

Supporting Information

NiSe₂/FeSe₂ heterostructured nanoparticles supported on rGO for efficient catalyst towards water electrolysis

Muhammad Ahmad,^a Baojuan Xi,^a Yu Gu,^a Hua Zhang^a and Shenglin Xiong^{*a}

^a School of Chemistry and Chemical Engineering, State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, P. R. China

*Correspondence author. Email: chexsl@sdu.edu.cn (S.L.X)

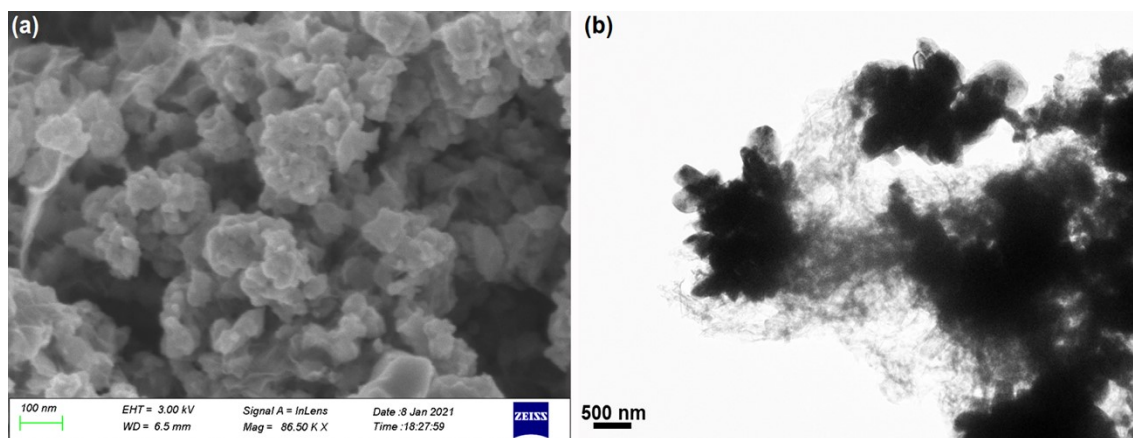


Figure S1. (a) FSEM and (b) TEM images of $\text{FeSe}_2@\text{rGO}$.

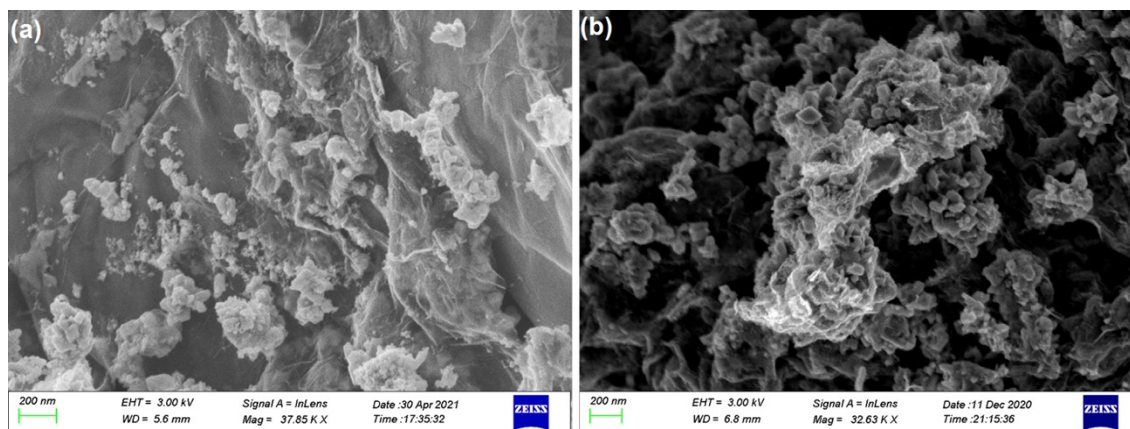


Figure S2. (a,b) FESEM images of NiSe₂@FeSe₂/rGO-2.

