Supporting Information

Catalytic Centers with Multiple Oxidation States: A Strategy for Breaking the Overpotential Ceiling from the Linear Scaling Relation in Oxygen Evolution

Ungsoo Kim,[a] Jinhong Mun,[b] Donghwan Koo,[a] Jihyung Seo,[a] Yunseong Choi,[a] Geunsik Lee,*[b] and Hyesung Park*[a]

[a]Department of Materials Science and Engineering, Graduate School of Semiconductor Materials and Devices Engineering, Perovtronics Research Center, Low Dimensional Carbon Materials Center, Ulsan National Institute of Science and Technology, Ulsan 44919, Republic of Korea

[b]Department of Chemistry, Center for Superfunctional Materials, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Republic of Korea

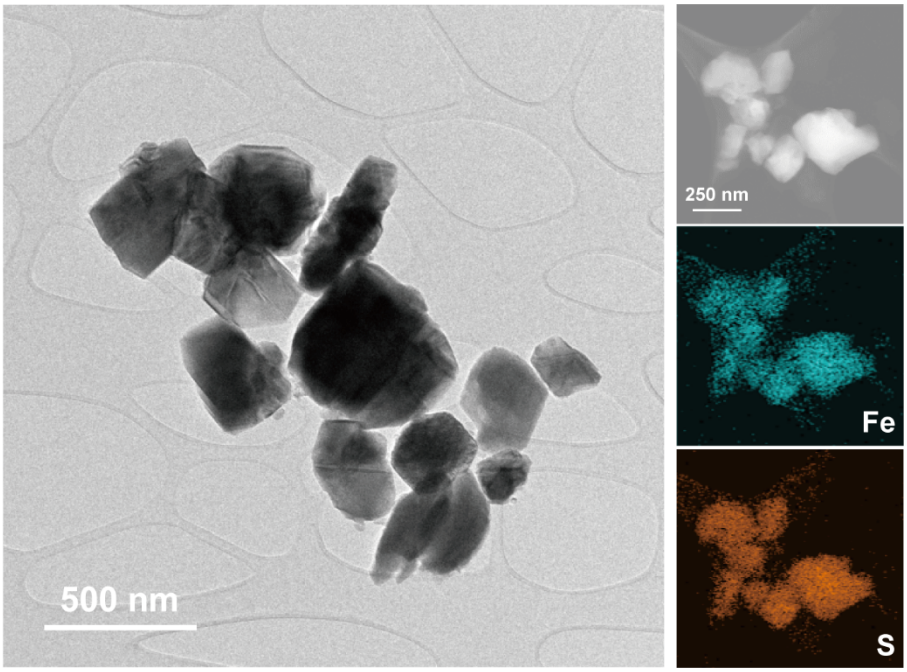

Fig. S1 Transmission electron microscopy and element mapping images of FeS_2.

