

Supplementary Information

Corrosion-etching strategy for fabricating RuO₂ coupled with defective NiFeZn(OH)_x for highly efficient hydrogen evolution reaction

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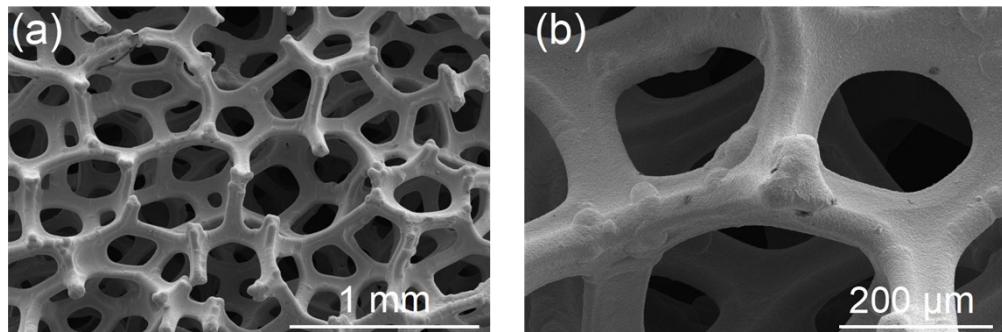


Fig. S1. Low (a) and high (b) resolution SEM images of NFF.

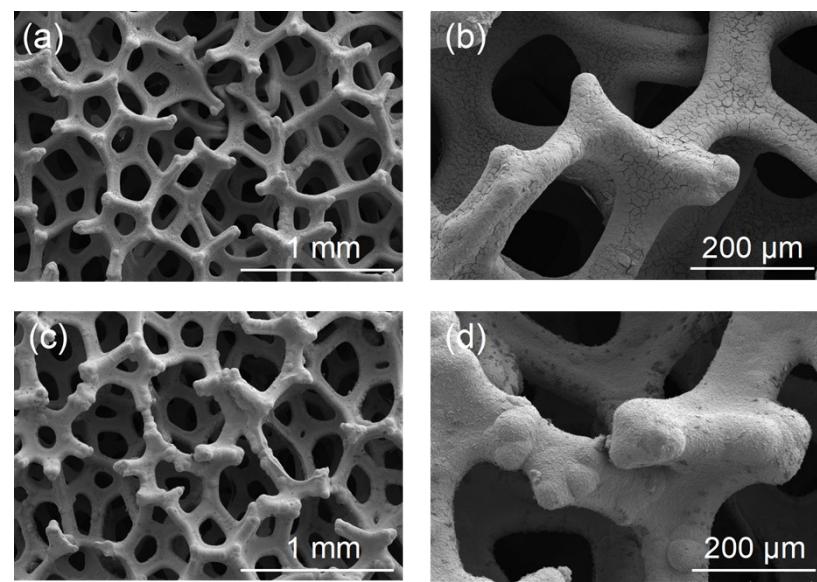


Fig. S2. SEM images of (a-b) NFF-Ru and (c-d) NFF-Ru-Zn.

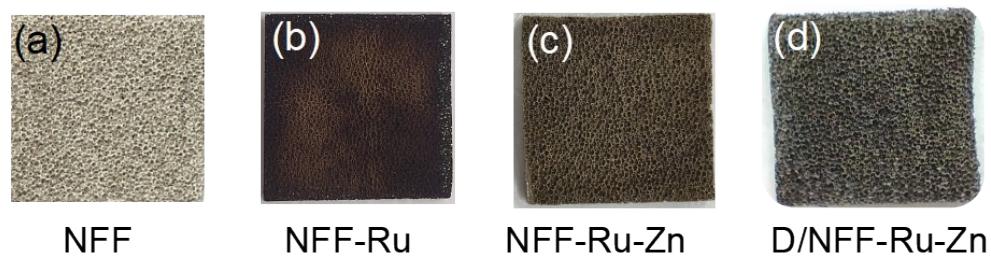


Fig. S3. Photographs of (a) NFF, (b) NFF-Ru, (c) NFF-Ru-Zn, and (d) D/NFF-Ru-Zn.

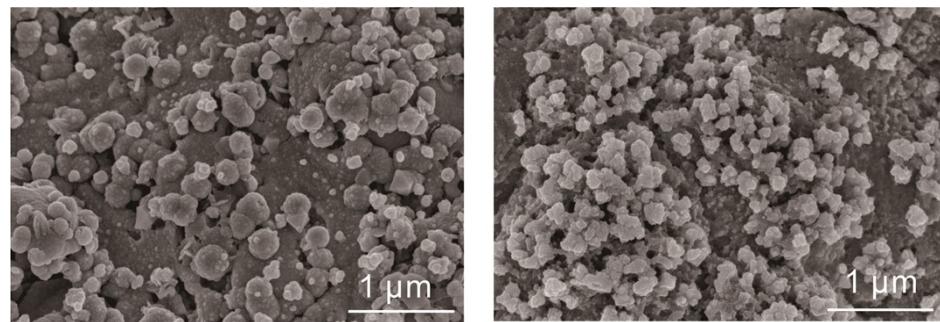


Fig. S4. SEM images of D/NFF-Ru-Zn.

