Supporting information

Engineering of interfacial active sites in composites of troilite phase nano-leaves interacting with nickel oxide adorned carbon nanotubes for robust overall water splitting

Sajjad Hussain‡[a,b], Zulfqar Ali Sheikh‡[c], Ghazanfar Nazir [b], Iftikhar Hussain[d], Shoyebmohamad F. Shaikh[e], Hyun-Seok Kim[f], Deok-Kee Kim[c], Jongwan Jung [a,b], Dhanasekaran Vikraman*[f]

[a.] Hybrid Materials Center (HMC), Sejong University, Seoul 05006, Republic of Korea.
[b.] Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 05006, Republic of Korea.
[c.] Department of Electrical Engineering and Department of Convergence Engineering for Intelligent Drone, Sejong University, Seoul 05006, Republic of Korea.
[d.] Department of Mechanical Engineering, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong.
[e.] Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia.
[f.] Division of Electronics and Electrical Engineering, Dongguk University-Seoul, Seoul 04620, Republic of Korea.

*Corresponding Author's E-mail: v.j.dhanasekaran@gmail.com
‡ These authors contributed equally.

S1. Characterization

X-ray photoelectron spectroscopy (XPS, Theta Probe by Thermo Fisher Scientific) was employed to establish the chemical composition and binding energy state of the composite structures. The morphology of prepared nanostructures was investigated using an X-ray energy dispersive spectrometer connected field-emission scanning electron microscope (FESEM, Hitachi, SU-8010). To examine the shape and microstructure of the material, JEOL JEM-ARM200F high-resolution transmission electron microscope (HR-TEM) was engaged. Renishaw System 3000 was engaged for the Raman analysis with a 514 nm excitation laser. Empyrean X-ray diffractometer equipped with Cu-Kα radiation (λ = 1.540 Å) was used for the structural analysis.

All potentials were adjusted to the reversible hydrogen electrode (RHE) using the equation: $E(RHE) = E(vs.\ Hg/HgO) + E^{o}(Hg/HgO) + 0.0592 \times pH$.

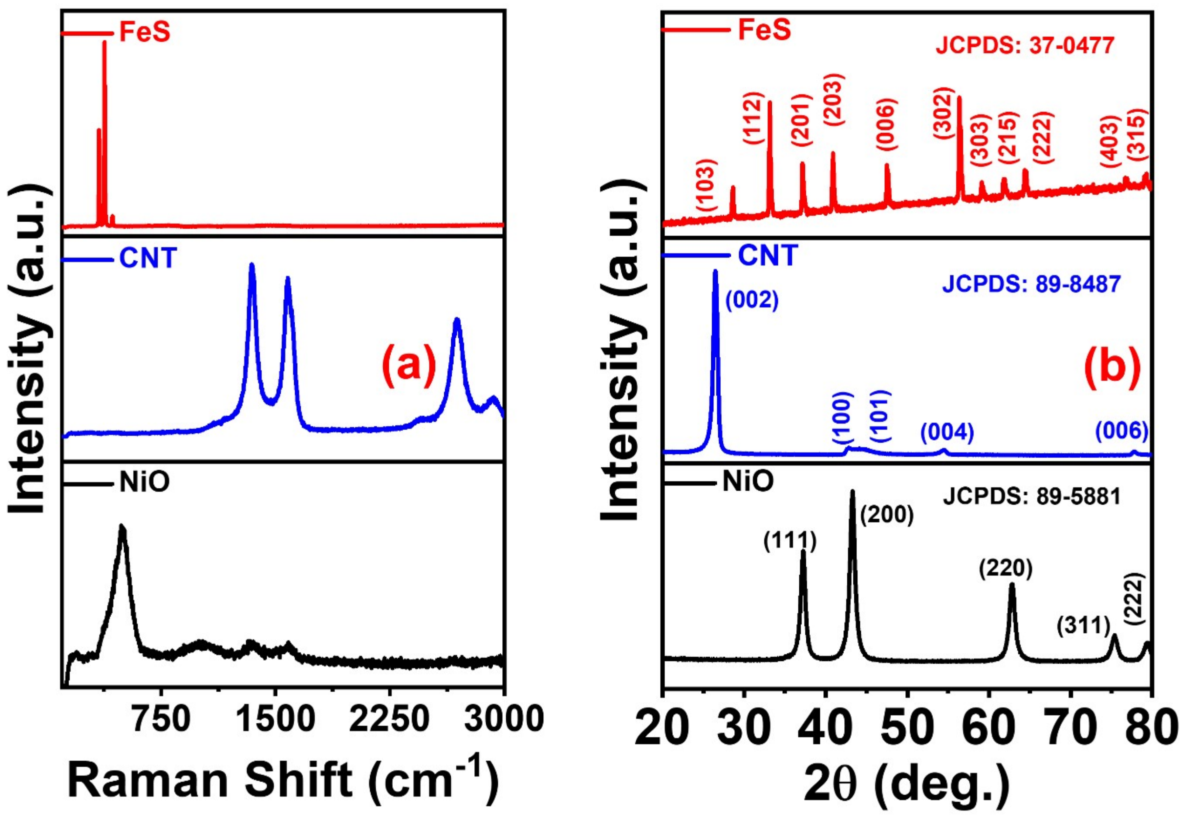

Figure S1. (a) Raman and (b) XRD spectra of pure FeS, NiO and CNT.

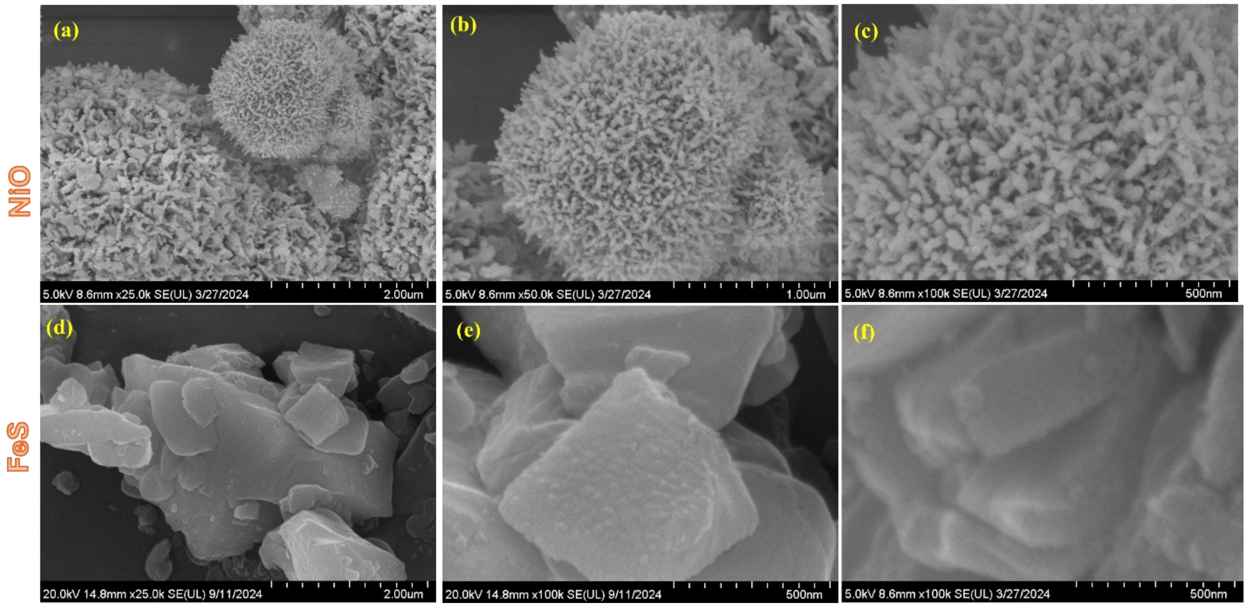

Figure S2. SEM images of (a-c) NiO and (d-f) FeS.