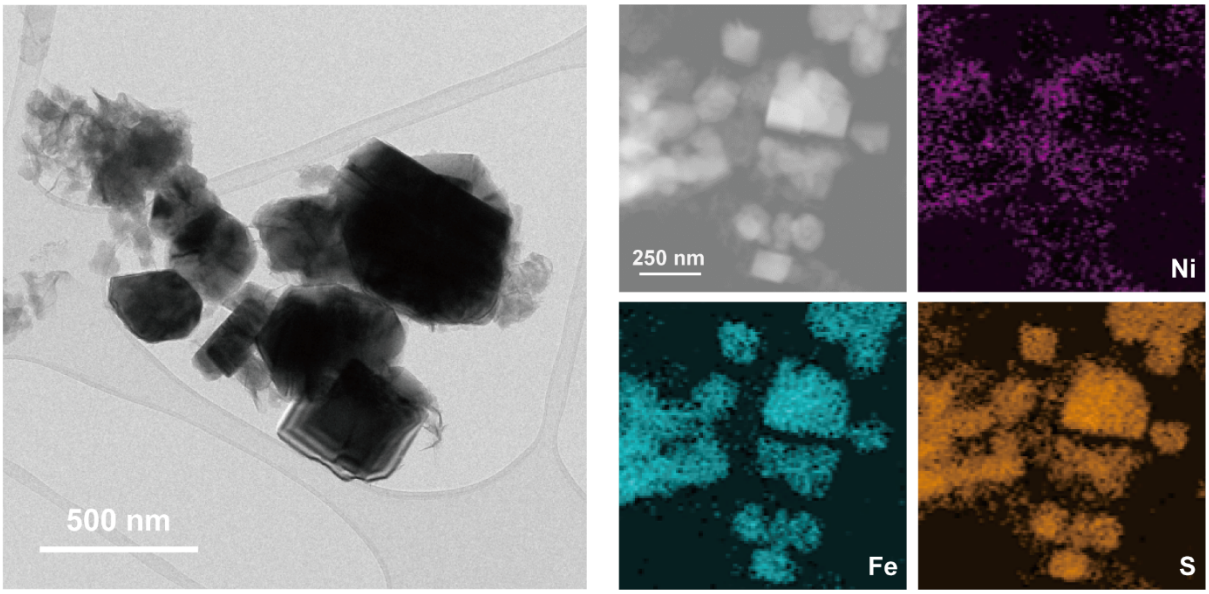

Fig. S2 Transmission electron microscopy and element mapping images of $NiFeS_2$.

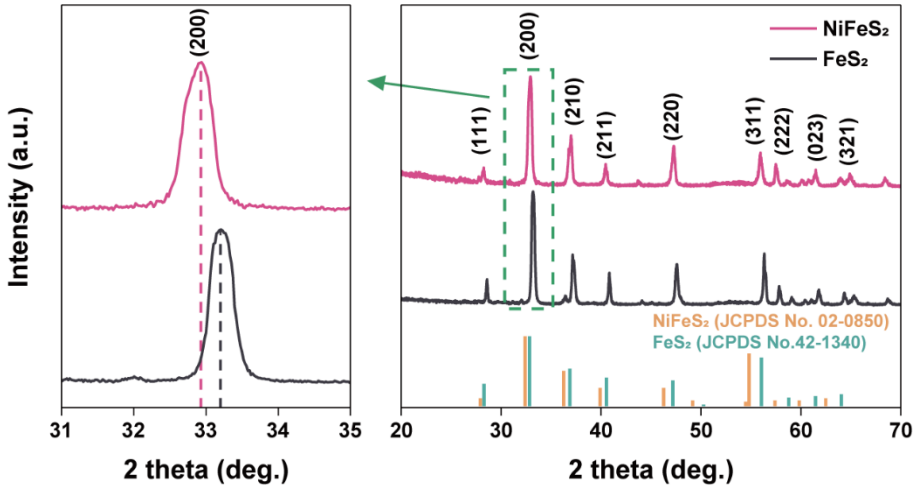

Fig. S3 X-ray diffraction patterns of FeS_2 and $NiFeS_2$.

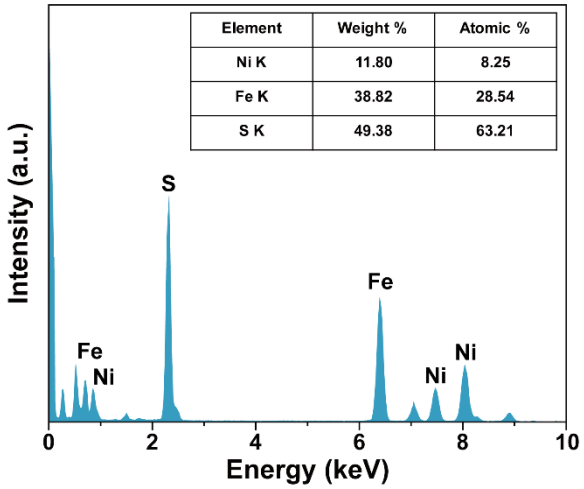

Fig. S4 Transmission electron microscopy-energy-dispersive X-ray spectrum of $NiFeS_2$ corresponding to Fig. S2. Inset: weights and atomic ratios of Ni, Fe, and S.