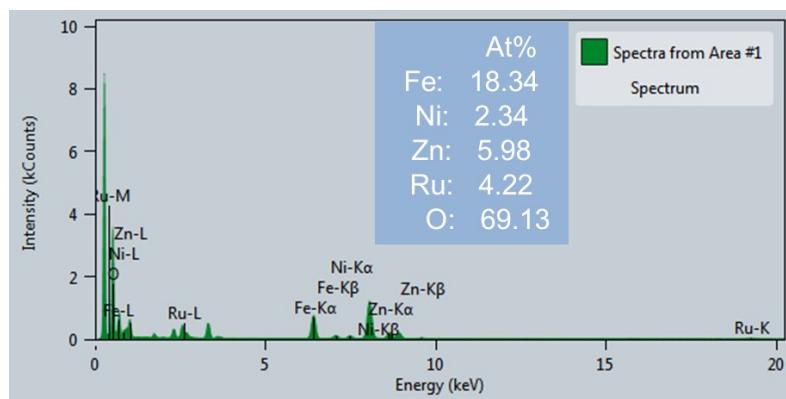


Fig. S5. EDX spectrum of the D/NFF-Ru-Zn.

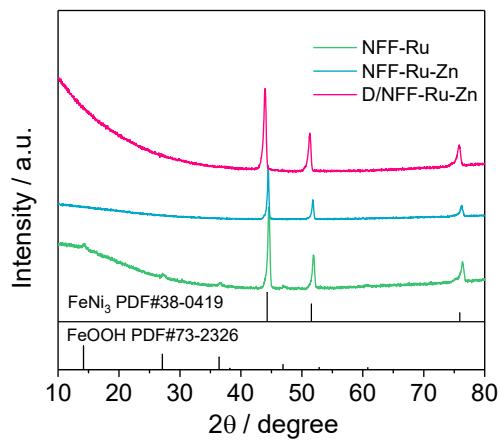


Fig. S6. XRD spectra of the NFF-Ru, NFF-Ru-Zn, and D/NFF-Ru-Zn.

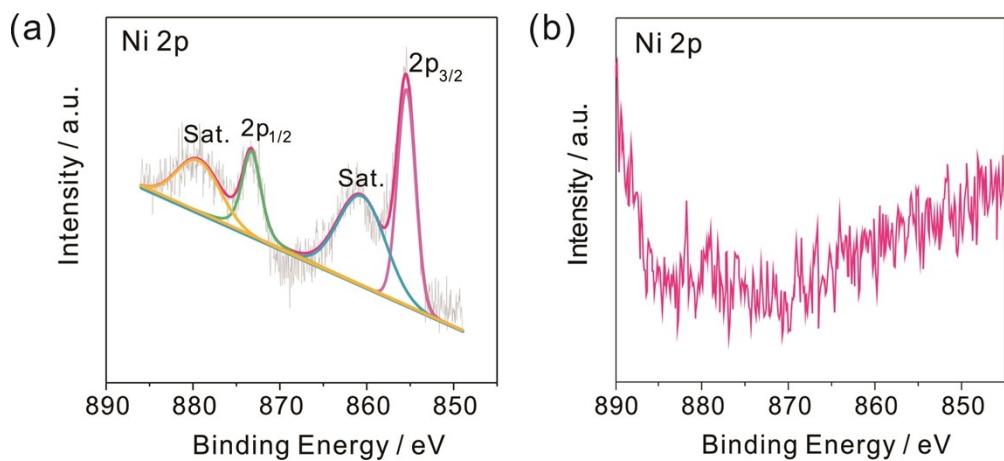


Fig. S7. Ni 2p XPS spectra of (a) D/NFF-Ru-Zn and (b) NFF-Ru-Zn.

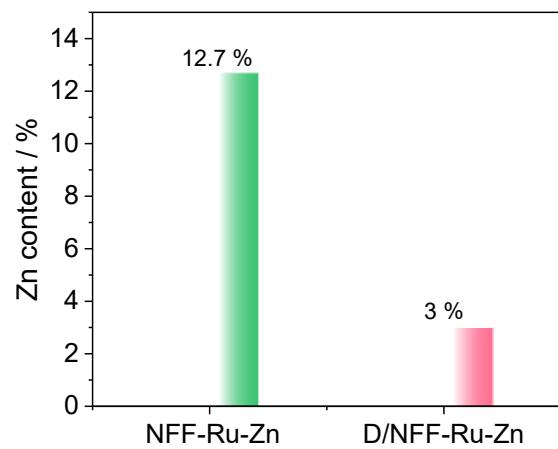


Fig. S8. Zn content in NFF-Ru-Zn and D/NFF-Ru-Zn obtained by XPS analysis.