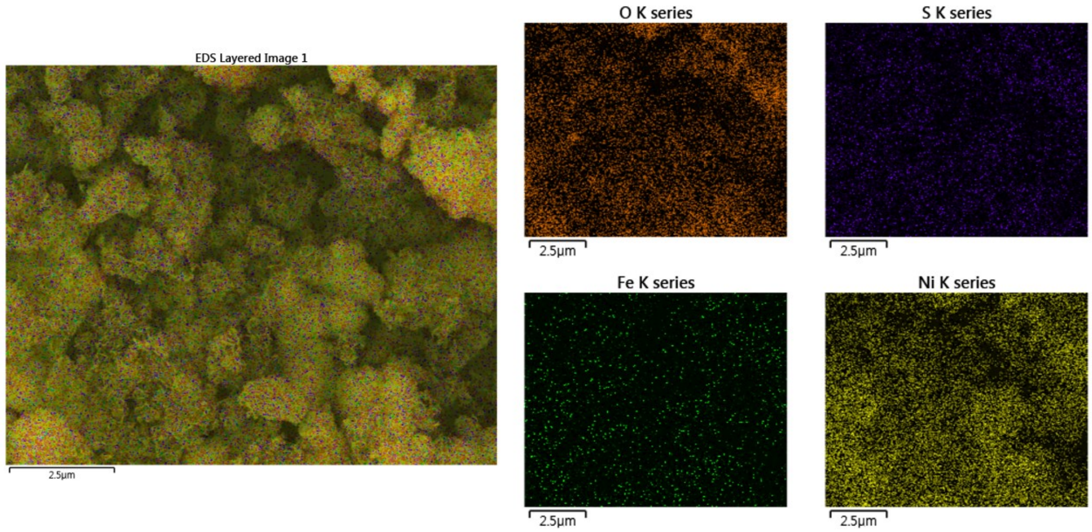

Figure S3. Elemental mapping of NF-2 composites

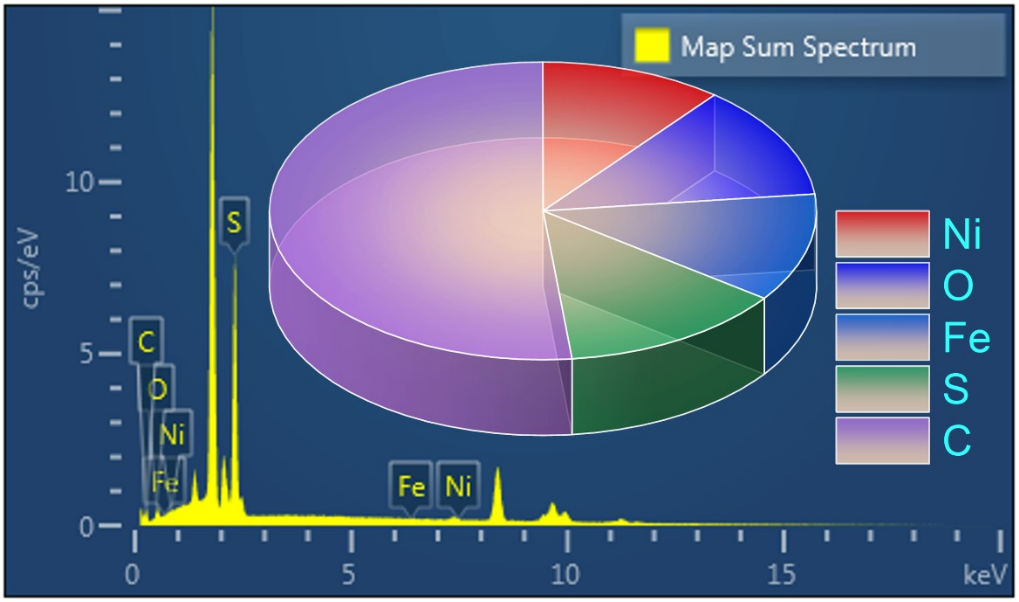

Figure S4. EDS spectrum of NFC-2 NiO/FeS@CNT hybrid composite along with element composition.

