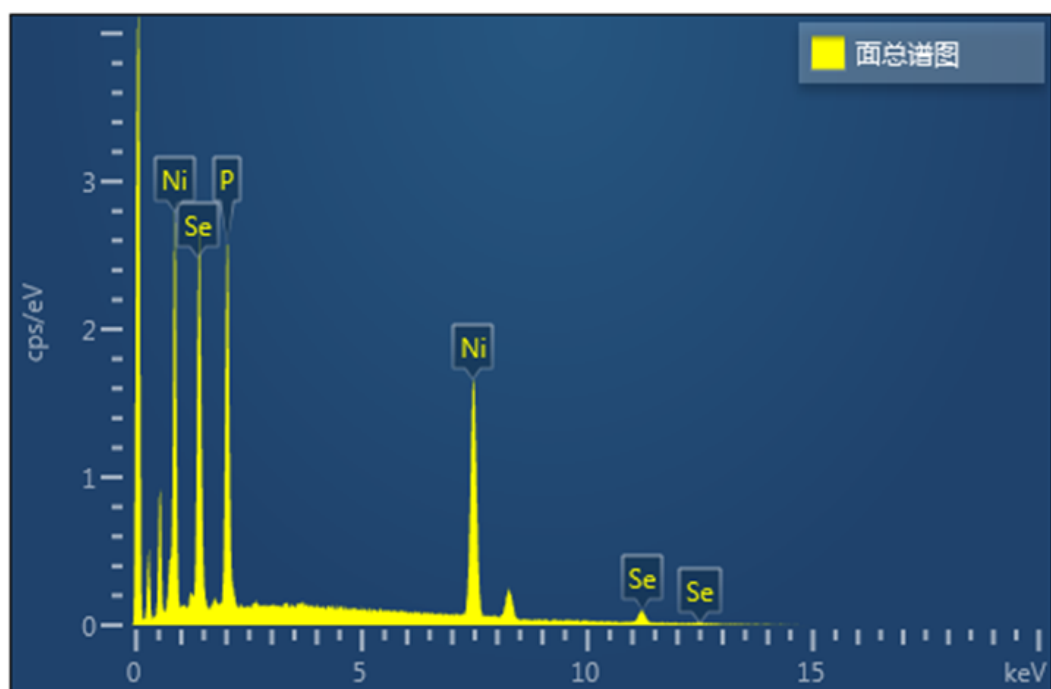


Figure S7 Energy spectrum for $\text{Ni}_5\text{P}_4\text{-Se}$ composites.

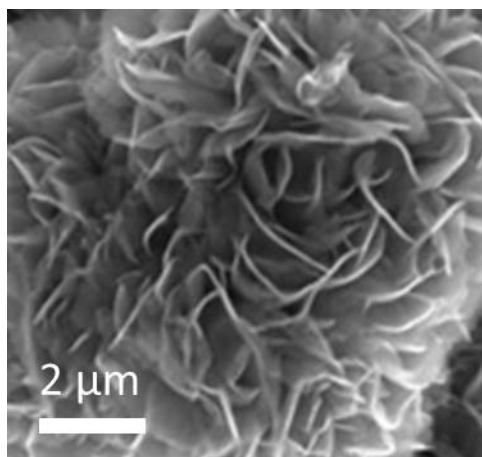


Figure S8 SEM image of $\text{Ni}_5\text{P}_4\text{-Se}$ catalyst after long cycles.

Table S1 Comparison of the catalytic activity of catalysts

Catalyst	Electrolyte	Overpotential (mV vs.RHE)	Tafel (mV dec ⁻¹)	Reference
PNi ₃ S ₂ /NF	1 M KOH	137	147	[1]
NiCo/Sm ₂ O ₃	1 M KOH	276	162	[2]
Ni ₂ P/LSCN	0.1 M KOH	339	105	[3]
NiFe LDH@DG	1 M KOH	270	110	[4]
Ni ₂ P nanofilms	0.1 M KOH	315	120	[5]
np-NiFeMoP	1 M KOH	223	180.3	[6]
FeP	1 M KOH	181	134	[7]
Cu _{0.3} Co _{1.7} P/NC	1 M KOH	220	122	[8]
Ni ₂ P	1 M KOH	183	-	[9]
CoNiP-1:1 NWs	1 M KOH	252	128	[10]
Ni₅P₄-Se	1 M KOH	128	163.14	This work