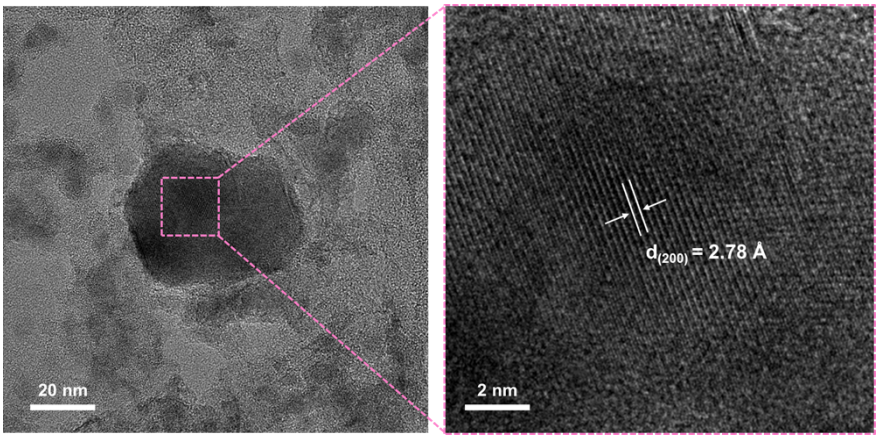

Fig. S5 High-resolution transmission electron microscopy image of $NiFeS_2$ in multiple-oxidation-state NiFe catalyst (MOS NiFe). Magnified image shows the lattice fringe of $NiFeS_2$.

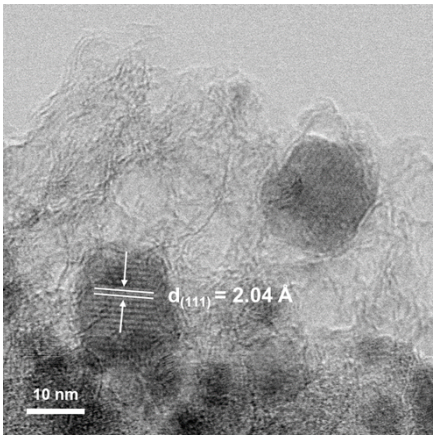

Fig. S6 High-resolution transmission electron microscopy image of Ni NPs in multiple-oxidation-state NiFe catalyst (MOS NiFe).

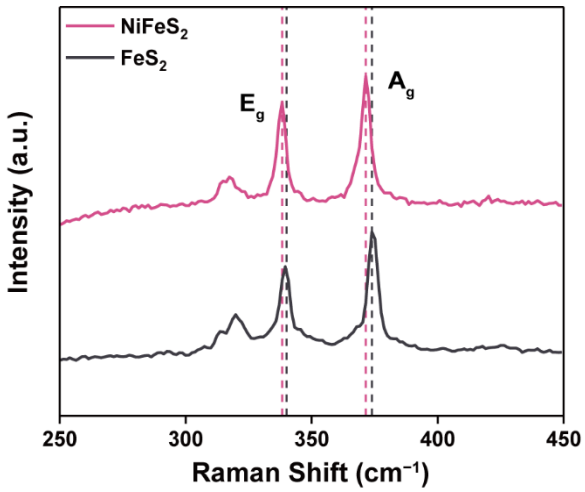

Fig. S7 Raman spectra of FeS_2 and $NiFeS_2$.

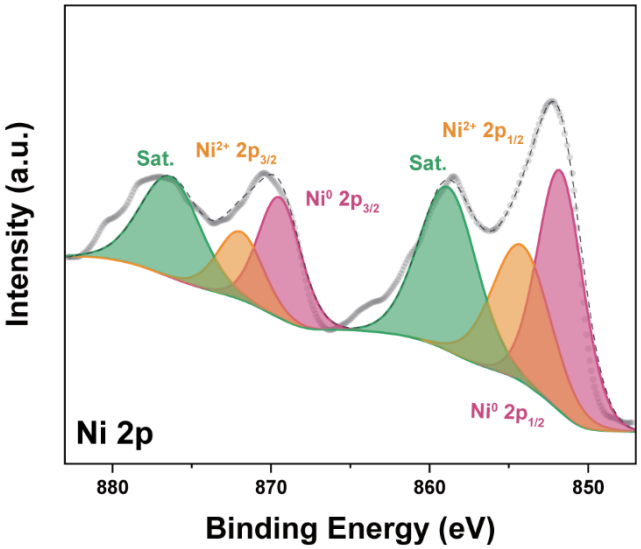

Fig. S8 High-resolution X-ray photoelectron spectroscopy spectrum of Ni 2p for Ni anchored on the carbon support (NiC).