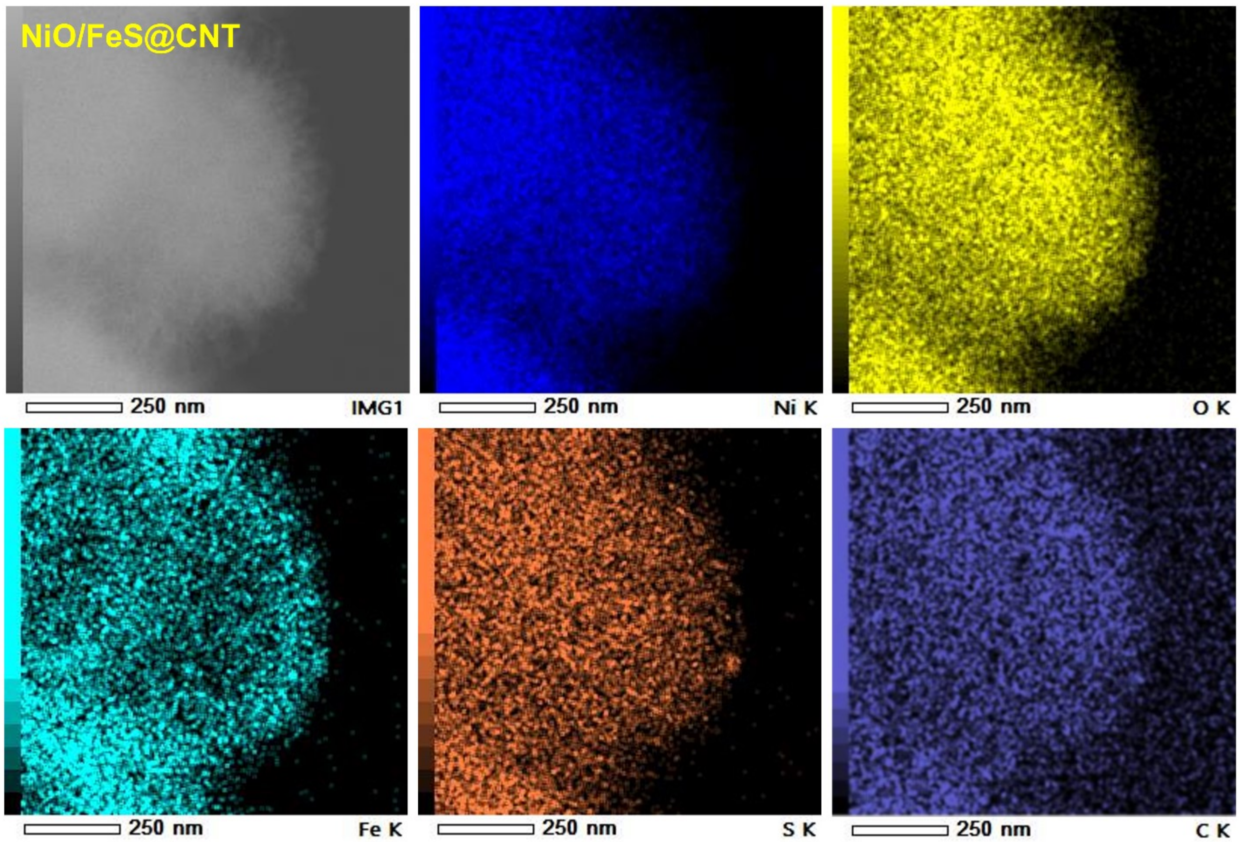

Figure S5. TEM elemental mapping of NFC-2 composites

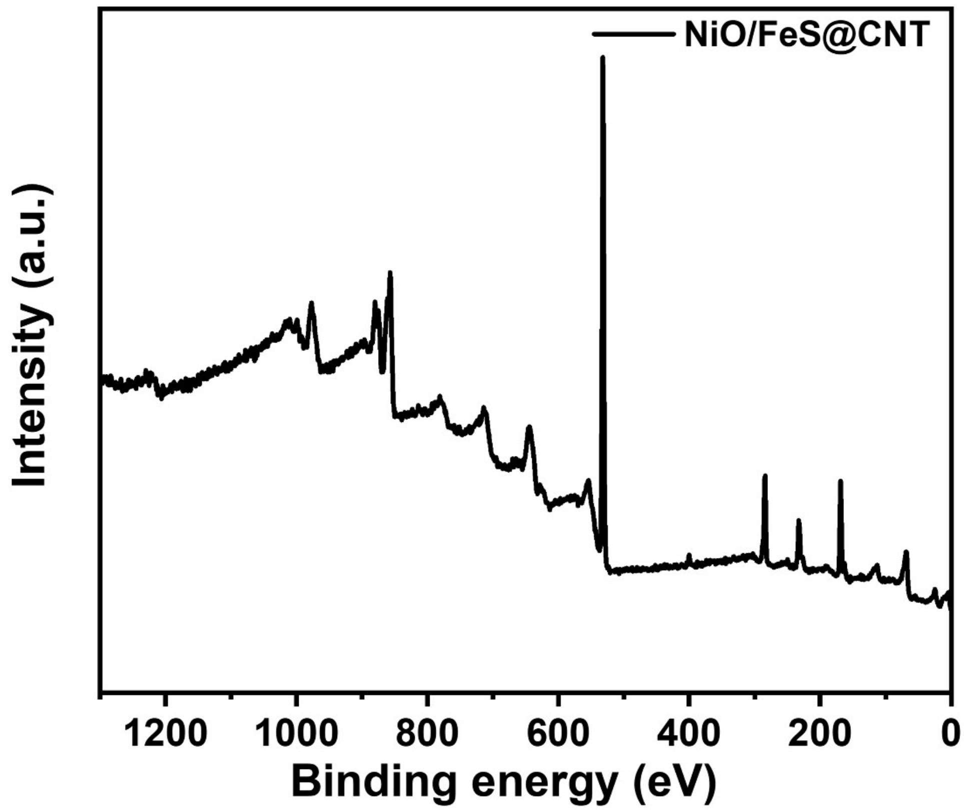

Figure S6. XPS survey scan of NFC-2 NiO/FeS@CNT hybrid composite.

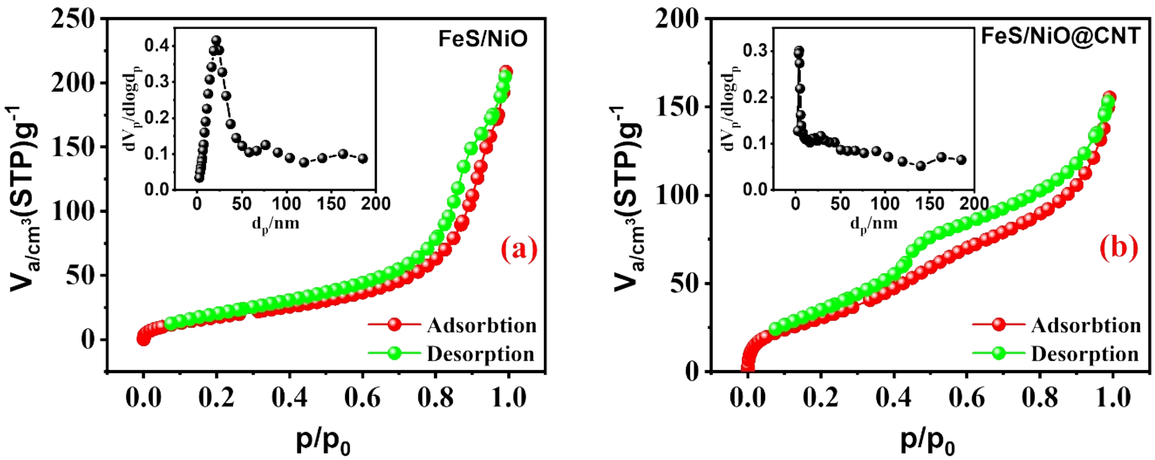

Figure S7. The BET and pore size distribution (inset) of (a) NF-2 NiO/FeS and (b) NFC-2 NiO/FeS@CNT hybrid composites.