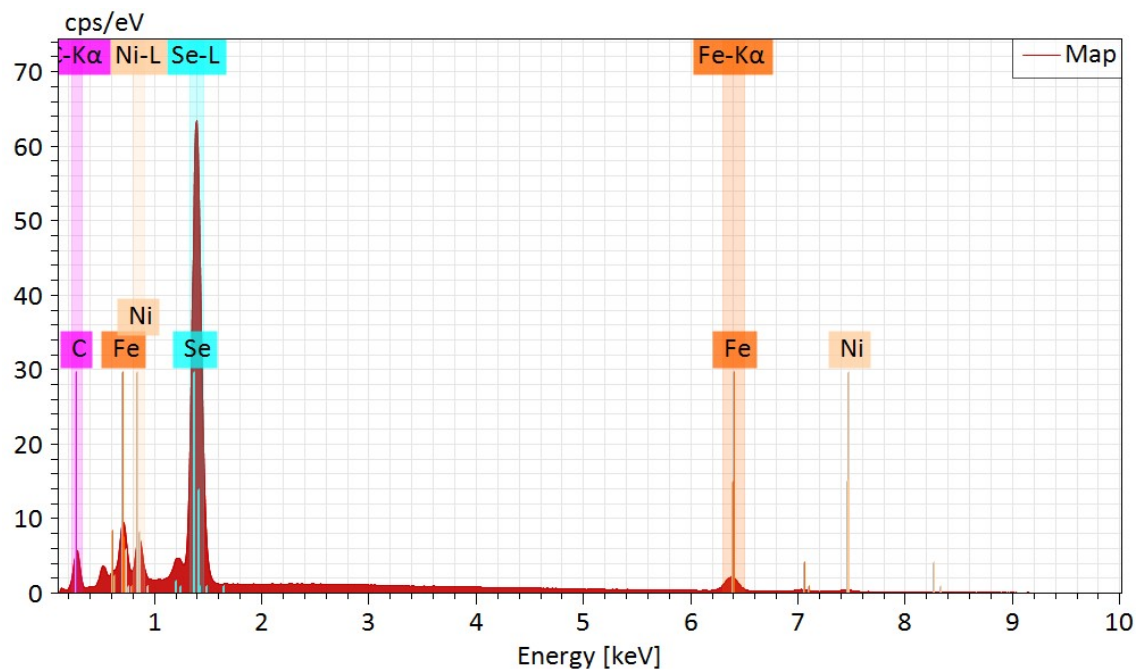


Figure S3. EDX spectrum of NiSe₂@FeSe₂/rGO-2.

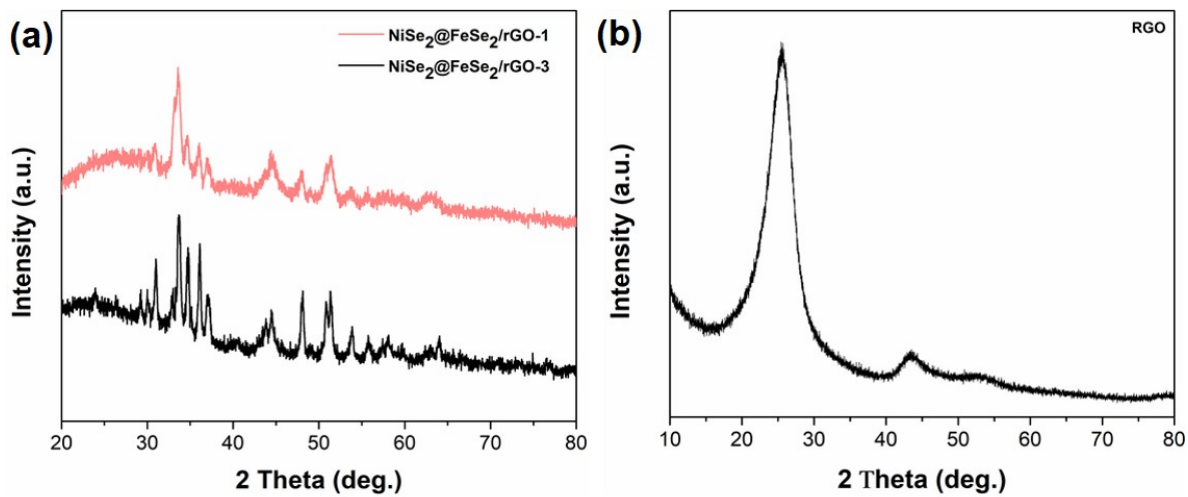


Figure S4. XRD patterns of (a) NiSe₂@FeSe₂/rGO-1, NiSe₂@FeSe₂/rGO-3 and (b) rGO.