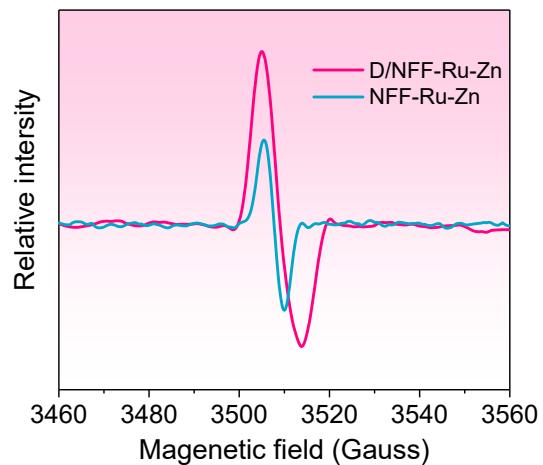


Fig. S9. Electron paramagnetic resonance of NFF-Ru-Zn and D/NFF-Ru-Zn.

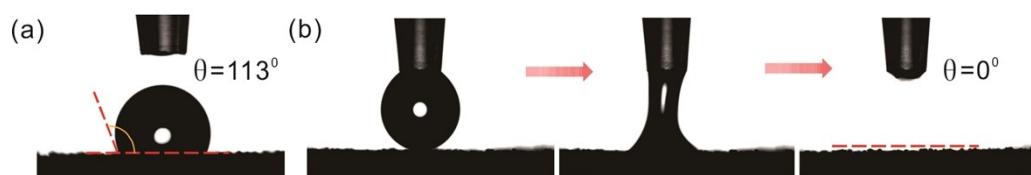


Fig. S10. Contact angles of (a) NFF and (b) D/NFF-Ru-Zn.

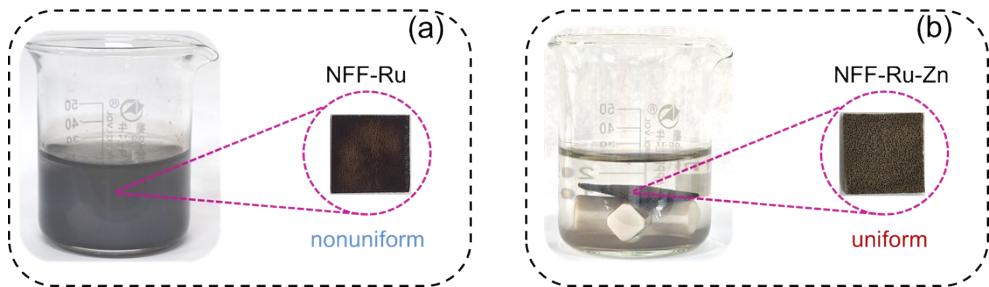


Fig. S11. Photographs of (a) NFF-Ru and (b) NFF-Ru-Zn.

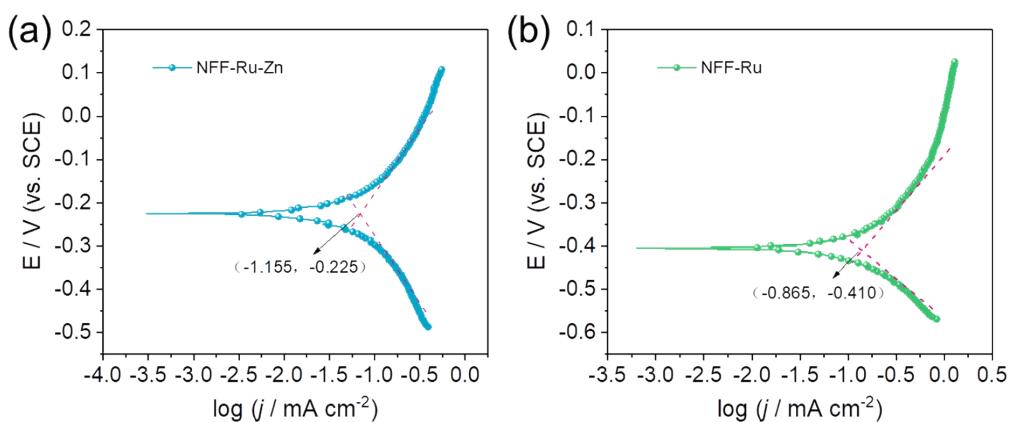


Fig. S12. Corrosion polarization curves of NFF in the solutions of (a) $\text{RuCl}_3\text{-ZnSO}_4$ and (b) RuCl_3 , respectively.