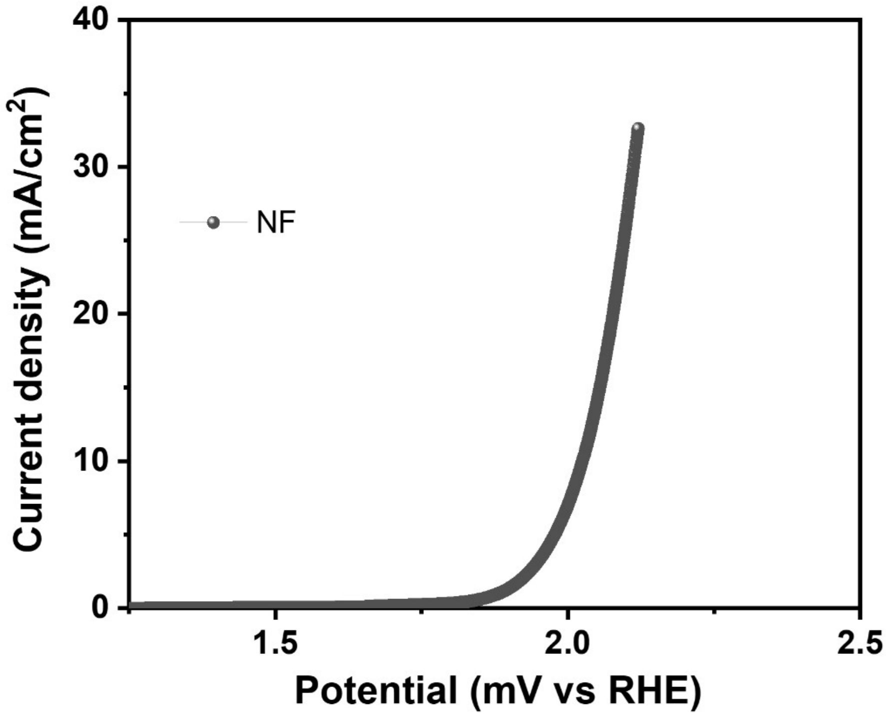

Figure S8. LSV OER profile of pure nickel foam

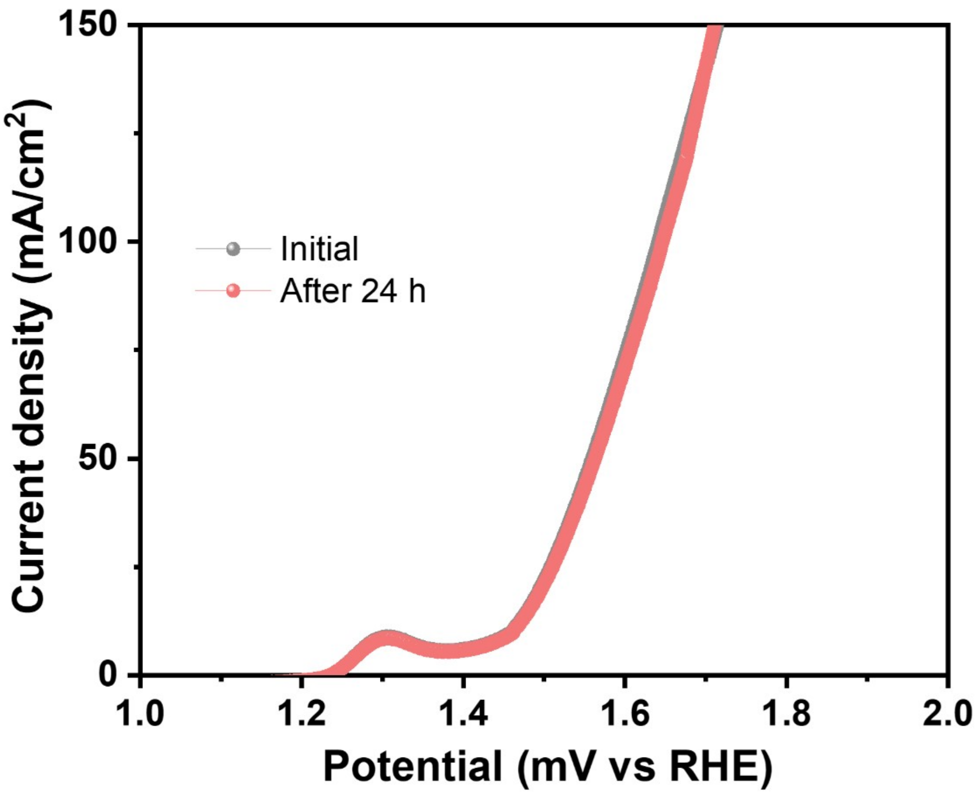

Figure S9. LSV profiles of NFC-2 NiO/FeS@CNT hybrid composites before and after 24-h continuous OER reaction