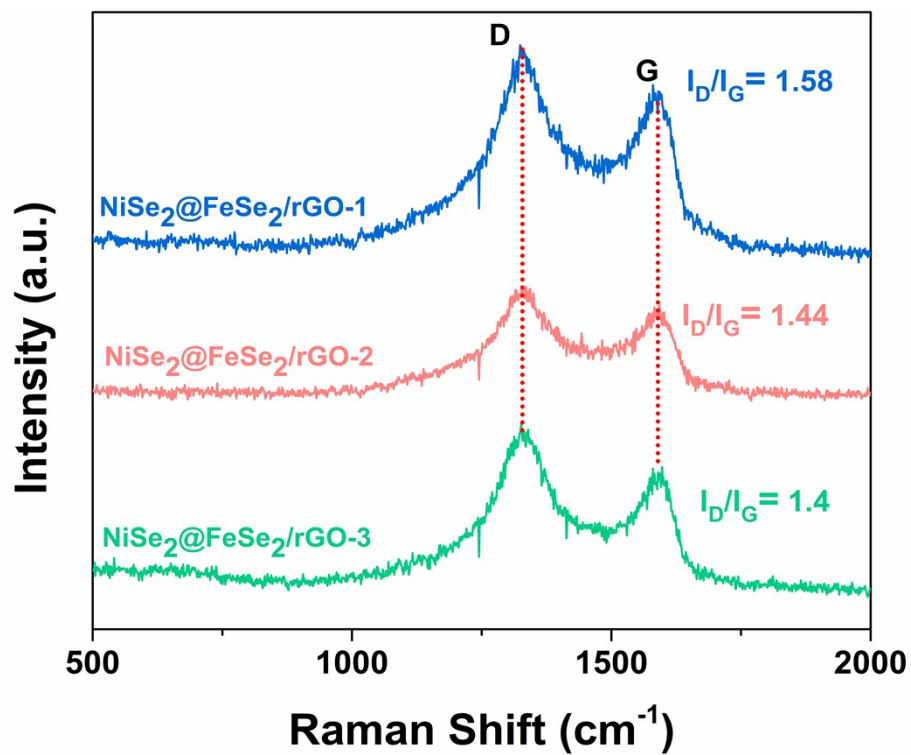


Figure S5. Raman spectra of different samples.

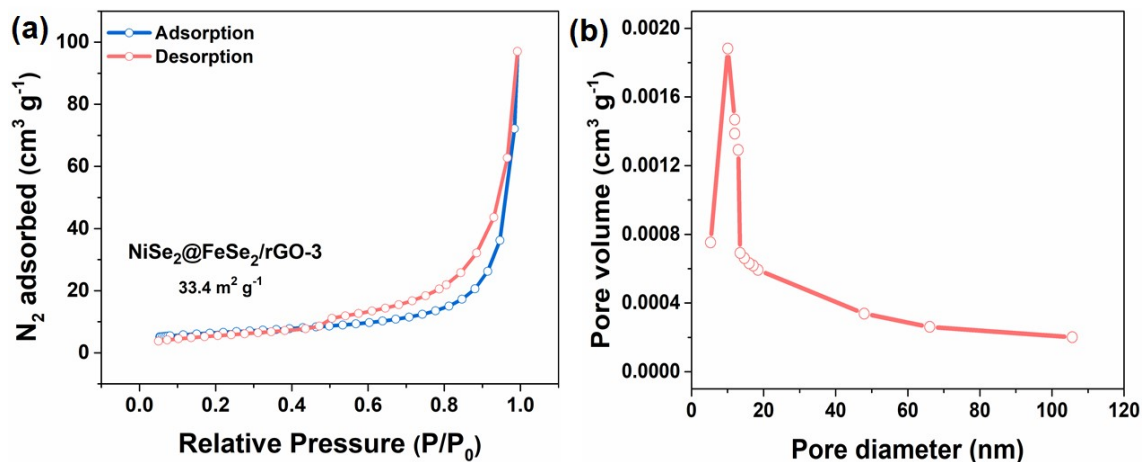


Figure S6. (a) N₂ sorption isotherm and (b) corresponding pore size distribution curve of NiSe₂@FeSe₂/rGO-3.

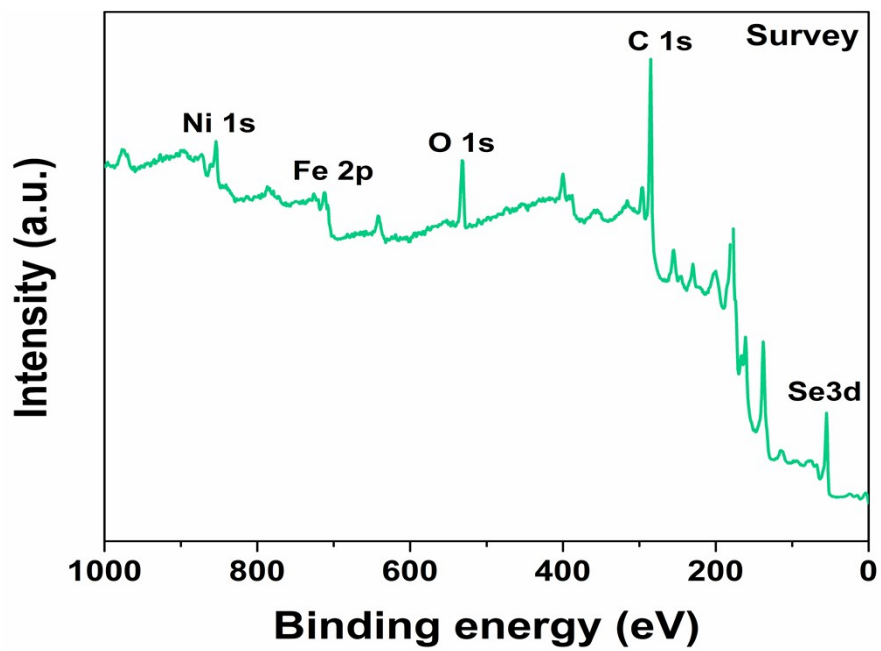


Figure S7. Survey spectrum of NiSe₂@FeSe₂/rGO-2.

