

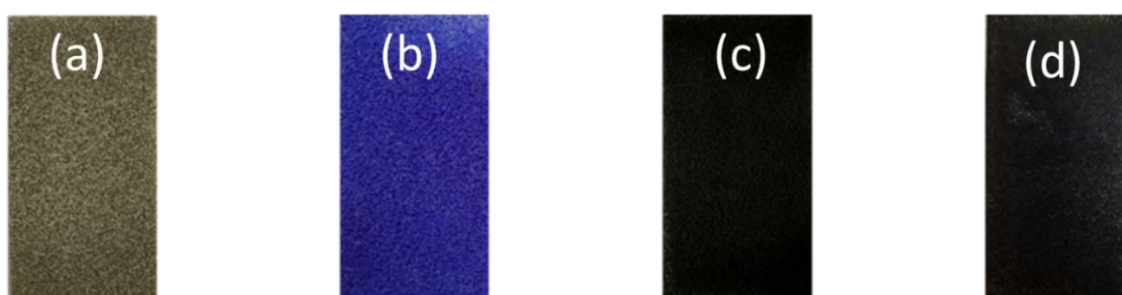
## Electronic Supplementary Information

### ZIF-67-Derived Co-N-C Supported Nickel Cobalt Sulfide as a Bifunctional Electrocatalyst for Sustainable Hydrogen Production via Alkaline Electrolysis

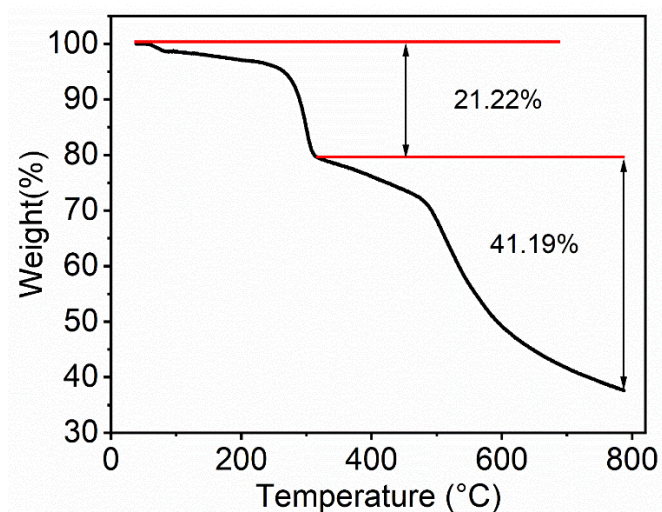
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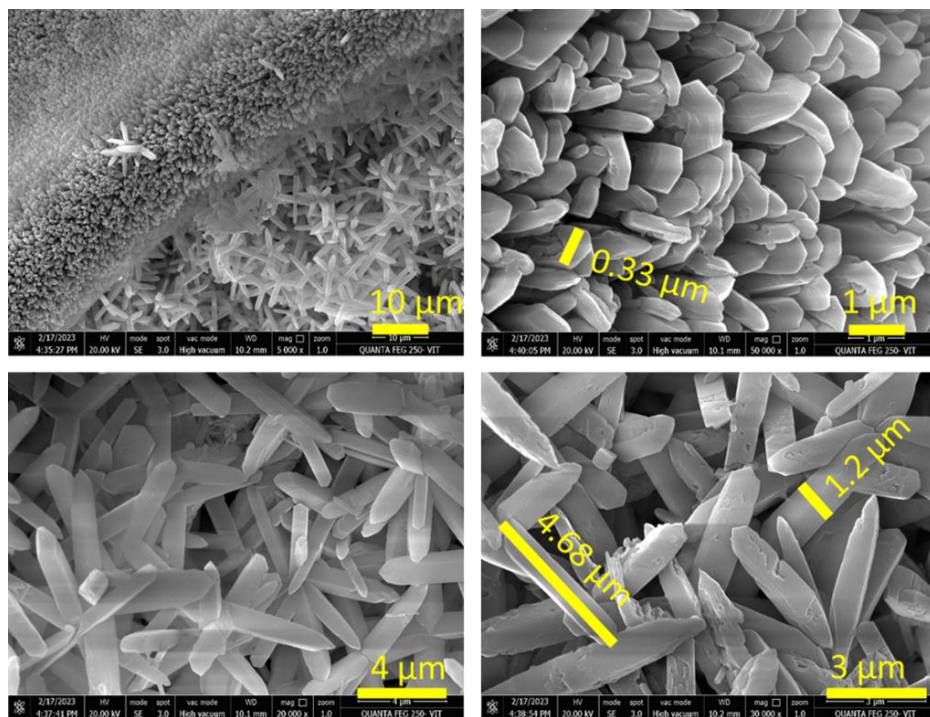
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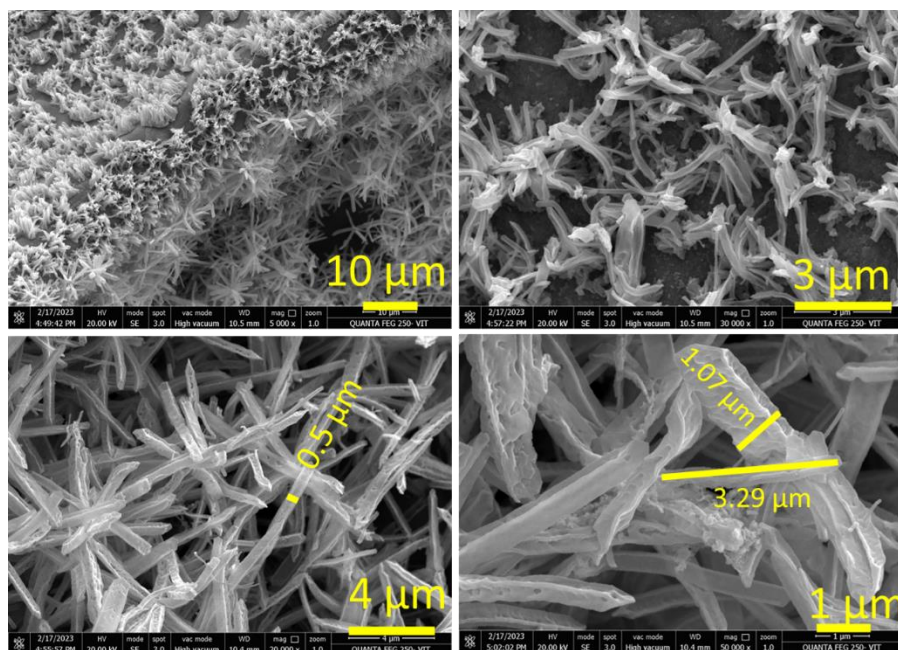
**Fig. S1** Digital images of (a) bare NF, (b) NF@ZIF-67, (c) NF@ZIF-67@NiCo<sub>2</sub>S<sub>4</sub>, (d) NF@Co-N-C@NiCo<sub>2</sub>S<sub>4</sub>.