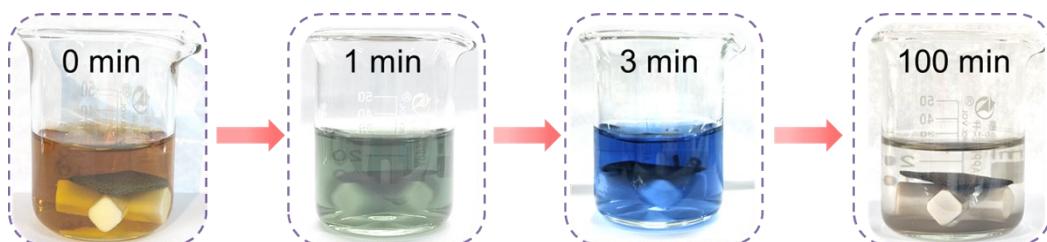


Fig. S13. Color changes of the “ $\text{RuCl}_3\text{-ZnSO}_4$ ” solution in the preparation of NFF-Ru-Zn.

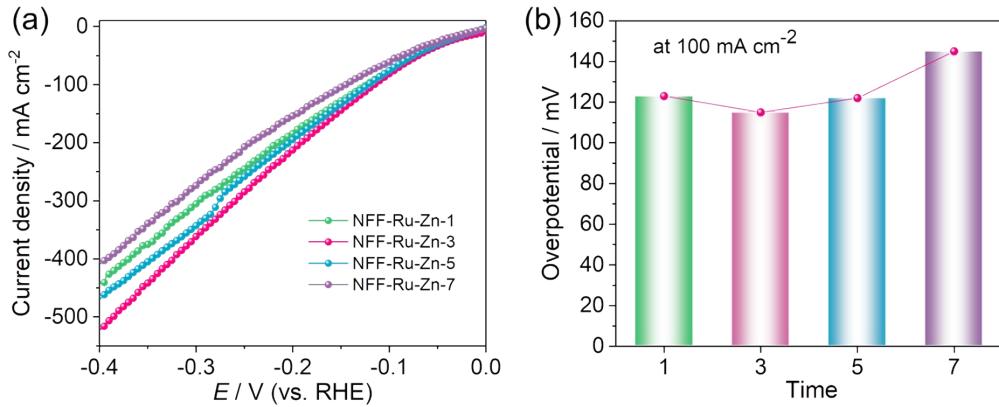


Fig. S14. (a) HER polarization curves of NFF-Ru-Zn under different corrosion time. (b) Comparison of overpotentials at the current density of 100 mA cm^{-2} .

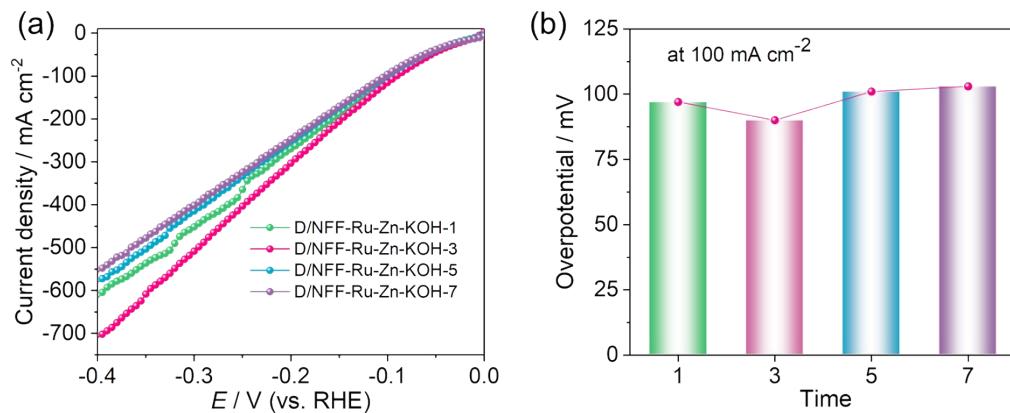


Fig. S15. (a) HER polarization curves of D/NFF-Ru-Zn under different etching time. (b) Comparison of overpotentials at the current density of 100 mA cm^{-2} .

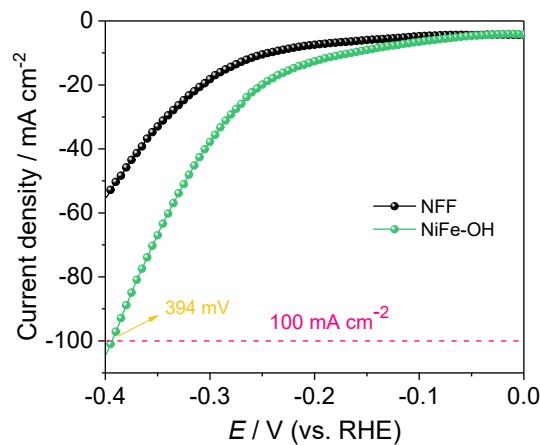


Fig. S16. HER polarization curves of NFF and NiFe-OH.