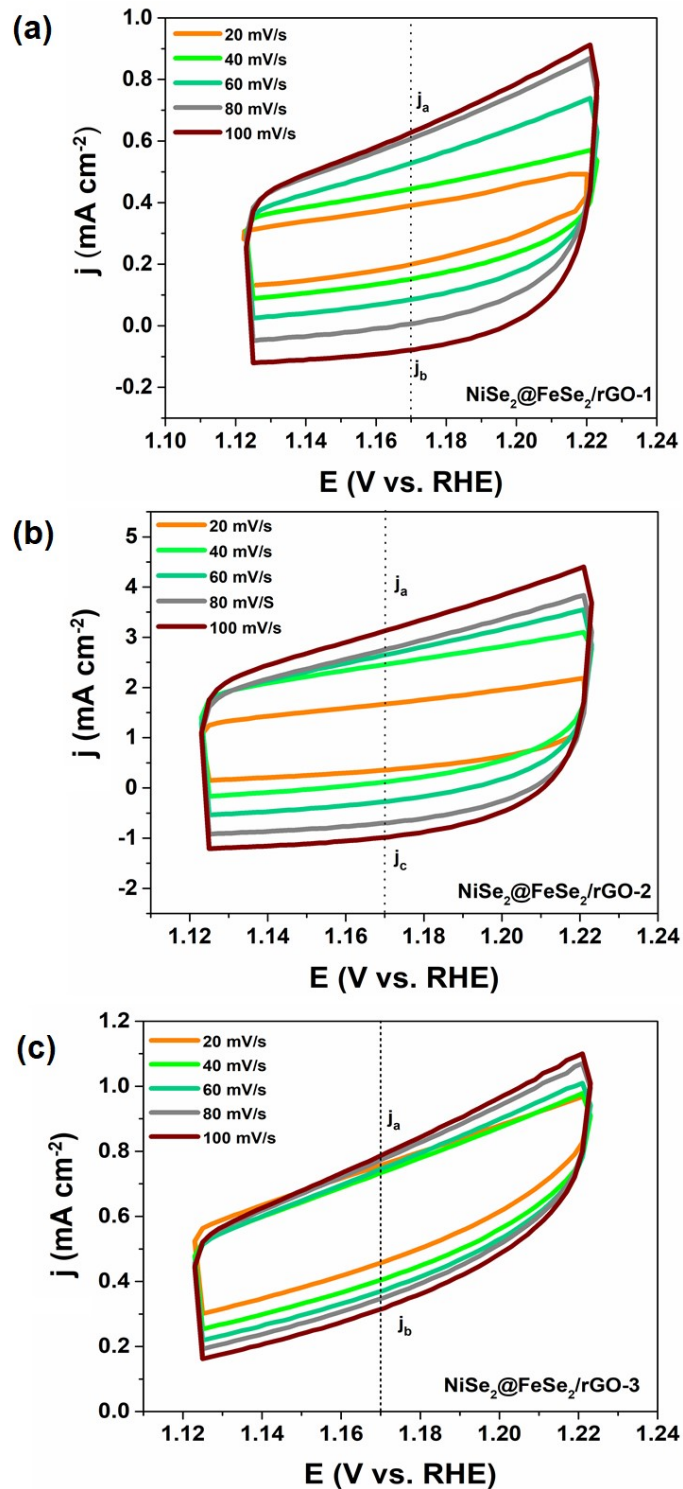


Figure S8. Cyclic voltammogram (CV) curves of (a) NiSe₂@FeSe₂/rGO-1 (b) NiSe₂@FeSe₂/rGO-2 and (c) NiSe₂@FeSe₂/rGO-3.