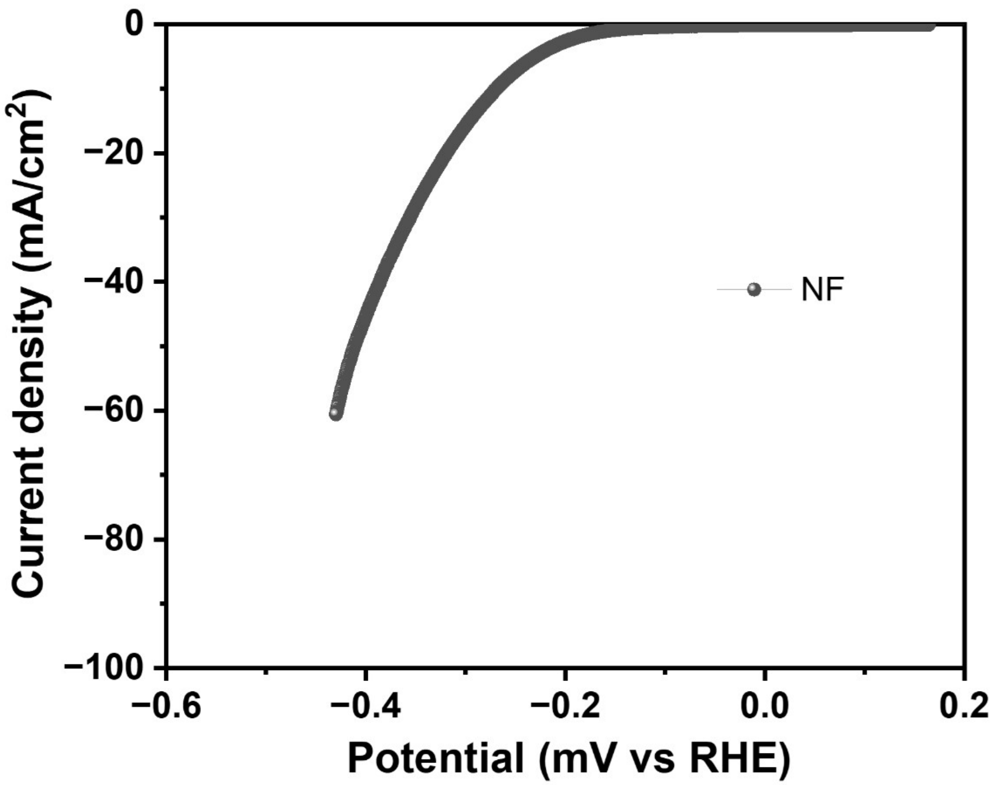

Figure S10. LSV HER profile of pure nickel foam

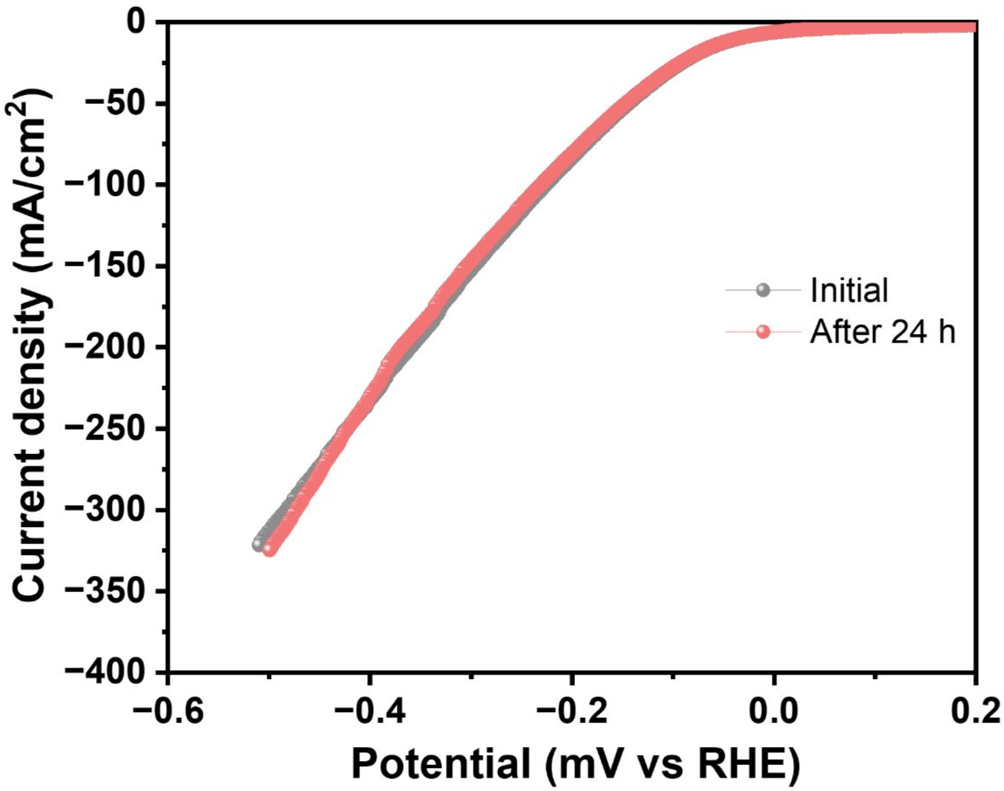

Figure S11. LSV profiles of NFC-2 NiO/FeS@CNT hybrid composites before and after 24-h continuous HER reaction

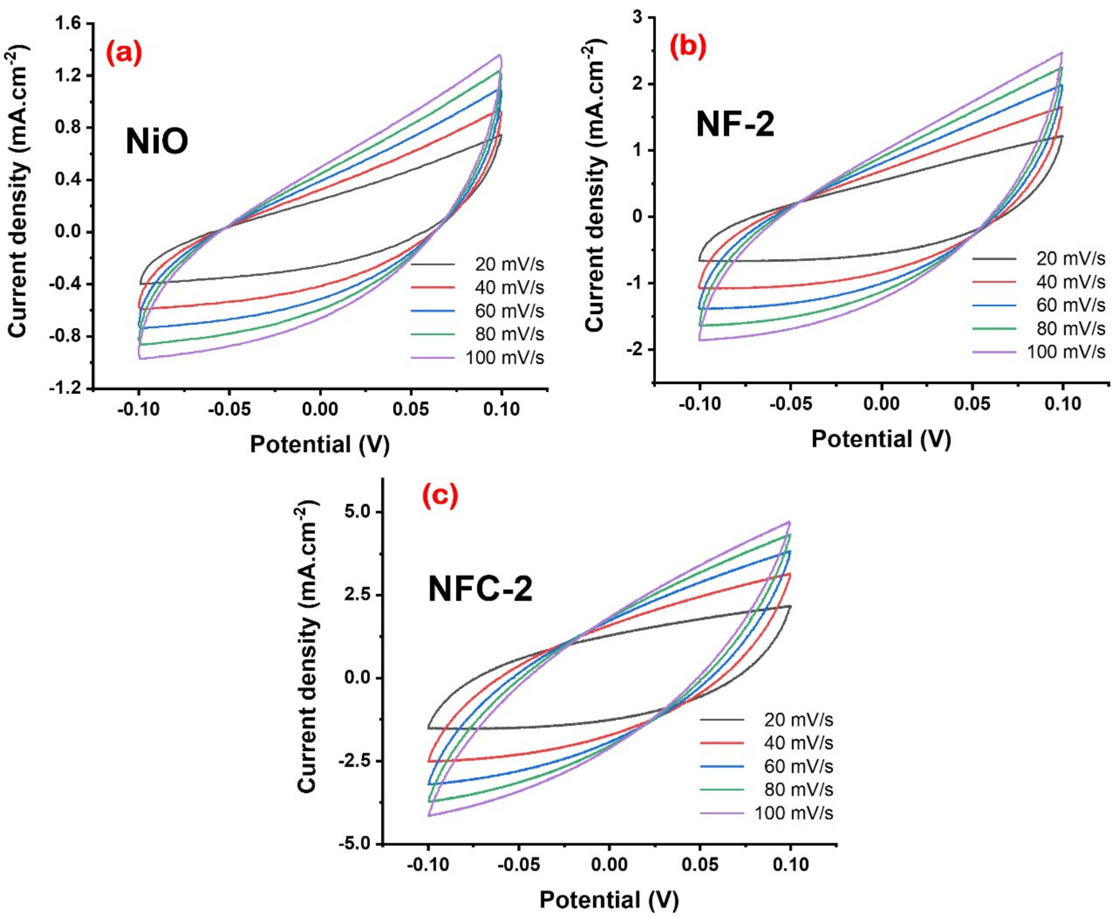

Figure S12. CVs at the different scan rate in the non-faradaic region for (a) NiO, (b) NF-2 and (c) NFC-2 electrocatalysts.

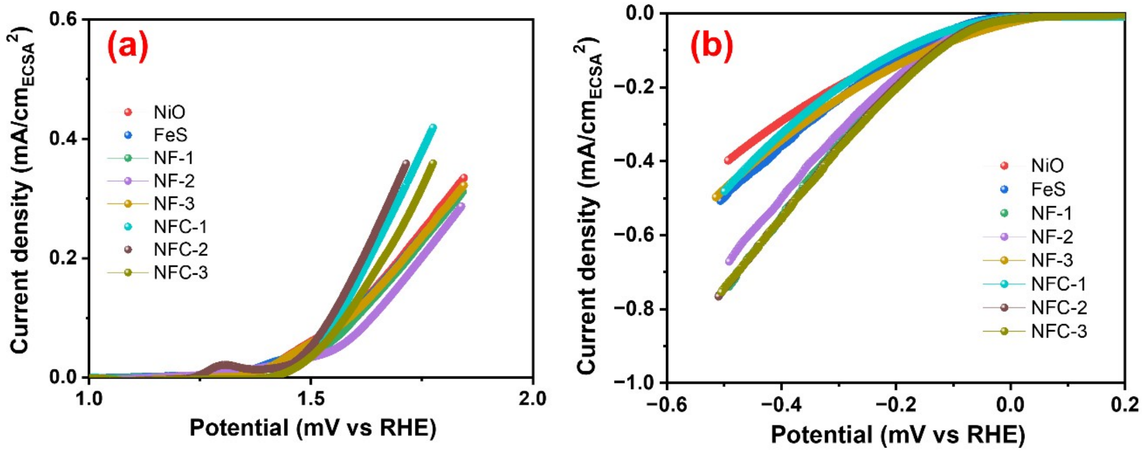

Figure S13. ECSA-normalized (a) OER and (b) HER activity of NiO, FeS, NF-1, NF-2, NF-3, NFC-1, NFC-2 and NFC-3 electrocatalysts