**Fig. S2** TGA analysis of ZIF-67.



**Fig. S3** FESEM images of NF@ZIF-67.



**Fig. S4** FESEM images of ZIF-67 after calcination (Co-N-C).

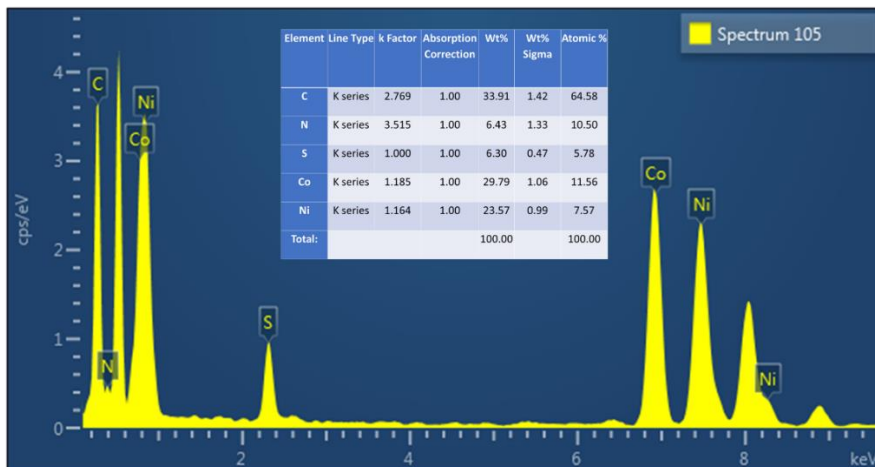


Fig. S5 EDS spectrum of NF@Co-N-C@NiCo<sub>2</sub>S<sub>4</sub>.