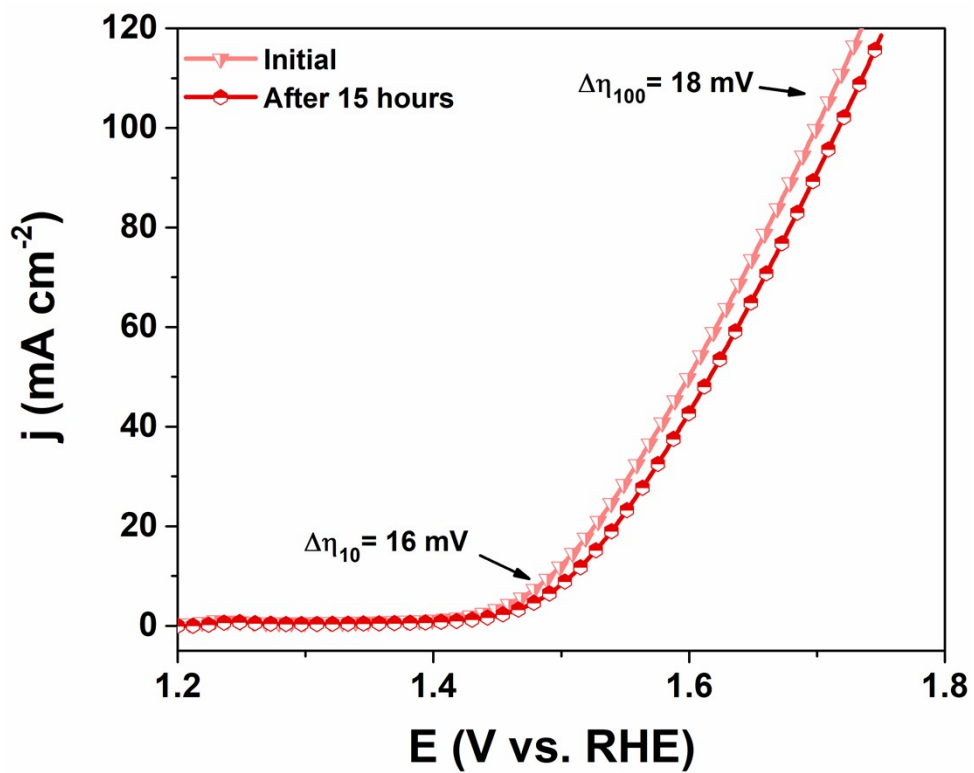


Figure S9. LSV curves of NiSe₂@FeSe₂/rGO-2 before and after chronoamperometric (i-t) measurements for OER.

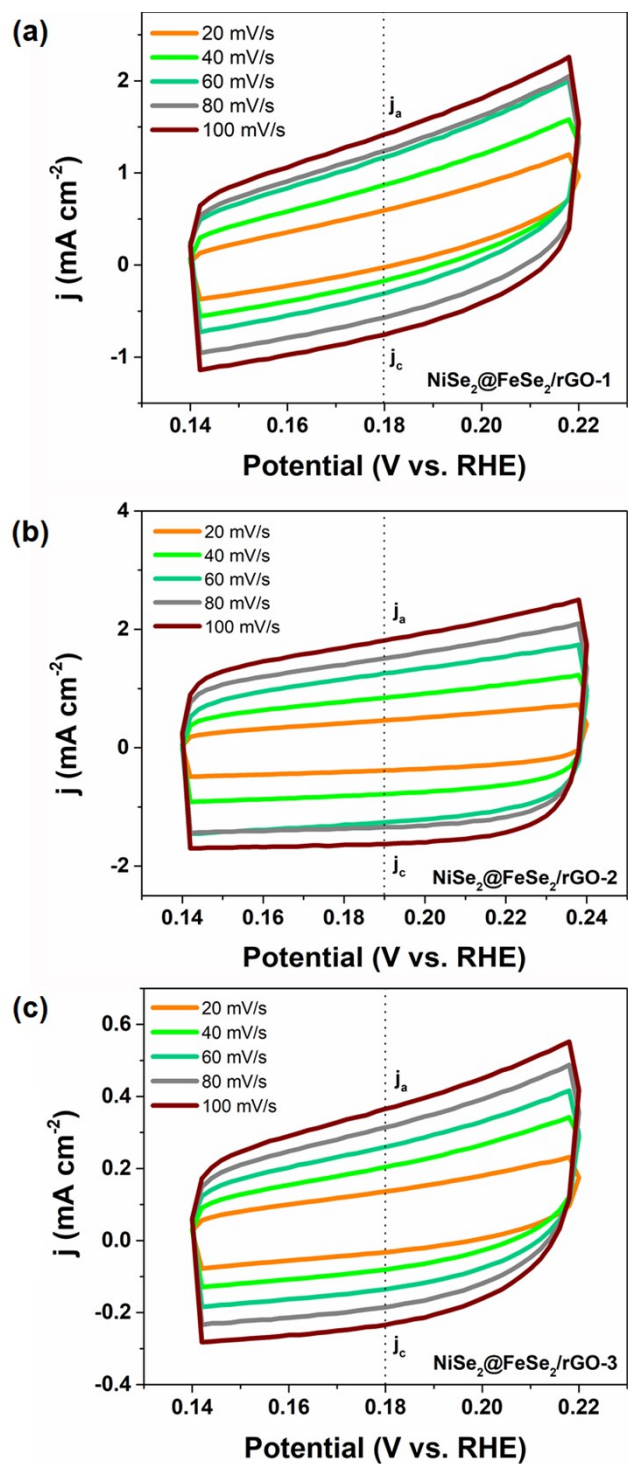


Figure S10. Cyclic voltammogram curves of (a) $\text{NiSe}_2@FeSe_2/rGO-1$ (b) $\text{NiSe}_2@FeSe_2/rGO-3$ and (c) $\text{NiSe}_2@FeSe_2/rGO-2$.