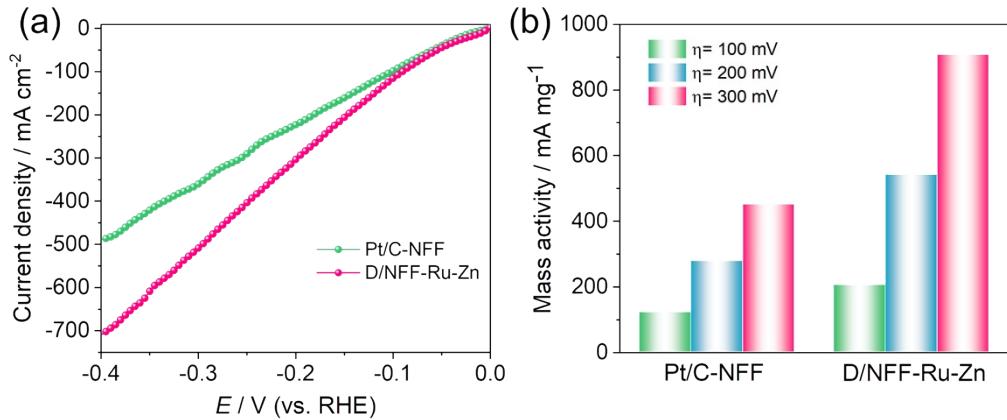


Fig. S17. (a) LSV polarization curves and (b) mass activity of D/NFF-Ru-Zn and Pt/C-NFF (40% Pt) at overpotentials of 100, 200, and 300 mV.

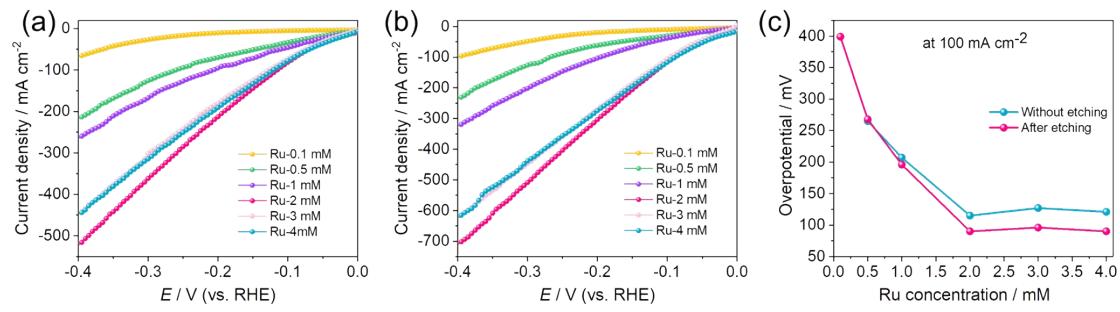


Fig. S18. HER polarization curves of (a) NFF-Ru-Zn and (b) D/NFF-Ru-Zn with different Ru concentrations. (c) Comparison of overpotentials at 100 mA cm⁻² for NFF-Ru-Zn and D/NFF-Ru-Zn with different Ru concentrations.

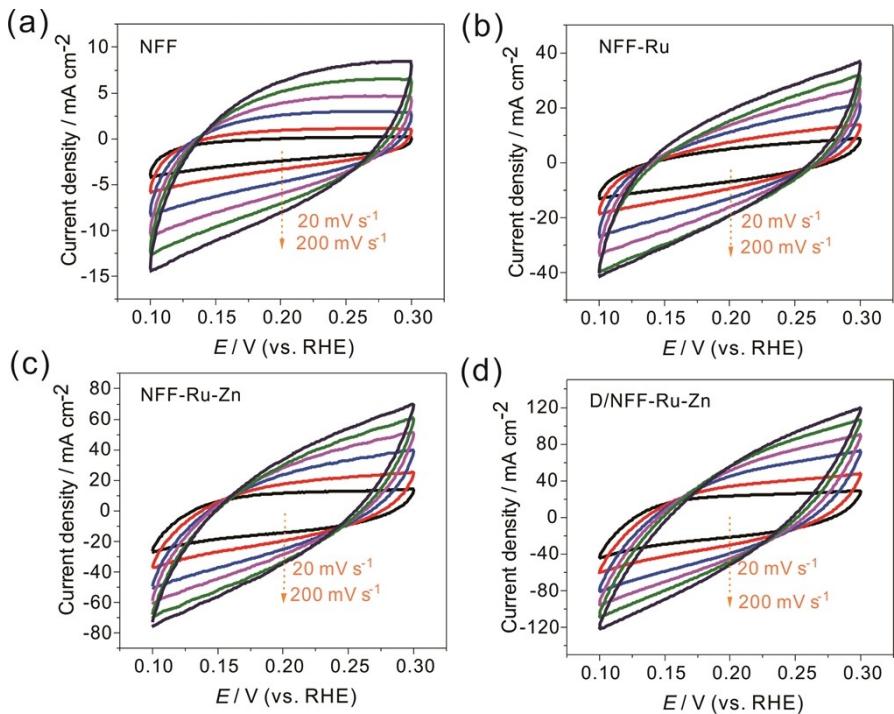


Fig. S19. CV curves of (a) NFF, (b) NFF-Ru, (c) NFF-Ru-Zn and (d) D/NFF-Ru-Zn catalysts in the potential range of 0.1~0.3 V with the scanning rates of 20~200 mV s⁻¹.