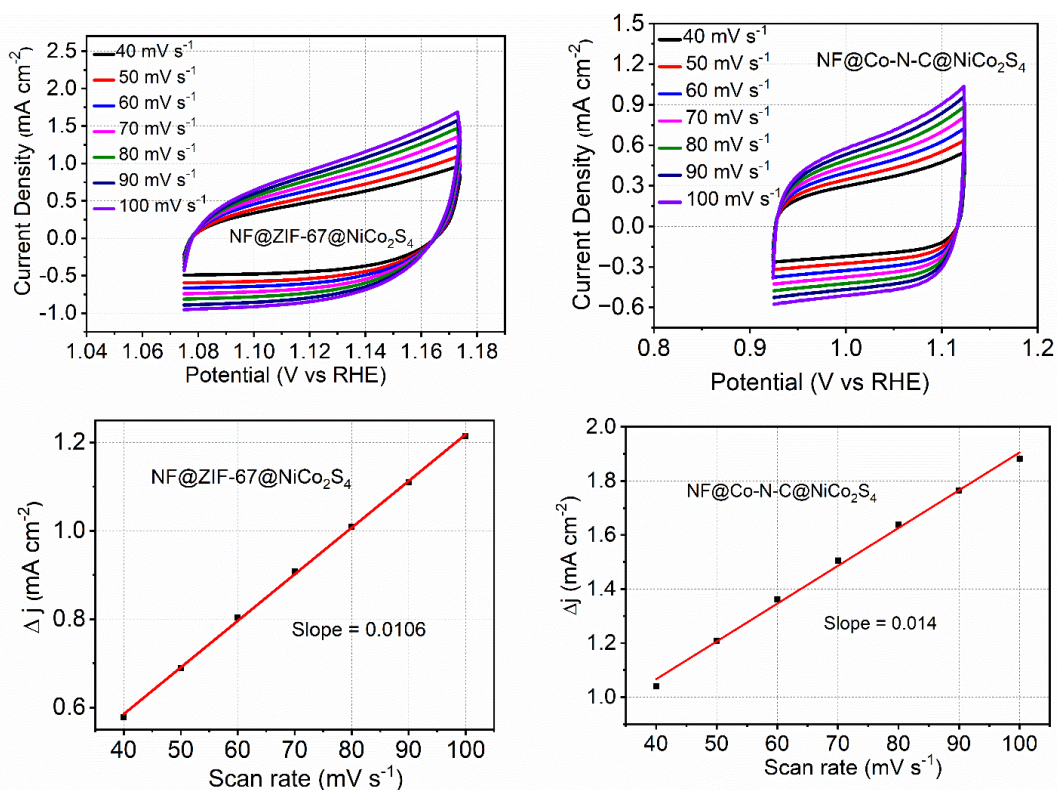


Fig. S6 (a and b) cyclic voltammograms at different scan rates ranging from 40 to 100 mV s<sup>-1</sup>  
 (c and d) Scan rate dependent current densities of the materials.