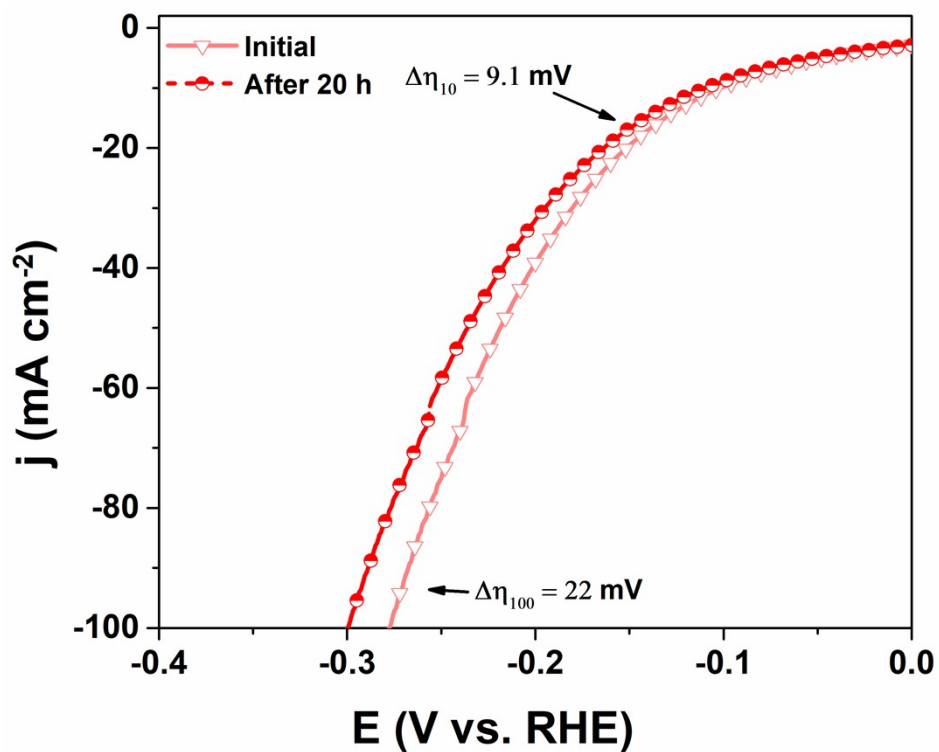


Figure S11. LSV curves of of NiSe₂@FeSe₂/rGO-2 recorded before and after chronoamperometric (i-t) measurements for HER.

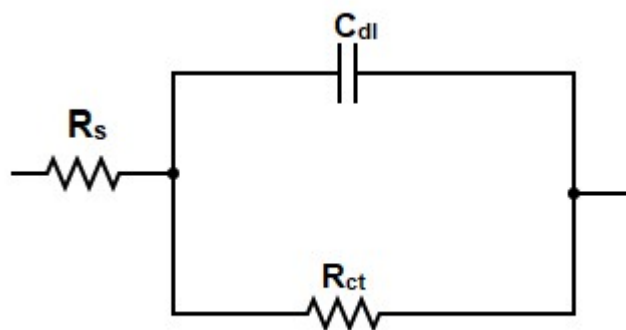


Figure S12. Equivalent circuit employed to calculate R_{ct} .

Table S1. Comparison of OER performances with previously reported catalysts.

Catalysts	Current density j (mA cm ⁻²)	Overpotential η (mV)	Refs.
NiSe ₂ @FeSe ₂ /rGO	10	260	This work
Ni _{0.85} Se/GS	10	302	[S1]
Ti@Ni _{0.85} Se	30	270	[S2]
NiSe-Ni _{0.85} Se/CP	10	300	[S3]
FeNi ₃ @NC	10	277	[S4]
Co _{0.95} Cr _{0.05} Fe ₂ O ₄	10	293.3	[S5]
Co ₃ O ₄	10	297	[S6]
NiSe@NiOOH/NF	50	332	[S7]
NiCo ₂ S ₄ /RGO	10	366	[S8]
Co-Mo-B	10	320	[S9]
β -Ni(OH) ₂	10	340	[S10]
Fe _{0.08} Ni _{0.77} Se	10	245	[S11]

Table S2. Comparison of HER performances with previously reported catalysts.