References

1. Ding, Y. H.; Li, H. Y.; Hou, Y., Phosphorus-doped nickel sulfides/nickel foam as electrode materials for electrocatalytic water splitting. *Int. J. Hydrog. Energy* **2018**, *43*, 19002-19009.
2. Liu, H. H.; Zeng, S.; He, P.; Dong, F. Q.; He, M. Q.; Zhang, Y.; Wang, S.; Li, C. X.; Liu, M. Z.; Jia, L. P., Samarium oxide modified Ni-Co nanosheets based three-dimensional honeycomb film on nickel foam: A highly efficient electrocatalyst for hydrogen evolution reaction. *Electrochim. Acta* **2019**, *299*, 405-414.
3. Wang, Y. R.; Wang, Z. J.; Jin, C.; Li, C.; Li, X. W.; Li, Y. F.; Yang, R. Z.; Liu, M. L., Enhanced overall water electrolysis on a bifunctional perovskite oxide through interfacial engineering. *Electrochim. Acta* **2019**, *318*, 120-129.
4. Jia, Y.; Zhang, L. Z.; Gao, G. P.; Chen, H.; Wang, B.; Zhou, J. Z.; Soo, M. T.; Hong, M.; Yan, X. C.; Qian, G. R.; Zou, J.; Du, A. J.; Yao, X. D., A Heterostructure Coupling of Exfoliated Ni-Fe Hydroxide Nanosheet and Defective Graphene as a Bifunctional Electrocatalyst for Overall Water Splitting. *Adv. Mater.* **2017**, *29*, 8.
5. Li, Y.; Cai, P. W.; Ci, S. Q.; Wen, Z. H., Strongly Coupled 3D Nanohybrids with Ni₂P/Carbon Nanosheets as pH-Universal Hydrogen Evolution Reaction Electrocatalysts. *ChemElectroChem* **2017**, *4*, 340-344.

6. Qian, H. X.; Li, K. Y.; Mu, X. B.; Zou, J. Z.; Xie, S. H.; Xiong, X. B.; Zeng, X. R., Nanoporous NiFeMoP alloy as a bifunctional catalyst for overall water splitting. *Int. J. Hydrog. Energy* **2020**, *45*, 16447-16457.
7. Lv, C. C.; Peng, Z.; Zhao, Y. X.; Huang, Z. P.; Zhang, C., The hierarchical nanowires array of iron phosphide integrated on a carbon fiber paper as an effective electrocatalyst for hydrogen generation. *J. Mater. Chem. A* **2016**, *4*, 1454-1460.
8. Song, J. H.; Zhu, C. Z.; Xu, B. Z.; Fu, S. F.; Engelhard, M. H.; Ye, R. F.; Du, D.; Beckman, S. P.; Lin, Y. H., Bimetallic Cobalt-Based Phosphide Zeolitic Imidazolate Framework: CoPx Phase-Dependent Electrical Conductivity and Hydrogen Atom Adsorption Energy for Efficient Overall Water Splitting. *Adv. Energy Mater.* **2017**, *7*, 9.
9. Read, C. G.; Callejas, J. F.; Holder, C. F.; Schaak, R. E., General Strategy for the Synthesis of Transition Metal Phosphide Films for Electrocatalytic Hydrogen and Oxygen Evolution. *ACS Appl. Mater. Interfaces* **2016**, *8*, 12798-12803.
10. Amorim, I.; Xu, J. Y.; Zhang, N.; Xiong, D. H.; Thalluri, S. M.; Thomas, R.; Sousa, J. P. S.; Araujo, A.; Li, H.; Liu, L. F., Bi-metallic cobalt-nickel phosphide nanowires for electrocatalysis of the oxygen and hydrogen evolution reactions. *Catal. Today* **2020**, *358*, 196-202.