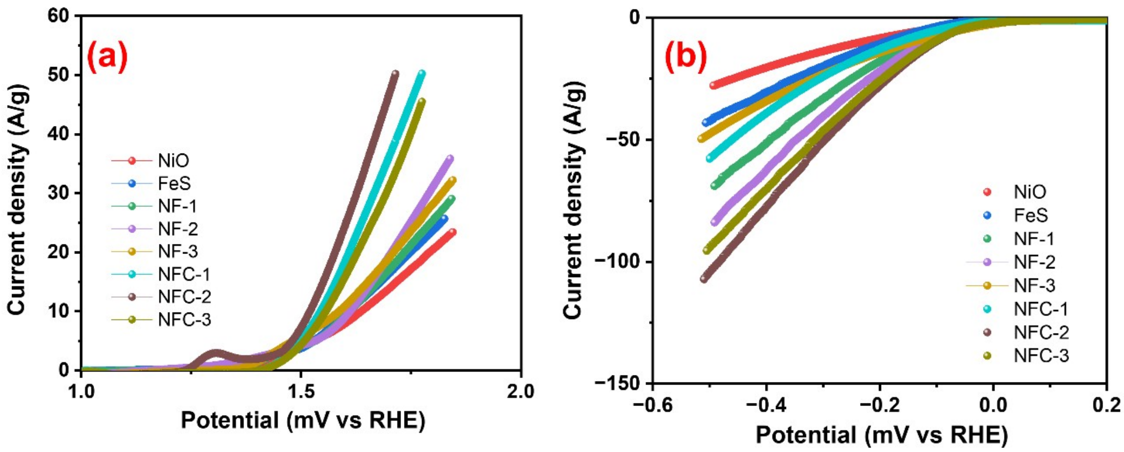

Figure S14. Mass ratio-normalized (a) OER and (b) HER activity of NiO, FeS, NF-1, NF-2, NF-3, NFC-1, NFC-2 and NFC-3 electrocatalysts.

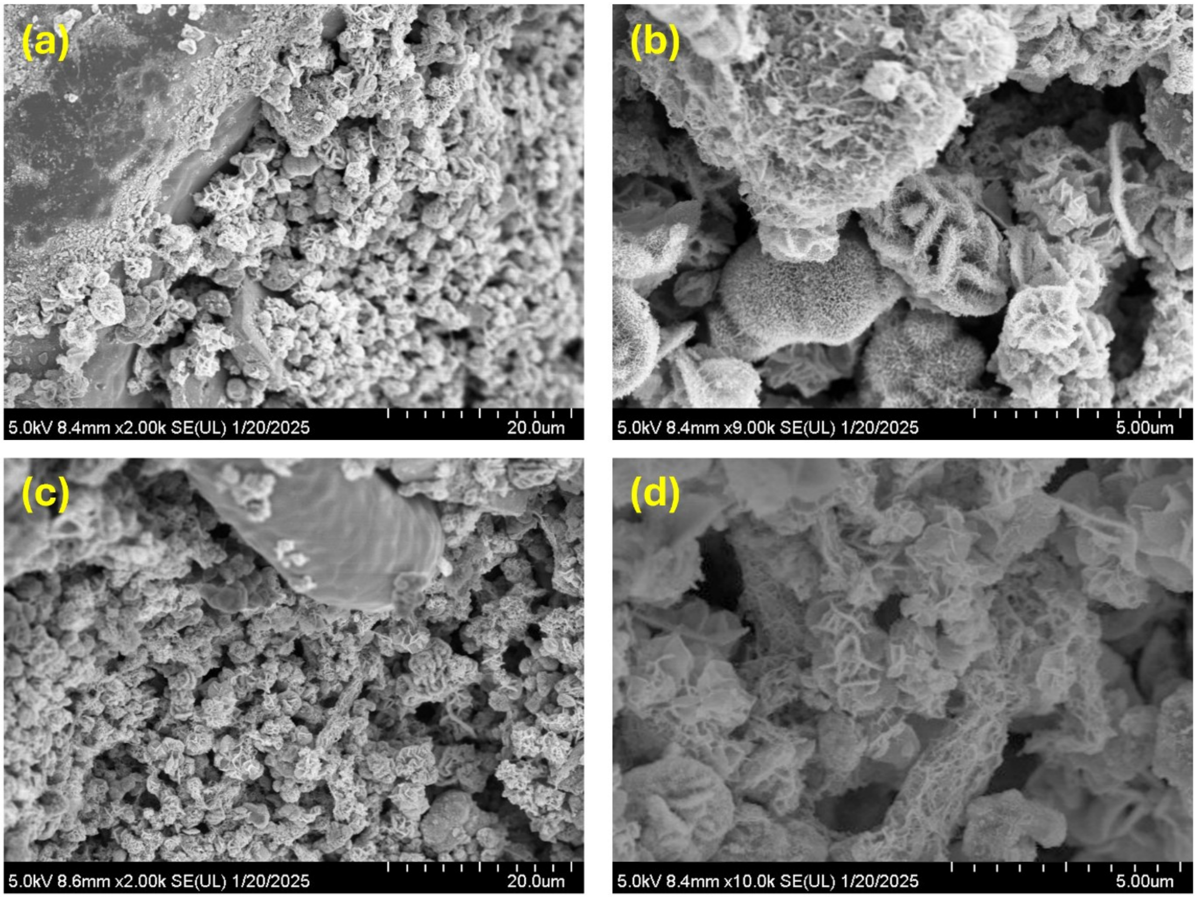

Figure S15. SEM images of NFC-2 NiO/FeS@CNT hybrid composites coated nickel foam (a-b) before and (c-d) after 24 h overall water splitting performance in alkaline medium.