Catalysts	Current density j (mA cm ⁻²)	Overpotential η (mV)	Refs.
NiSe ₂ @FeSe ₂ /rGO	10	101	This work
Ni _{0.85} Se/GS	10	200	[S1]
Ti@Ni _{0.85} Se	30	120	[S2]
NiSe-Ni _{0.85} Se/CP	10	101	[S3]
Fe _{0.08} Ni _{0.77} Se/CNT ₃	10	108	[S11]
Ni ₂ Fe ₂ N/Ni ₃ Fe	10	74	[S12]
SnS ₂ -MoS ₂	10	240	[S13]
2D i-WC-G	10	120	[S14]
Co@CNF	10	196	[S15]
Ni ₁ Co ₁ -P	10	169	[S16]
Mo ₂ C@NC@MoS _x	10	249	[S17]

Table S3 Comparison of overall watersplitting performances with previously reported catalysts.

catalysts	current density j (mA cm ⁻²)	overall water splitting performance (V)	Refs.
NiSe ₂ @FeSe ₂ /rGO	10	1.57	This work
Ni _{0.85} Se/GS	10	1.7	[S1]
Ti@Ni _{0.85} Se	10	1.66	[S2]
NiSe-Ni _{0.85} Se/CP	10	1.62	[S3]
Fe _{0.08} Ni _{0.77} Se/CNT ₃	10	1.53	[S11]
NiMoP ₂	10	1.5	[S18]
NiS/Ni ₂ P/CC	10	1.67	[S19]
α -Co(OH) ₂	10	1.72	[S20]
α -NiOOH	10	1.66	[S21]
Ni-Fe-P	10	1.486	[S22]
MoO ₂	30	1.65	[S23]

References

- [1] X. Wu, D. He, H. Zhang, H. Li, Z. Li, B. Yang, Z. Lin, L. Lei and X. Zhang, Ni_{0.85}Se as an efficient non-noble bifunctional electrocatalyst for full water splitting, *Int. J. Hydrogen Energy*, 2016, **41**, 10688–10694.
- [2] C. Yang, J. Zhang, G. Gao, D. Liu, R. Liu, R. Fan and Y. Wang, 3D Metallic Ti@Ni_{0.85}Se with triple hierarchy as high-efficiency electrocatalyst for overall water splitting, *ChemSusChem*, 2019, **12**, 2271–2277.

- [3] Y. Chen, Z. Ren, H. Fu, X. Zhang, G. Tian and H. Fu, NiSe-Ni_{0.85}Se heterostructure nanoflake arrays on carbon paper as efficient electrocatalysts for overall water splitting, *Small* 2018, **14**, e1800763.
- [4] D. Chen, J. Zhu, X. Mu, R. Cheng, W. Li, S. Liu, Z. Pu, C. Lin and S. Mu, Nitrogen-Doped carbon coupled FeNi₃ intermetallic compound as advanced bifunctional electrocatalyst for OER, ORR and zn-air batteries, *Appl. Catal. B* 2020, **268**, 118729.
- [5] S. Pan, J. Yu, Y. Zhang and B. Li, Pulsed laser deposited Cr-doped CoFe₂O₄ thin film as highly efficient oxygen evolution reaction electrode, *Mater. Lett.* 2020, **262**, 127027.
- [6] J. Du, C. Li and Q. Tang, Oxygen vacancies enriched Co₃O₄ nanoflowers with single layer porous structures for water splitting, *Electrochim. Acta* 2020, **331**, 135456.
- [7] X. Li, G. -Q. Han, Y.-R. Liu, B. Dong, W. -H. Hu, X. Shang, Y. -M. Chai and C.-G. Liu, NiSe@NiOOH coreshell hyacinth-like nanostructures on nickel foam synthesized by in situ electrochemical oxidation as an efficient electrocatalyst for the oxygen evolution reaction, *ACS Appl. Mater. Interfaces*, 2016, **8**, 20057–20066.
- [8] C. Shuai, Z. Mo, X. Niu, X. Yang, G. Liu, J. Wang, N. Liu and R. Guo, Hierarchical NiCo₂S₄ nanosheets grown on graphene to catalyze the oxygen evolution reaction, *J. Mater. Sci.*, 2020, **55**, 1627–1636.