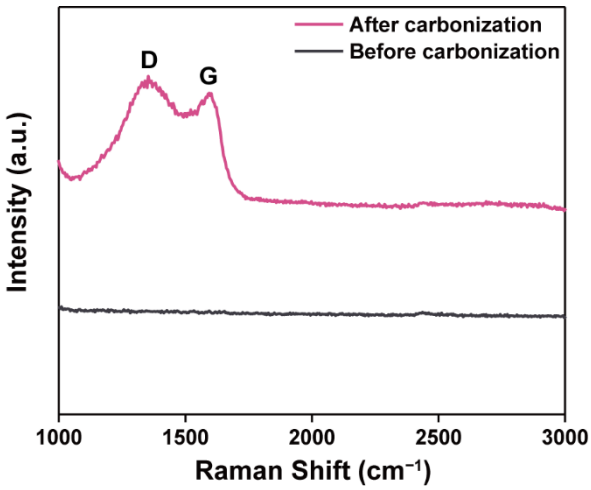

Fig. S9 Raman spectra of $NiFeS_2$ (before carbonization) and the multiple-oxidation-state NiFe catalyst (MOS NiFe) (after carbonization).

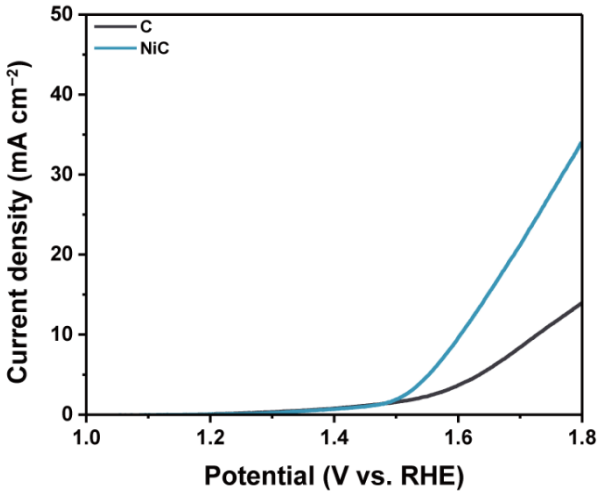

Fig. S10 Oxygen evolution reaction performance of Ni anchored on the carbon support (NiC).

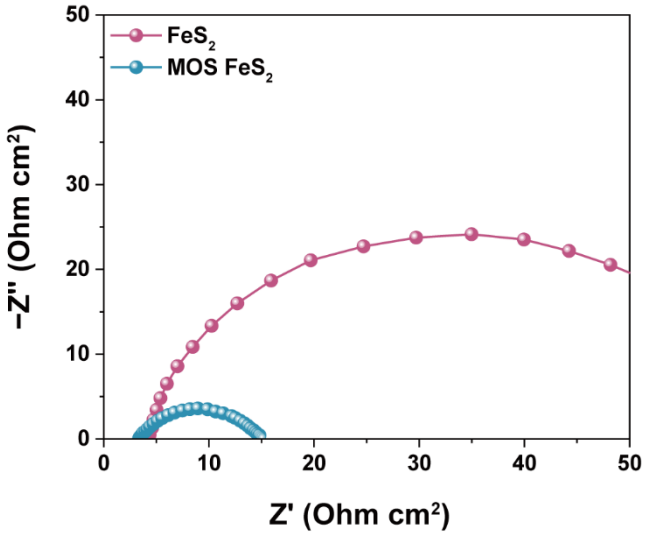

Fig. S11 Nyquist plots for FeS_2 and multiple-oxidation-state FeS_2.