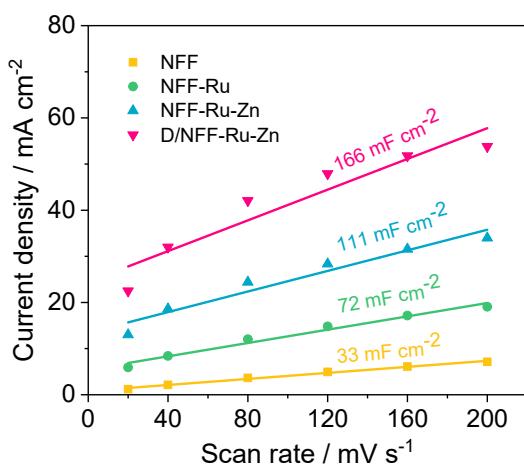


Fig. S20. The C_{dl} values of samples at various scanning rates.

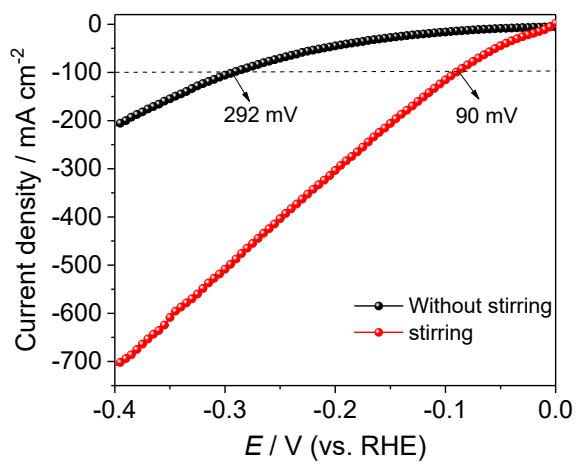


Fig. S21. HER polarization curves of D/NFF-Ru-Zn catalyst with and without stirring.

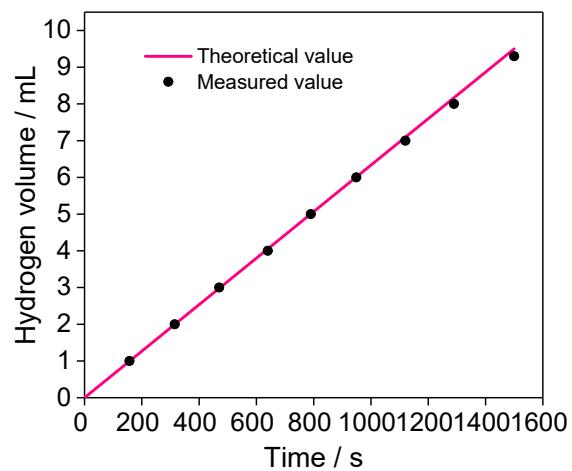


Fig. S22. The volume of theoretical H₂ and experimentally measured H₂ along with the reaction time.