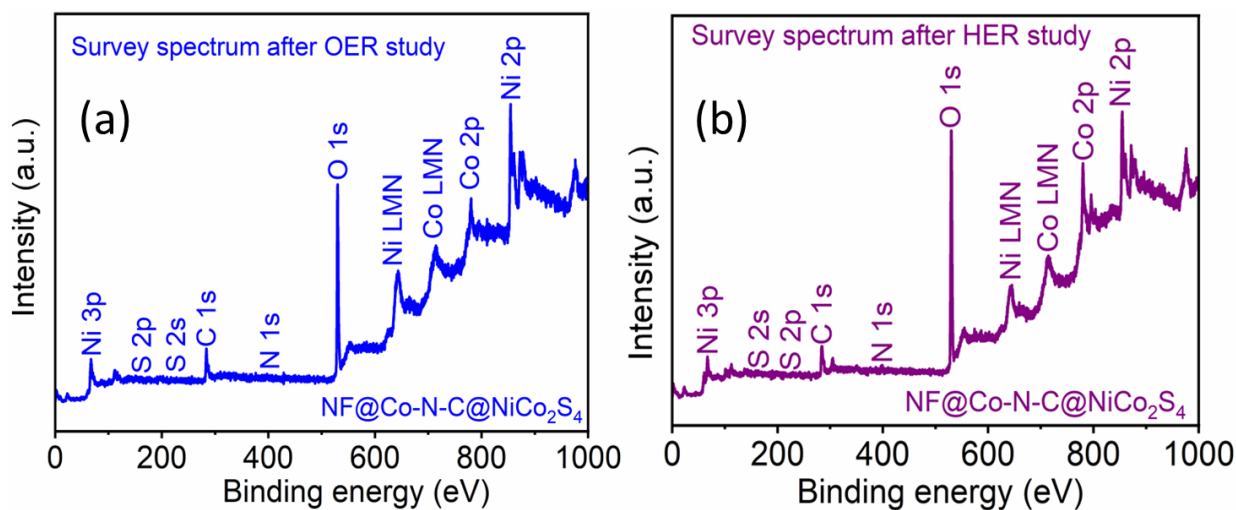


Fig. S7 XPS survey spectrum of NF@Co-N-C@NiCo<sub>2</sub>S<sub>4</sub> after (a) OER and (b) HER studies.

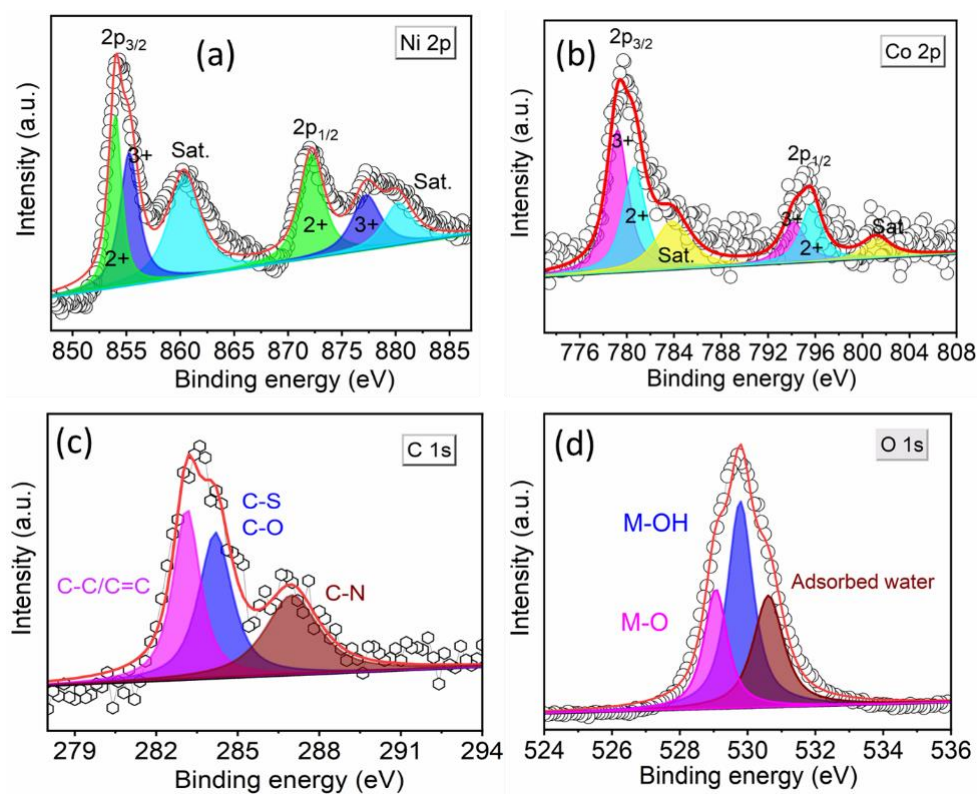
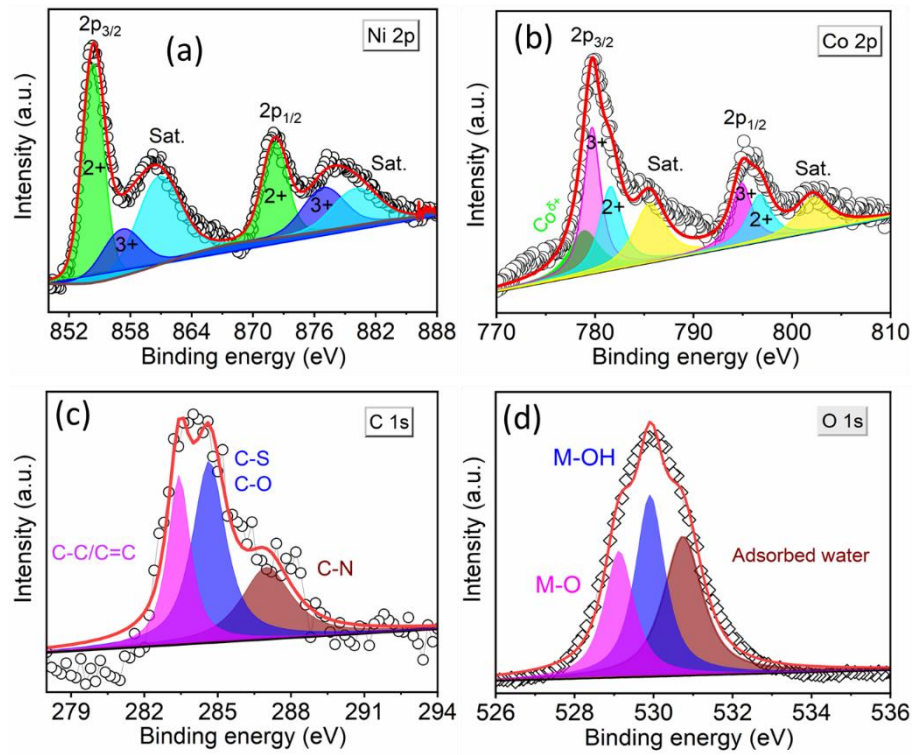