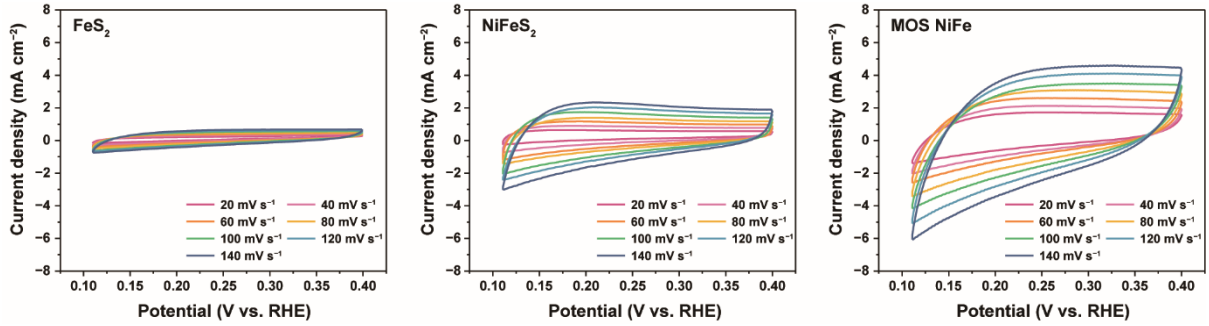

Fig. S12 Cyclic voltammetry (CV) curves at different scan rates for FeS_2, $NiFeS_2$, and the multiple-oxidation-state NiFe catalyst (MOS NiFe). The anodic and cathodic current densities were obtained at a potential of 0.3 V.

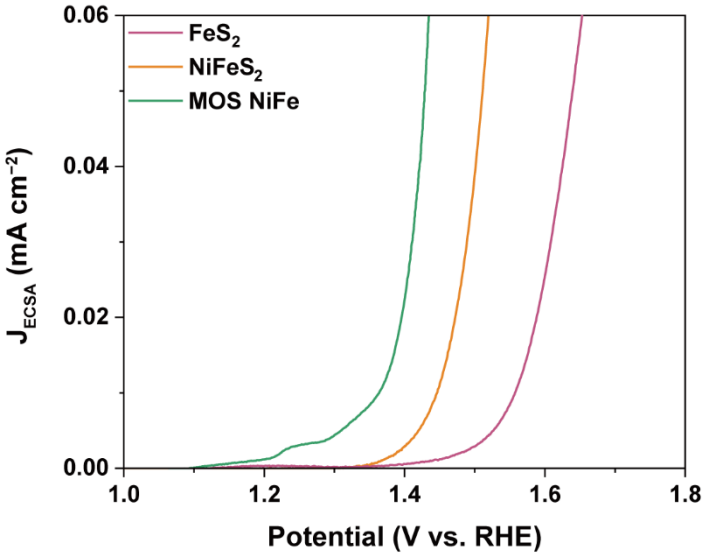

Fig. S13 Polarization curves normalized to electrochemical active surface area for FeS_2, $NiFeS_2$, and the multiple-oxidation-state NiFe catalyst.

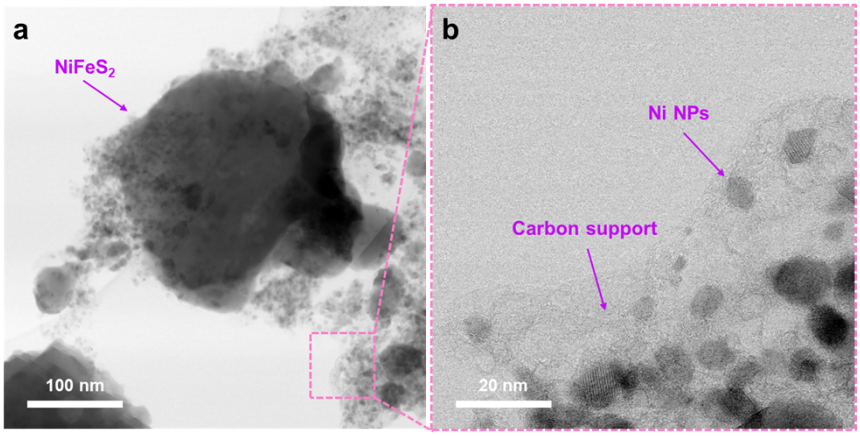

Fig. S14 (a) High-resolution transmission electron microscopy (HR-TEM) image of the multiple-oxidation-state NiFe catalyst (MOS NiFe). (b) Magnified HR-TEM image taken from the marked region in (a). These images were obtained after the chronopotentiometry stability test operated at different current densities for up to 60 h.