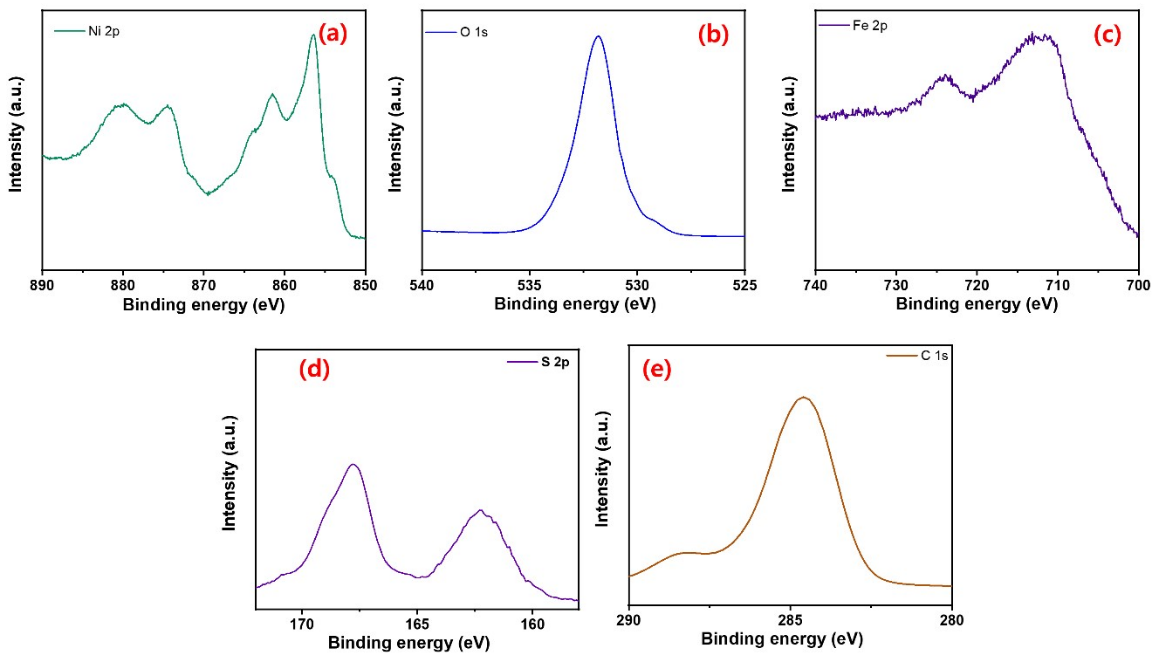

Figure S16. XPS profiles of after the 24 h overall water splitting reaction (a) Ni 2p; (b) O 1s; (c) Fe 2p; (d) S 2p and (e) C 1s binding energy for the NFC-2 FeS/NiO@CNT hybrid composite.

Table S1. OER catalytic performances of various electrocatalysts

Electrocatalyst	Electrolyte	η (mV)@ 10 mA/cm^2	Tafel Slope (mV·dec^{-1})	Ref
Pure nickel foam	**1M KOH**	**850 @ 10 mA/cm^2**	**265**	**This work**
NFC-2 NiO/FeS@CNT	**1M KOH**	**218 @ 10 mA/cm^2**	**52**	
$Ni_3S_4/NiS_2/FeS_2$	1M KOH	230 @ 10 mA/cm^2	49	[1]
Mo–FeS nanosheets	1M KOH	210 @ 10 mA/cm^2	50	[2]
NiS_2/FeS_2/NC	1M KOH	231 @ 10 mA/cm^2	44.29	[3]
NiO@Ni/WS_2/CC	1M KOH	347 @ 50 mA/cm^2	108.9	[4]
$Ni_{0.7}Fe_{0.3}S_2$	1M KOH	198 @ 10 mA/cm^2	56	[5]
Ni-doped O-incorporated FeS_2	1M KOH	255@100 mA/cm	58.29	[6]
Ce-FeS_2/Ni_3S_2	1M KOH	190 @ 10 mA/cm^2	96.1	[7]
FeS/Ni_3S_2@NF	1M KOH	192@10 mA/cm	70	[8]
FeS_2/FeOOH-ZnO@N	1M KOH	177@10 mA/cm	105.79	[9]
core-shell FeS_2@FeOOH	1M KOH	170@10 mA/cm	60	[10]
FeS_2/CoS_2 NSs	1M KOH	302@10 mA/cm	42	[11]
Ni-Fe-LDH/Li_2S_8-140	1M KOH	246@10 mA/cm	38.89	[12]
1T-Co-WS_2/$NiTe_2$/Ni	1M KOH	290@30 mA/cm	98	[13]
NiS_2/FeS_2/NC	1M KOH	231@10 mA/cm	44.29	[3]
Fe_3O_4-FeS_2	1M KOH	253@10 mA/cm	48	[14]
γ-Fe_2O_3@FeS_2@C	1M KOH	268@10 mA/cm	54	[15]
FeS_2@MXene	1M KOH	240@10 mA/cm	58.6	[16]
Co–FeS_2/CoS_2	1M KOH	278@10 mA/cm	73	[17]
NiFeS@Ti_3C_2 MXene/NF	1M KOH	290@20 mA/cm	45	[18]
Ni_3S_2/$FeNi_2S_4$ hybrid	1M KOH	210@20 mA/cm	36.2	[19]

Ni_2FeS@NSC	1M KOH	247@10 mA/cm	150	[20]
Ni_3S_2–$Fe_5Ni_4S_8$	1M KOH	240@100 mA/cm	48.1	[21]
FeS_2/TiO_2	1M KOH	230@100 mA/cm	48.1	[22]
NiFeS/NF	1M KOH	215@100 mA/cm	56.37	[23]
$NaFeS_2$/NF	1M KOH	370@200 mA/cm	90	[24]
$CuFeS_2$/rGO	1M KOH	176@10 mA/cm	216	[25]

Table S2. HER catalytic performances of various electrocatalysts

Electrocatalyst	Electrolyte	η (mV)	Tafel Slope ($mV\cdot dec^{-1}$)	Ref
Pure nickel foam	**1M KOH**	**340 @ 10 mA/cm^2**	**141**	**This work**
NFC-2 NiO/FeS@CNT	**1M KOH**	**64@10 mA/cm^2**	**38**	
FeS_2@MXene	1M KOH	87@10 mA/cm^2	97.7	[16]
NiO–$NiMoO_4$/mCNTs	1M KOH	109 @10 mA/cm^2	49.2	[26]
FeS_2/CoS_2 NSs	1M KOH	78.2@10 mA/cm^2	44	[11]
$Ni_{0.7}Fe_{0.3}S_2$	1M KOH	155@10 mA/cm^2	109	[5]
Co-MoS_2@Mo_2CTx	1M KOH	112@10 mA/cm^2	82	[27]
FeS/Ni_3S_2@NF	1M KOH	130@10 mA/cm^2	124	[8]
FeS_2/FeOOH-ZnO@N	1M KOH	74@10 mA/cm^2	93.96	[9]
Ni-doped O-incorporated FeS_2	1M KOH	157@10 mA/cm^2	112.5	[6]
NiS_2/FeS_2/NC	1M KOH	172 @ 10 mA/cm^2	68.56	[3]
$Ni_3S_4/NiS_2/FeS_2$	1M KOH	196@10 mA/cm^2	110	[1]
Co–FeS_2/CoS_2	0.5 M H_2SO_4	103@10 mA/cm^2	56	[17]
NiFeS@Ti_3C_2 MXene/NF	1M KOH	180@20 mA/cm^2	177	[18]
$Ni_3S_2/FeNi_2S_4$ hybrid	1M KOH	50@20 mA/cm^2	117	[19]
1T-Co-$WS_2/NiTe_2$/Ni	1M KOH	88@10 mA/cm	68	[13]
Ni_2FeS@NSC	1M KOH	271@10 mA/cm	102	[20]
NiFeS/NF	1M KOH	196@100 mA/cm	102.93	[23]
$NaFeS_2$/NF	1M KOH	220@100 mA/cm	31	[24]