Fig. S8 XPS high-resolution spectra of NF@Co-N-C@NiCo<sub>2</sub>S<sub>4</sub> for (a) Ni 2p, (b) Co 2p, (c) C 1s, (d) O 1s after OER study.



**Fig. S9** XPS high-resolution spectra of NF@Co-N-C@NiCo<sub>2</sub>S<sub>4</sub> for (a) Ni 2p, (b) Co 2p, (c) C 1s, (d) O 1s after HER study.

**Table S1** Comparison of OER performance of NF@ZIF-67@NiCo<sub>2</sub>S<sub>4</sub> and NF@Co-N-C@NiCo<sub>2</sub>S<sub>4</sub> with other electrocatalysts in 1.0 M KOH.

Catalysts	j (mA cm <sup>-2</sup> )	η (mV vs RHE)	Tafel slope (mV dec <sup>-1</sup> )	Electrolyte	References
CoNi@C on NF	100	355	55.6	1 M KOH	S1
Fe <sub>3</sub> C-Co-NC on NF	50	338	59	1 M KOH	S2
NiCoDH/NiCoS	20	303	77.6	1 M KOH	S3
V <sub>s</sub> -NiCo <sub>2</sub> S <sub>4</sub> /N,S-rGO	10	340	43.8	0.1 M KOH	S4
Ni <sub>3</sub> S <sub>2</sub> /VG@NiCo LDHs	100	320	67	1 M KOH	S5
CoS <sub>x</sub> /Ni <sub>3</sub> S <sub>2</sub> @NF	10	1.572	105.4	1 M KOH	S6
	50	1.863			
Co <sub>3</sub> S <sub>4</sub> @rGO	10	151	59	0.5 M H <sub>2</sub> SO <sub>4</sub>	S7
NiCoS-3	10	320	58.8	1.0 M KOH	S8
NiCo <sub>2</sub> S <sub>4</sub> NW/NF	10	260	40.1	1.0 M KOH	S9
Ni <sub>0.7</sub> Fe <sub>0.3</sub> S <sub>2</sub>	10	198	56	1.0 M KOH	S10
Ni <sub>3</sub> S <sub>2</sub> /NF	10	260	-	1.0 M KOH	S11
NiFeS-2	10	286	56.3	1.0 M KOH	S12
FeOOH decorated on Ni	20	267	79	1.0 M KOH	S13
MOF					
NDA/MWCNTs-a	10	285	73	1.0 M KOH	S14
NiFe-Se/CFP	10	281 mV	40.93	1.0 M KOH	S15
Ni-Fe-Se/N-CNTs	10	215	97.1	1.0 M KOH	S16
powder					
NiFeSe@NiSe O@CC	10	270	63.2	1.0 M KOH	S17
NiFe-based selenide	10	216	36	1.0 M KOH	S18
powder					
NiSe <sub>2</sub> NPs/	10	324	47.47	1.0 M KOH	S19
(Co.Ni)Se <sub>2</sub> @NiFe LDH	10	277	75	1.0 M KOH	S20
Ni-Co-S-P	10	280	78	1.0 M KOH	S21
(Co <sub>1-x</sub> Ni <sub>x</sub> )(S <sub>1-y</sub> P <sub>y</sub> ) <sub>2</sub> /G	10	285	105	1.0 M KOH	S22