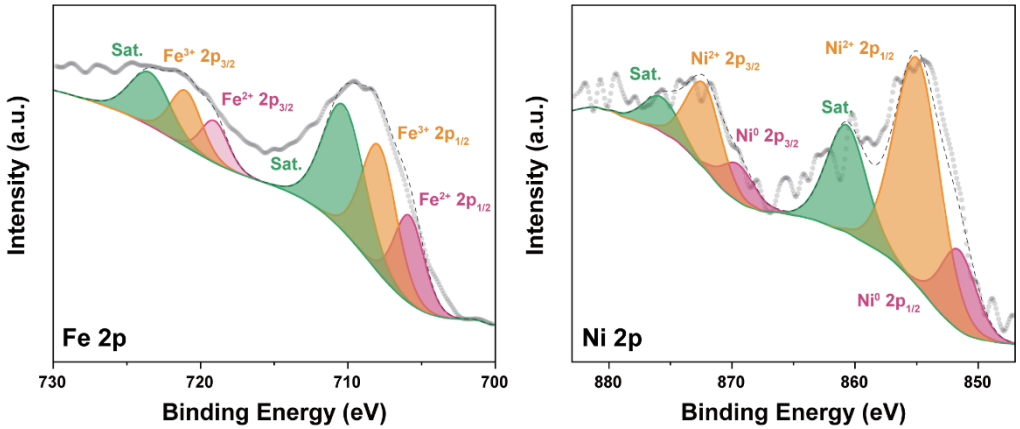

Fig. S15 High-resolution X-ray photoelectron spectroscopy spectra of Fe 2p and Ni 2p for the multiple-oxidation-state NiFe catalyst (MOS NiFe) after the chronopotentiometry stability test operated at different current densities for up to 60 h.