Table S3. Comparison of overall water splitting performances of various electrocatalysts

Electrocatalyst	Electrolyte	η (V) @ 10 mA/cm^2	Ref
NFC-2 NiO/FeS@CNT	**1 M KOH**	**1.465**	**This work**
NiO–$NiMoO_4$/mCNTs	1M KOH	1.57	[26]
$Ni_3S_4/NiS_2/FeS_2$	1M KOH	1.68	[1]
FeS/Ni_3S_2@NF	1M KOH	1.51	[8]
NiFeS@Ti_3C_2 MXene/NF	1M KOH	1.85	[18]
$Ni_{0.7}Fe_{0.3}S_2$	1M KOH	1.62	[5]
FeS_2/FeOOH-ZnO@N	1M KOH	1.41	[9]
FeS_2/CoS_2 NSs	1M KOH	1.47	[11]
Ni-doped O-incorporated FeS_2	1M KOH	1.58	[6]
FeS_2@MXene	1M KOH	1.57	[16]
NiS_2/FeS_2/NC	1M KOH	1.58	[3]
$Ni_3S_2/FeNi_2S_4$ hybrid	1M KOH	1.55	[19]

References

1. W. Wang, W. Wang, Y. Xu, X. Ren, X. Liu and Z. Li, *Applied Surface Science*, 2021, **560**, 149985.
2. Z. Shao, H. Meng, J. Sun, N. Guo, H. Xue, K. Huang, F. He, F. Li and Q. Wang, *ACS Applied Materials & Interfaces*, 2020, **12**, 51846-51853.
3. S. Wang, P. Ning, S. Huang, W. Wang, S. Fei, Q. He, J. Zai, Y. Jiang, Z. Hu and X. Qian, *Journal of Power Sources*, 2019, **436**, 226857.
4. D. Wang, Q. Li, C. Han, Z. Xing and X. Yang, *ACS Central Science*, 2018, **4**, 112-119.
5. J. Yu, G. Cheng and W. Luo, *Journal of materials chemistry A*, 2017, **5**, 15838-15844.
6. S. Shit, S. Bolar, N. C. Murmu and T. Kuila, *ACS sustainable chemistry & engineering*, 2019, **7**, 18015-18026.
7. J. Wu, D. Wu, W. Yuan, Y. Luo, Z. Han, X. Xu, S. Chang, M. Wen and C. Huang, *Chemical Engineering Journal*, 2025, 161821.
8. H. Li, S. Yang, W. Wei, M. Zhang, Z. Jiang, Z. Yan and J. Xie, *Journal of Colloid and Interface Science*, 2022, **608**, 536-548.
9. Y. Yang, Y. Chen, Y. Xiong, Y. He, Q. Sun, D. Xu and Z. Hu, *Journal of Alloys and Compounds*, 2024, 174525.
10. C. Yue, X. Zhang, J. Yin, H. Zhou, K. Liu and X. Liu, *Applied Catalysis B: Environmental*, 2023, **339**, 123171.
11. Y. Li, J. Yin, L. An, M. Lu, K. Sun, Y. Q. Zhao, D. Gao, F. Cheng and P. Xi, *Small*, 2018, **14**, 1801070.
12. Y. Lu, F. Ma, J. Mao, H. Zhang, J. Wang, X. Liu, X. Ren and R. Chen, *Journal of Alloys and Compounds*, 2023, **960**, 170842.
13. D. R. Paudel, U. N. Pan, R. B. Ghising, P. P. Dhakal, V. A. Dinh, H. Wang, N. H. Kim and J. H. Lee, *Nano Energy*, 2022, **102**, 107712.
14. M. J. Wang, X. Zheng, L. Song, X. Feng, Q. Liao, J. Li, L. Li and Z. Wei, *Journal of Materials Chemistry A*, 2020, **8**, 14145-14151.
15. K. Chen, R. Rajendiran, D. H. Lee, J. Diao and O. L. Li, *Journal of Alloys and Compounds*, 2021, **885**, 160986.
16. Y. Xie, H. Yu, L. Deng, R. Amin, D. Yu, A. E. Fetohi, M. Y. Maximov, L. Li, K. El-

Khatib and S. Peng, *Inorganic Chemistry Frontiers*, 2022, **9**, 662-669.

17. K. Wang, W. Guo, S. Yan, H. Song and Y. Shi, *RSC advances*, 2018, **8**, 28684-28691.
18. D. Chanda, K. Kannan, J. Gautam, M. M. Meshesha, S. G. Jang, V. A. Dinh and B. L. Yang, *Applied Catalysis B: Environmental*, 2023, **321**, 122039.
19. Y. Wu, Y. Li, M. Yuan, H. Hao, X. San, Z. Lv, L. Xu and B. Wei, *Chemical Engineering Journal*, 2022, **427**, 131944.
20. J. Chang, S. Zang, F. Song, W. Wang, D. Wu, F. Xu, K. Jiang and Z. Gao, *Applied Catalysis A: General*, 2022, **630**, 118459.
21. Y. Wu, Y. Li, Z. Lü, L. Xu and B. Wei, *Journal of Materials Science*, 2020, **55**, 15963-15974.
22. Z. Chen, R. Zheng, S. Deng, W. Wei, W. Wei, B.-J. Ni and H. Chen, *Journal of Materials Chemistry A*, 2021, **9**, 25032-25041.
23. J. Chen, L. Zhang, J. Li, X. He, Y. Zheng, S. Sun, X. Fang, D. Zheng, Y. Luo and Y. Wang, *Journal of Materials Chemistry A*, 2023, **11**, 1116-1122.
24. V. Dileepkumar, C. Pratapkumar, R. Viswanatha, B. M. Basavaraja, R. R. Maphanga, M. Chennabasappa, N. Srinivasa, S. Ashoka, Z. Chen and S. Rtimi, *Chemical Engineering Journal*, 2021, **426**, 131315.
25. S. Swathi, R. Yuvakkumar, G. Ravi, M. Thambidurai, H. D. Nguyen and D. Velauthapillai, *ACS Applied Nano Materials*, 2023, **6**, 6538-6549.
26. Q. Xue, Y. Wu, J. Hao, L. Ma, Y. Dang, J.-J. Zhu and Y. Zhou, *ACS Applied Materials & Interfaces*, 2023, **15**, 31470-31477.
27. J. Liang, C. Ding, J. Liu, T. Chen, W. Peng, Y. Li, F. Zhang and X. Fan, *Nanoscale*, 2019, **11**, 10992-11000.