FeCoNiP <sub>0.5</sub> S <sub>0.5</sub>	100	285	69	1.0 M KOH	S23
Ru@NiCo-MOF HPNs	10	284	78.8	1.0 M KOH	S24
NF@ZIF-67@NiCo <sub>2</sub> S <sub>4</sub>	50	248	68	1.0 M KOH	
	100	361	68	1.0 M KOH	This work
NF@Co-N-C@NiCo <sub>2</sub> S <sub>4</sub>	50	239	66	1.0 M KOH	
	100	300	66	1.0 M KOH	This work

**Table S2** Comparison of HER performance of NF@ZIF-67@NiCo<sub>2</sub>S<sub>4</sub> and NF@Co-N-C@NiCo<sub>2</sub>S<sub>4</sub> with other electrocatalysts in 1.0 M KOH.

Catalysts	j (mA cm <sup>-2</sup> )	$\eta$ (mV vs RHE)	Tafel slope (mV dec <sup>-1</sup> )	Electrolyte	Reference
Ni-MOF/NC-800	10	369	127.1	1.0 M KOH	S25
Fe-Co-CN/rGO-700	10	215	-	1.0 M KOH	S26
NiCo <sub>2</sub> S <sub>4</sub> NW/NF	10	260	67	1.0 M KOH	S9
Ni <sub>3</sub> S <sub>2</sub> -CNFs/CC	20	300	-	1.0 M KOH	S30
NF@ZIF-67@NiCo <sub>2</sub> S <sub>4</sub>	20	230	139	1.0 M KOH	This work
NF@Co-N-C@NiCo <sub>2</sub> S <sub>4</sub>	20	229	131	1.0 M KOH	This work

**Table S3** Comparison of Overall water splitting performance of NF@ZIF-67@NiCo<sub>2</sub>S<sub>4</sub> and NF@Co-N-C@NiCo<sub>2</sub>S<sub>4</sub> with other electrocatalysts in 1.0 M KOH.

Catalysts	j (mA cm <sup>-2</sup> )	$\eta$ (mV vs RHE)	Reference
Co-NCNTFs//NF	10	1.62	S27
FeCoNi@FeNC	10	1.63	S28
Co(S <sub>x</sub> Se <sub>1-x</sub> ) <sub>2</sub>	10	1.63	S36
NiS/Ni <sub>2</sub> P/CC	10	1.67	S37

Ni-Co-S-P	10	1.61	S21
(Co <sub>1-x</sub> Ni <sub>x</sub> )(S <sub>1-y</sub> P <sub>y</sub> ) <sub>2</sub> /G	10	285	S38
Ni <sub>0.33</sub> Co <sub>0.67</sub> S <sub>2</sub>	5	1.65	S29
NiCo <sub>2</sub> S <sub>4</sub> NW/NF	10	1.63	S9
NiCo(OH) <sub>2</sub> /NF	10	1.65	S29
N, O and S tridoped carbon-encapsulated	10	1.6	S31
Ni <sub>3</sub> S <sub>4</sub> /NF	10	1.61	S32
Ni <sub>0.7</sub> Fe <sub>0.3</sub> S <sub>2</sub>	10	1.625	S33
Ni Co-LDH/NF	10	1.66	S34
NiCo <sub>2</sub> S <sub>4</sub> /N-rGO	10	1.63	S35
Ni <sub>3</sub> S <sub>2</sub> /VG@NiCo LDHs	10	1.66	S5
NF@ZIF67@NiCo <sub>2</sub> S <sub>4</sub>   NF@ZIF- 67@NiCo <sub>2</sub> S <sub>4</sub>	10	1.62	This work
NF@Co-N-C@NiCo <sub>2</sub> S <sub>4</sub> (+)  NF@Co-N- C@NiCo <sub>2</sub> S <sub>4</sub> (-)	10	1.59	This work