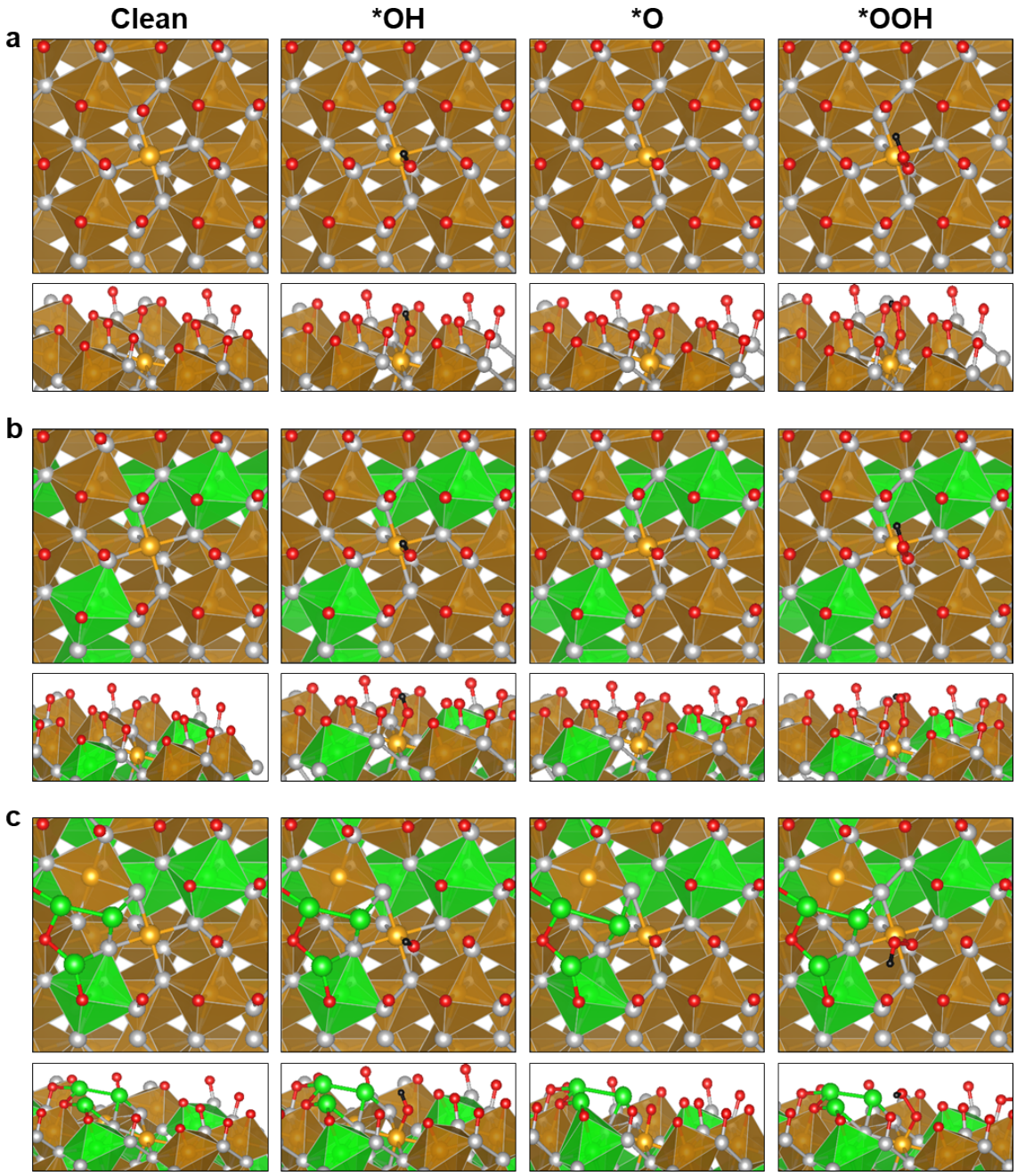

Fig. S16 Optimized structures of each intermediate on the surface layer of (a) FeS_2, (b) $NiFeS_2$, and (c) the multiple-oxidation-state NiFe catalyst (MOS NiFe). The colors indicate the following elements: iron (orange), nickel (green), sulfur (gray), oxygen (red), and hydrogen (black).

Table S1. Comparison of the oxygen evolution reaction performance of the multiple-oxidation-state NiFe catalyst (MOS NiFe) with state-of-the-art Ni- and Fe-based electrocatalysts.

Catalyst	Electrolyte	η at 10 mA cm^{-2} (mV)	Tafel slope (mV dec^{-1})	Ref.
MOS NiFe	**1.0 M KOH**	**160**	**53**	**This work**
NiFe-OH-F-SR	1.0 M KOH	176	22.6	1
CS-NiFeCu	1.0 M KOH	180	33	2
a-LNF (t-d)	1.0 M KOH	183	36	3
CoFe@NiFe-200/NF	1.0 M KOH	190	45.71	4
$Ni_{0.8}Fe_{0.2}$-AHNA	1.0 M KOH	190	34.7	5
Fe^{2+}-NiFe-LDH	1.0 M KOH	195	40.3	6
Ultrathin LDH	1.0 M KOH	210	31	7
MoS_2/NiFe-LDH	1.0 M KOH	210	46	8
$Fe_{0.5}Ni_{0.5}$@N-GR	1.0 M KOH	210	62	9
WC_x-FeNi	1.0 M KOH	211	56	10
NiFe LDH@NiCoP/NF	1.0 M KOH	220	88.2	11
NiFe/$(NiFe)_3S_2$	1.0 M KOH	224	46	12
NiFeMo-N_2	1.0 M KOH	226	26.7	13
hcp-NiFe@NC	1.0 M KOH	226	41	14
NiFe-NFF	1.0 M KOH	227	38.9	15
NiFe-LDH/MXene/NF	1.0 M KOH	229	44	16
MIL-53(FeNi)/NF	1.0 M KOH	233	31.3	17
Ni_2Fe_1@PANI-KOH900	1.0 M KOH	240	82	18
Ni_2-Fe_1-O	1.0 M KOH	244	39	19
DR-Ni_3FeN/N-G	1.0 M KOH	250	38	20
LDH-UF	1.0 M KOH	254	32	21
$NiFe_x/NiFe_2O_4$@NC	1.0 M KOH	262	51.4	22
Ni SAs/Fe-NiOOH	1.0 M KOH	269	33.4	23
NiFeCr-6:2:1	1.0 M KOH	280	130	24