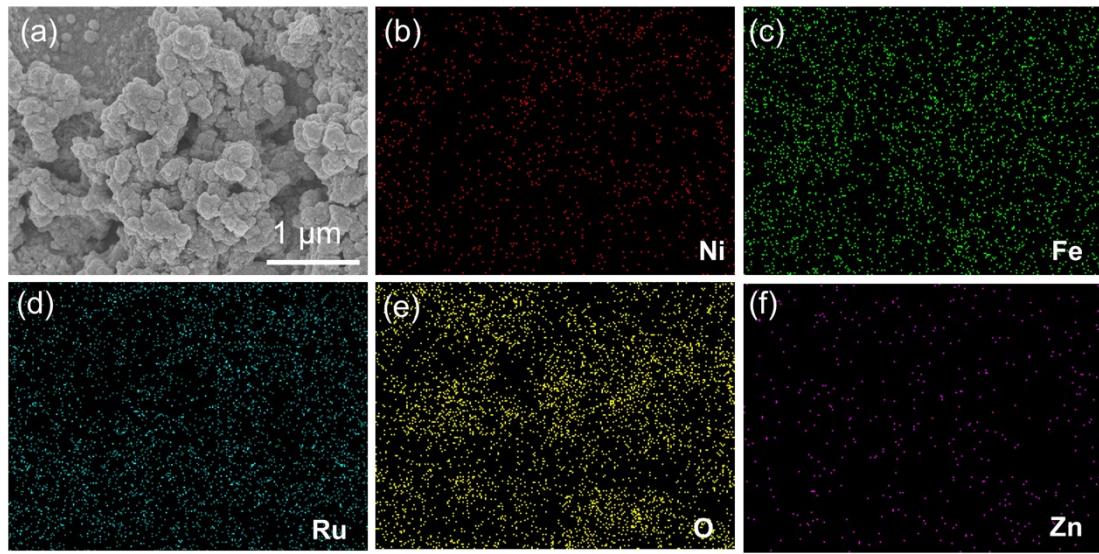


Fig. S23. (a) SEM images, (b-f) corresponding mapping images of Ni, Fe, Ru, O and Zn elements in the D/NFF-Ru-Zn after HER stability test for 100 h.

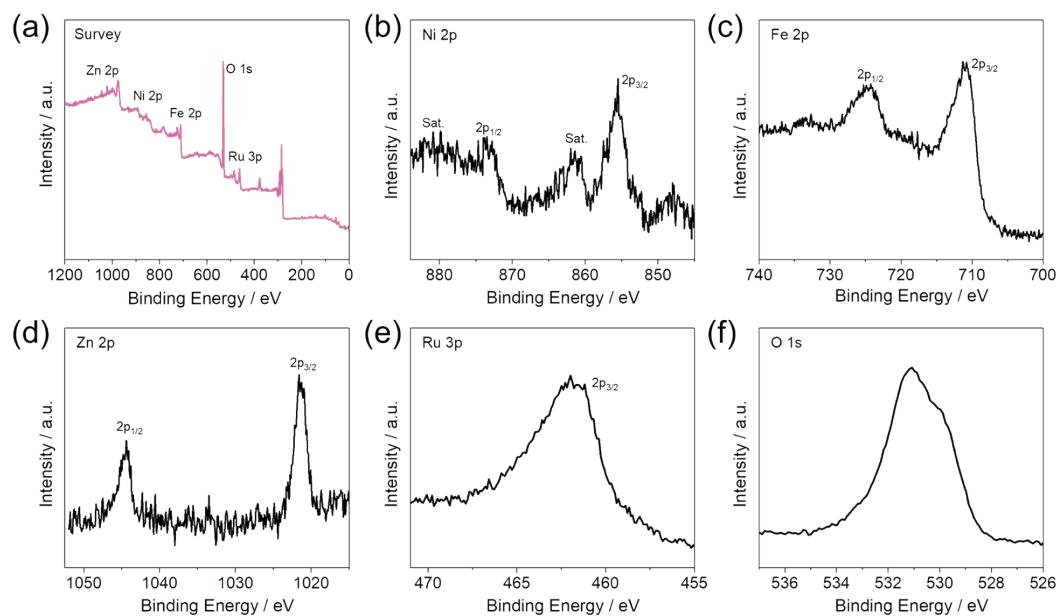


Fig. S24. (a) The XPS survey spectrum, (b) Ni 2p, (c) Fe 2p, (d) Zn 2p, (e) Ru 3p and (f) O 1s spectra of the D/NFF-Ru-Zn after HER stability test for 100 h.

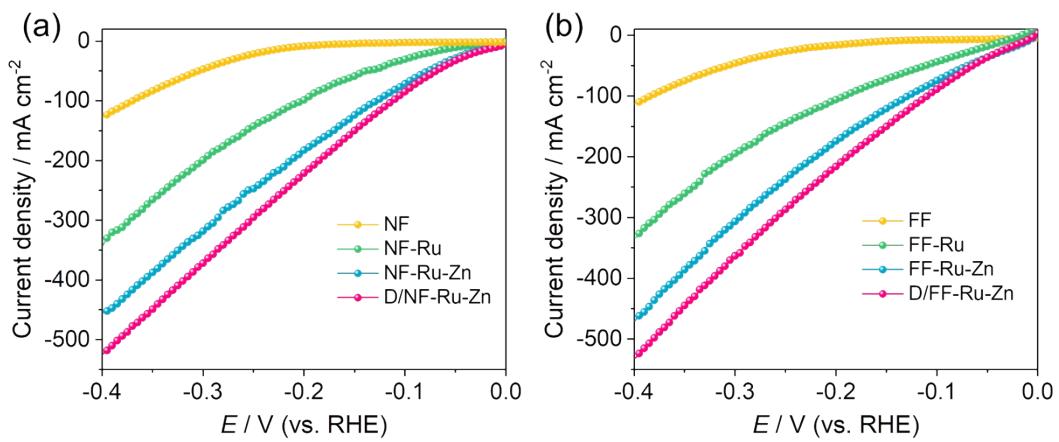


Fig. S25. HER polarization curves of samples derived from (a) Ni foam (NF) and (b) Fe foam (FF) substrates prepared by corrosion-etching strategy.