- [9] S. Gupta, N. Patel, R. Fernandes, S. Hanchate, A. Miotello and D.C. Kothari, Co-Mo-B nanoparticles as a non-precious and efficient bifunctional electrocatalyst for hydrogen and oxygen evolution, *Electrochim. Acta*, 2017, **232**, 64–71.
- [10] N. Kim, D. Lim, Y. Choi, S.E. Shim and S.-H. Baeck, β -Ni(OH)₂ nanoplates with oxygen vacancies as efficient catalysts for the oxygen evolution reaction, *Electrochim. Acta*, 2019, **324**, 134868.
- [11] G. Liu, C. Shuai, Z. Mo, R. Guo, N. Liu, Q. Dong, J. Wang, H. Pei, W. Liu and X. Guo, Fe-doped Ni_{0.85}Se nanospheres interspersed into carbon nanotubes as efficient and stable electrocatalyst for overall water splitting, *Electrochim. Acta*, 2021, **385**, 138452.
- [12] Y. Hu, T. Xiong, M.-S.J.T. Balogun, Y. Huang, D. Adekoya, S. Zhang and Y. Tong, Enhanced metallicity boosts hydrogen evolution capability of dual-bimetallic Ni–Fe nitride nanoparticles *Mater. Today Phys.*, 2020, **15**, 100267.
- [13] T. Ali, X. Wang, K. Tang, Q. Li, S. Sajjad, S. Khan, S.A. Farooqi and C. Yan, SnS₂ quantum dots growth on MoS₂: atomic-level heterostructure for electrocatalytic hydrogen evolution, *Electrochim. Acta*, 2019, **300**, 45–52.
- [14] M. Zeng, Y. Chen, J. Li, H. Xue, R.G. Mendes, J. Liu, T. Zhang, M.H. Rummeli and L. Fu, 2D WC single crystal embedded in graphene for enhancing hydrogen evolution reaction, *Nano Energy*, 2017, **33**, 356–362.
- [15] H. Su, H.-H. Wang, B. Zhang, K.-X. Wang, X.-H. Li and J.-S. Chen, Enriching Co nanoparticles inside carbon nanofibers via nanoscale assembly of metal–organic complexes for highly efficient hydrogen evolution, *Nano Energy*, 2016, **22**, 79–86.

- [16] C. Shuai, Z. Mo, X. Niu, P. Zhao, Q. Dong, Y. Chen, N. Liu and R. Guo, Nickel/cobalt bimetallic phosphides derived metal-organic frameworks as bifunctional electrocatalyst for oxygen and hydrogen evolution reaction, *J. Alloys Compd.*, 2020, **847**, 156514.
- [17] J. -Q. Chi, X. Shang, S. -S. Lu, B. Dong, Z. -Z. Liu, K. -L. Yan, W. -K. Gao, Y. -M. Chai and C.-G. Liu, Mo₂C@NC@MoS_x porous nanospheres with sandwich shell based on MoO₄²⁻-polymer precursor for efficient hydrogen evolution in both acidic and alkaline media, *Carbon*, 2017, **124**, 555–564.
- [18] X. -D. Wang, H.-Y. Chen, Y.-F. Xu, J.-F. Liao, B.-X. Chen, H.-S. Rao, D.-B. Kuang and C.-Y. Su, Self-supported NiMoP₂ nanowires on carbon cloth as an efficient and durable electrocatalyst for overall water splitting, *J. Mater. Chem. A* 2017, **5**, 7191–7199.
- [19] X. Xiao, D. Huang, Y. Fu, M. Wen, X. Jiang, X. Lv, M. Li, L. Gao, S. Liu, M. Wang, C. Zhao and Y. Shen, Engineering NiS/Ni₂P heterostructures for efficient electrocatalytic water splitting, *ACS Appl. Mater. Interfaces* 2018, **10**, 4689–4696.
- [20] P. Guo, J. Wu, X. -B. Li, J. Luo, W. -M. Lau, H. Liu, X. -L. Sun and L.-M. Liu, A highly stable bifunctional catalyst based on 3D Co(OH)₂@NCNTs@NF towards overall water-splitting, *Nano Energy*, 2018, **47**, 96–104.
- [21] Q. Zhang, C. Zhang, J. Liang, P. Yin and Y. Tian, Orthorhombic α-NiOOH nanosheet arrays: phase conversion and efficient bifunctional electrocatalysts for full Water splitting, *ACS Sustain. Chem. Eng.*, 2017, **5**, 3808–3818.

- [22] C. Xuan, Z. Peng, K. Xia, J. Wang, W. Xiao, W. Lei, M. Gong, T. Huang and D. Wang, Self-supported ternary Ni-Fe-P nanosheets derived from metal-organic frameworks as efficient overall water splitting electrocatalysts, *Electrochim. Acta*, 2017, **258**, 423–432.
- [23] W. Wang, Z. Yang, F. Jiao and Y. Gong, (P, W)-co doped MoO₂ nanoflowers on nickel foam as an efficient bifunctional electrocatalyst for overall water splitting, *Appl. Surf. Sci.* 2020, **529**, 146987.