References

1. B. Zhang, K. Jiang, H. Wang and S. Hu, *Nano Lett.*, 2019, **19**, 530–537.
2. P. Zhang, L. Li, D. Nordlund, H. Chen, L. Fan, B. Zhang, X. Sheng, Q. Daniel and L. Sun, *Nat. Commun.*, 2018, **9**, 381.
3. G. Chen, Y. Zhu, H. M. Chen, Z. Hu, S. F. Hung, N. Ma, J. Dai, H. J. Lin, C. T. Chen, W. Zhou and Z. Shao, *Adv. Mater.*, 2019, **31**, 1900883.
4. R. Yang, Y. Zhou, Y. Xing, D. Li, D. Jiang, M. Chen, W. Shi and S. Yuan, *Appl. Catal. B*, 2019, **253**, 131–139.
5. C. Liang, P. Zou, A. Nairan, Y. Zhang, J. Liu, K. Liu, S. Hu, F. Kang, H. J. Fan and C. Yang, *Energy Environ. Sci.*, 2020, **13**, 86−95.
6. Z. Cai, D. Zhou, M. Wang, S. M. Bak, Y. Wu, Z. Wu, Y. Tian, X. Xiong, Y. Li, W. Liu, S. Siahrostami, Y. Kuang, X. Q. Yang, H. Duan, Z. Feng, H. Wang and X. Sun, *Angew. Chem., Int. Ed.*, 2018, **57**, 9392.
7. C. Kuai, Y. Zhang, D. Wu, D. Sokaras, L. Mu, S. Spence, D. Nordlund, F. Lin and X.-W. Du, *ACS Catal.*, 2019, **9**, 6027.
8. P. Xiong, X. Zhang, H. Wan, S. Wang, Y. Zhao, J. Zhang, D. Zhou, W. Gao, R. Ma, T. Sasaki and G. Wang, *Nano Lett.*, 2019, **19**, 4518.
9. P. Liu, D. Gao, W. Xiao, L. Ma, K. Sun, P. Xi, D. Xue and J. Wang, *Adv. Funct. Mater.*, 2018, **28**, 1706928.
10. S, Li, B. Chen, Y. Wang, M.-Y. Ye, P. A. v. Aken, C. Cheng and A. Thomas, *Nat. Mater.*, 2021, **20**, 1240–1247.
11. H. Zhang, X. Li, A. Hähnel, V. Naumann, C. Lin, S. Azimi, S. L. Schweizer, A. W. Maijenburg and R. B. Wehrspohn, *Adv. Funct. Mater.*, 2018, **28**, 1706847.
12. C. T. Hsieh, X. F. Chuah, C. L. Huang, H. W. Lin, Y. A. Chen and S. Y. Lu, *Small Methods*, 2019, **3**, 1900234.
13. B. C. Moon, W. H. Choi, K. H. Kim, D. G. Park, J. W. Choi and J. K. Kang, *Small*, 2019, **15**, 1804764.
14. C. Wang, H. Yang, Y. Zhang and Q. Wang, *Angew. Chem., Int. Ed.*, 2019, **58**, 6099.
15. C. Cao, D. D. Ma, Q. Xu, X. T. Wu and Q. L. Zhu, *Adv. Funct. Mater.*, 2019, **29**, 1807418.
16. M. Yu, Z. Wang, J. Liu, F. Sun, P. Yang and J. Qiu, Nano Energy, 2019, **63**, 103880.
17. F. Sun, G. Wang, Y. Ding, C. Wang, B. Yuan and Y. Lin, *Adv. Energy Mater.*, 2018,

8, 1800584.

18. J. Zhang, M. Zhang, L. Qiu, Y. Zeng, J. Chen, C. Zhu, Y. Yu and Z. Zhu, *J. Mater. Chem. A*, 2019, **7**, 19045.

19. C. Dong, T. Kou, H. Gao, Z. Peng and Z. Zhang, *Adv. Energy Mater.*, 2018, **8**, 1701347.

20. S. Zhao, M. Li, M. Han, D. Xu, J. Yang, Y. Lin, N.-E. Shi, Y. Lu, R. Yang, B. Liu, Z. Dai and J. Bao, *Adv. Funct. Mater.*, 2018, **28**, 1706018.

21. Y. Zhao, X. Zhang, X. Jia, G. I. N. Waterhouse, R. Shi, X. Zhang, F. Zhan, Y. Tao, L.-Z. Wu, C.-H. Tung, D. O'Hare and T. Zhang, *Adv. Energy Mater.*, 2018, **8**, 1703585.

22. J. Zhao, X. Zhang, M. Liu, Y.-Z. Jiang, M. Wang, Z.-Y. Li and Z. Zhou, *J. Mater. Chem. A*, 2019, **7**, 21338.

23. H. Liu, X. Xu, H. Xu, S. Wang, Z. Niu, Q. Jia, L. Yang, R. Gao, L. Zheng and D. Gao, *Appl. Catal. B*, 2021, **297**, 120451.

24. Y. Yang, L. Dang, M. J. Shearer, H. Sheng, W. Li, J. Chen, P. Xiao, Y. Zhang, R. J. Hamers and S. Jin, *Adv. Energy Mater.*, 2018, **8**, 1703189.