Table S1. Comparison of overpotentials and Tafel slopes with recently reported HER catalysts at 100 mA cm⁻² in 1.0 M KOH.

Catalysts	Overpotential / mV	Tafel slope / mV dec ⁻¹	References
D/NFF-Ru-Zn	90	41	This work
A-NiCo LDH/NF	151	57	1
NC/Ni ₃ Mo ₃ N/NF	136	41.5	2
V-FeP	149	40.97	3
NiFe/NF	132	33.2	4
F-Co ₂ P/Fe ₂ P/IF	151.8	115.01	5
Co ₄ N-CeO ₂ /NF	149	56.8	6
CF@Ru-CoCH NWs	121	65	7
TiO ₂ @CoCH	187	80	8
Sn-Ni(OH) ₂	298	65.5	9
F, P-Fe ₃ O ₄ /IF	179.5	127.9	10
NiCo ₂ N	149	78.7	11
NiCoP-NWAs/NF	197	54	12
Ni _{1.8} Cu _{0.2} -P/NF	245	70	13
200-SMN/NF	278	72.9	14
V-Ni ₃ S ₂ /NW	350	112	15

References

- 1 H. Yang, Z. Chen, P. Guo, B. Fei and R. Wu, *Appl. Catal. B-Environ.*, 2020, **261**, 118240.
- 2 Y. Chen, J. Yu, J. Jia, F. Liu, Y. Zhang, G. Xiong, R. Zhang, R. Yang, D. Sun, H. Liu and W. Zhou, *Appl. Catal. B-Environ.*, 2020, **272**, 118956.
- 3 X.-Y. Zhang, F.-T. Li, Z.-N. Shi, B. Dong, Y.-W. Dong, Z.-X. Wu, L. Wang, C.-G. Liu and Y.-M. Chai, *J. Colloid Interface Sci.*, 2022, **615**, 445-455.
- 4 L. Xu, L. Cao, W. Xu and Z. Pei, *Appli. Surf. Sci.*, 2020, **503**, 144122.
- 5 X.-Y. Zhang, Y.-R. Zhu, Y. Chen, S.-Y. Dou, X.-Y. Chen, B. Dong, B.-Y. Guo, D.-P. Liu, C.-G. Liu and Y.-M. Chai, *Chem. Eng. J.*, 2020, **399**, 125831.
- 6 M. Lu, D. Chen, B. Wang, R. Li, D. Cai, H. Tu, H. Yang, Y. Zhang and W. Han, *J. Mater. Chem. A*, 2021, **9**, 1655-1662.
- 7 J. Li, Q. Zhou, Z. Shen, S. Li, J. Pu, C. Zhong, M. Cao, X. Jin, H. Zhang, Y. Wang and H. Ma, *Electrochim. Acta*, 2020, **331**, 135367.
- 8 L. Yuan, S. Liu, S. Xu, X. Yang, J. Bian, C. Lv, Z. Yu, T. He, Z. Huang, D. W. Boukhvalov, C. Cheng, Y. Huang and C. Zhang, *Nano Energy*, 2021, **82**, 105732.
- 9 J. Jian, X. Kou, H. Wang, L. Chang, L. Zhang, S. Gao, Y. Xu and H. Yuan, *ACS Appl. Mater. Interfaces*, 2021, **13**, 42861-42869.
- 10 X.-Y. Zhang, F.-T. Li, R.-Y. Fan, J. Zhao, B. Dong, F.-L. Wang, H.-J. Liu, J.-F. Yu, C.-G. Liu and Y.-M. Chai, *J. Mater. Chem. A*, 2021, **9**, 15836-15845.
- 11 L. Yu, S. Song, B. McElhenney, F. Ding, D. Luo, Y. Yu, S. Chen and Z. Ren, *J. Mater. Chem. A*, 2019, **7**, 19728-19732.
- 12 J. Li, G. Wei, Y. Zhu, Y. Xi, X. Pan, Y. Ji, I. V. Zatovsky and W. Han, *J. Mater. Chem. A*, 2017, **5**, 14828-14837.
- 13 S. Chu, W. Chen, G. Chen, J. Huang, R. Zhang, C. Song, X. Wang, C. Li and K. Ostrikov, *Appl. Catal. B-Environ.*, 2019, **243**, 537-545.
- 14 Z. Cui, Y. Ge, H. Chu, R. Baines, P. Dong, J. Tang, Y. Yang, P. M. Ajayan, M. Ye and J. Shen, *J. Mater. Chem. A*, 2017, **5**, 1595-1602.
- 15 Y. Qu, M. Yang, J. Chai, Z. Tang, M. Shao, C. T. Kwok, M. Yang, Z. Wang, D. Chua, S. Wang, Z. Lu and H. Pan, *ACS Appl. Mater. Interfaces*, 2017, **9**, 5959-5967.