## References

- S1 X. Zhang, J. Luo, K. Wan, D. Plessers, B. Sels, J. Song, L. Chen, T. Zhang, P. Tang, J. R. Morante, J. Arbiol and J. Fransaer, *J. Mater. Chem. A*, 2019, **7**, 1616-1628.
- S2 H. Wang, C. Sun, E. Zhu, C. Shi, J. Yu and M. Xu, *J. Alloys Compd.*, 2023, **948**, 169728.
- S3 H. Zhao, Y. Yang, X. Dai, H. Qiao, J. Yong, X. Luan, L. Yu, C. Luan, Y. Wang and X. Zhang, *Electrochim. Acta*, 2019, **295**, 1085-1092.
- S4 X. Feng, Q. Jiao, Q. Li, Q. Shi, Z. Dai, Y. Zhao, H. Li, C. Feng, W. Zhou and T. Feng, *Electrochim. Acta*, 2020, **331**, 135356.
- S5 X. Zhang, J. Fan, X. Lu, Z. Han, C. Cazorla, L. Hu, T. Wu, D. Chu, *Chem. Eng. J.*, 2021, **415**, 129048.



- S6 S. Shit, S. Chhetri, W. Jang, N. C. Murmu, H. Koo, P. Samanta and T. Kuila, *ACS Appl. Mater. Interfaces*, 2018, **10**, 27712-27722.
- S7 R. S. Kumar, S. C. Karthikeyan, S. Ramakrishnan, S. Vijayapradeep, A. Rhan Kim, J.-S. Kim and D. J. Yoo, *Chem. Eng. J.*, 2023, **451**, 138471.
- S8 Z. Yu, Y. Bai, S. Zhang, Y. Liu, N. Zhang and K. Sun, *Int. J. Hydrogen Energy*, 2018, **43**, 8815-8823.
- S9 A. Sivanantham, P. Ganesan and S. Shanmugam, *Adv. Funct. Mater.*, 2016, **26**, 4661-4672.
- S10 J. Yu, G. Cheng and W. Luo, *J. Mater. Chem. A*, 2017, **5**, 15838-15844.
- S11 L. Feng, G. Yu, Y. Wu, G. Li, H. Li, Y. Sun, T. Asefa, W. Chen and X. Zou, *J. Am. Chem. Soc.*, 2015, **137**, 14023-14026.
- S12 B. Q. Li, S. Y. Zhang, C. Tang, X. Cui and Q. Zhang, *Small*, 2017, **13**, 1700610.
- S13 J. Yao, Y. Ji, L. Pei, S. Tan, F. Ren, *New J. Chem.*, 2022, **46**, 9650.
- S14 S. Kiran, G. Yasmeen, Z. Shafiq, A. Abbas, S. Manzoor, D. Hussain, R. A. Pashameah, E. Alzahrani, A. K. Alanazi and M. N. Ashiq, *Fuel*, 2023, **331**, 125881.
- S15 Y. Guo, C. Zhang, J. Zhang, K. Dastafkan, K. Wang, C. Zhao and Z. Shi, *ACS Sustainable Chem. Eng.*, 2021, **9**, 2047-2056.
- S16 Y. Feng, S. Wang, H. Wang, Y. Zhong, Y. Hu, *J. Mater. Sci.*, 2020, **55**, 13927-13937.
- S17 G. Yilmaz, C. F. Tan, Y.-F. Lim and G. W. Ho, *Adv. Energy Mater.*, 2019, **9**, 1802983.
- S18 C. Xuan, K. Xia, W. Lei, W. Xia, W. Xiao, L. Chen, H. L. Xin and D. Wang, *Electrochim. Acta*, 2018, **291**, 64-72.
- S19 Y. Guo, C. Zhang, J. Zhang, K. Dastafkan, K. Wang, C. Zhao and Z. Shi, *ACS Sustainable Chem. Eng.*, 2021, **9**, 2047-2056.

- S20 J.-G. Li, H. Sun, L. Lv, Z. Li, X. Ao, C. Xu, Y. Li and C. Wang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 8106-8114.
- S21 Y. Tian, Z. Lin, J. Yu, S. Zhao, Q. Liu, J. Liu, R. Chen, Y. Qi, H. Zhang, R. Li, J. Li and J. Wang, *ACS Sustainable Chem. Eng.*, 2019, **7**, 14639-14646.
- S22 H. J. Song, H. Yoon, B. Ju, G.-H. Lee, D.-W. Kim, *Adv. Energy Mater.*, 2018, **8**, 1802319.
- S23 X. Wang, W. Ma, C. Ding, Z. Xu, H. Wang, X. Zong and C. Li, *ACS Catal.*, 2018, **8**, 9926-9935.
- S24 D. Liu, H. Xu, C. Wang, H. Shang, R. Yu, Y. Wang, J. Li, X. Li and Y. Du, *Inorg. Chem.*, 2021, **60**, 5882-5889.
- S25 J.-L. Liu, X.-Y. Zhou, L. Qin, Y.-Q. Wang, H.-J. Zhu, G. Ni, M.-L. Ma and M.-D. Zhang, *J. Mol. Struct.*, 2022, **1252**, 132184.
- S26 W. Fang, J. Wang, Y. Hu, X. Cui, R. Zhu, Y. Zhang, C. Yue, J. Dang, W. Cui, H. Zhao and Z. Li, *Electrochim. Acta*, 2021, **365**, 137384.
- S27 Q. Yuan, Y. Yu, Y. Gong and X. Bi, *ACS Appl. Mater. Interfaces*, 2020, **12**, 3592-3602.
- S28 Q. Zhang, R. F. Webster, S. Cheong, R. D. Tilley, X. Lu and R. Amal, *Part. Part. Syst. Charact.*, 2019, **36**, 1800252.
- S29 M. Li, X. Deng, K. Xiang, Y. Liang, B. Zhao, J. Hao, J.-L. Luo and X.-Z. Fu, *ChemSusChem*, 2020, **13**, 914-921.
- S30 B. Zhao, J. Liu, X. Wang, C. Xu, P. Sui, R. Feng, L. Wang, J. Zhang, J.-L. Luo and X.-Z. Fu, *NanoEnergy*, 2021, **80**, 10553.
- S31 S. Huang, Y. Meng, S. He, A. Goswami, Q. Wu, J. Li, S. Tong, T. Asefa and M. Wu, *Adv. Funct. Mater.*, 2017, **27**, 1606585.
- S32 J. T. Ren and Z. Y. Yuan, *ACS Sustainable Chem. Eng.*, 2017, **5**, 7203-7210.

- S33 J. Yu, G. Cheng and W. Luo, *J. Mater. Chem. A*, 2017, **5**, 15838-15844.
- S34 W. Liu, J. Bao, M. Guan, Y. Zhao, J. Lian, J. Qiu, L. Xu, Y. Huang, J. Qian and H. Li, *Dalton Trans.*, 2017, **46**, 8372-8376.
- S35 H. S. Lee, J. Pan, G. S. Gund and H. S. Park, *Adv. Mater. Interfaces*, 2020, **7**, 2000138.
- S36 X. Zhang, J. Luo, K. Wan, D. Plessers, B. Sels, J. Song, L. Chen, T. Zhang, P. Tang, J. R. Morante, J. Arbiol and J. Fransaer, *Adv. Funct. Mater.*, 2017, **27**, 1701008.
- S37 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, *ACS Appl. Mater. Interfaces*, 2018, **10**, 4689-4696.
- S38 H. J. Song, H. Yoon, B. Ju, G. H. Lee and D. W. Kim, *Adv. Energy Mater.*, 2018, **8**, 1802319.