

Supporting Information

Multivalent cation-modified Ni_xS_y for highly efficient and stable oxygen evolution electrocatalysis

Wei Yuan^a, Jicheng Wu^a, Guojian Jiang^{a,b,c,d,e,f,}, Dandan Wu^{a,*}, Xiaowei Xu^a,
Shufang Chang^a*

^aSchool of Materials Science and Engineering, Shanghai Institute of Technology, 100 Haiquan Road, Shanghai 201418, R. P. China.

^bState Key Laboratory of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, P. R. China.

^cState Key Laboratory of Crystal Materials, Shandong University, Jinan, Shandong, 250100, P. R. China.

^dInfrared and Low Temperature Plasma Key Laboratory of Anhui Province, college of Electronic Countermeasures, NUDT, Hefei 230037, P. R. China.

^eState Key Laboratory of Mineral Processing, Beijing 102628, P. R. China.

^fState Key Lab Advanced Metals and Materials, Beijing 100083, P. R. China.

Corresponding author: guojianjiang@sit.edu.cn; wdan1008@163.com

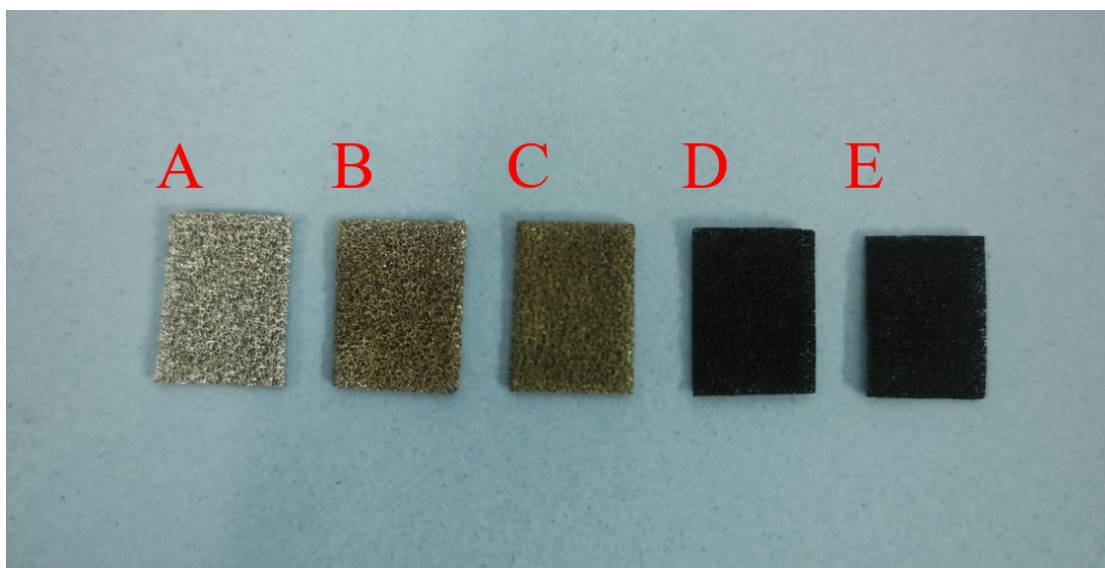


Fig. S1 Photograph of (A) bare Ni foam (B) NiFe-LDHs (C) NiFeV-LDHs (D) (Ni, Fe)₃S₄-NiS and (E) (Ni, Fe, V)₃S₄-NiS.

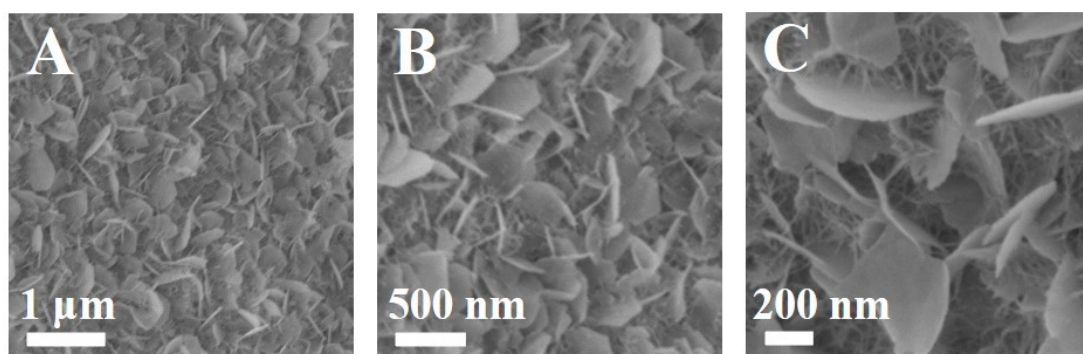


Fig. S2 SEM images of NiFe-LDHs.

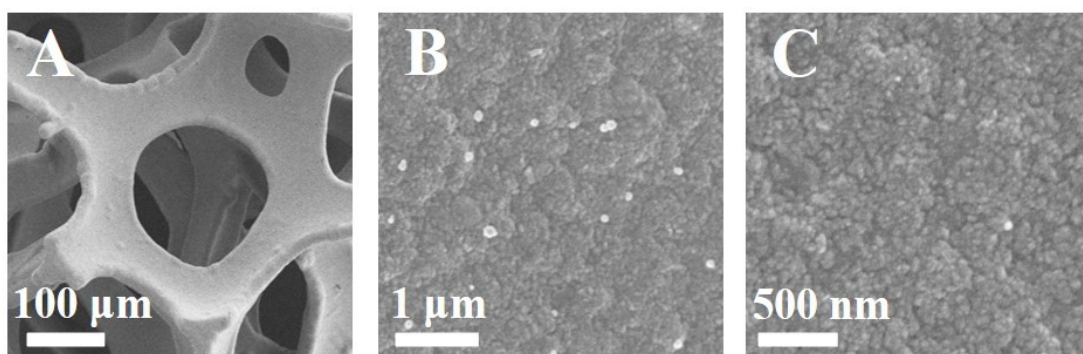


Fig. S3 SEM images of (Ni, Fe)₃S₄-NiS.

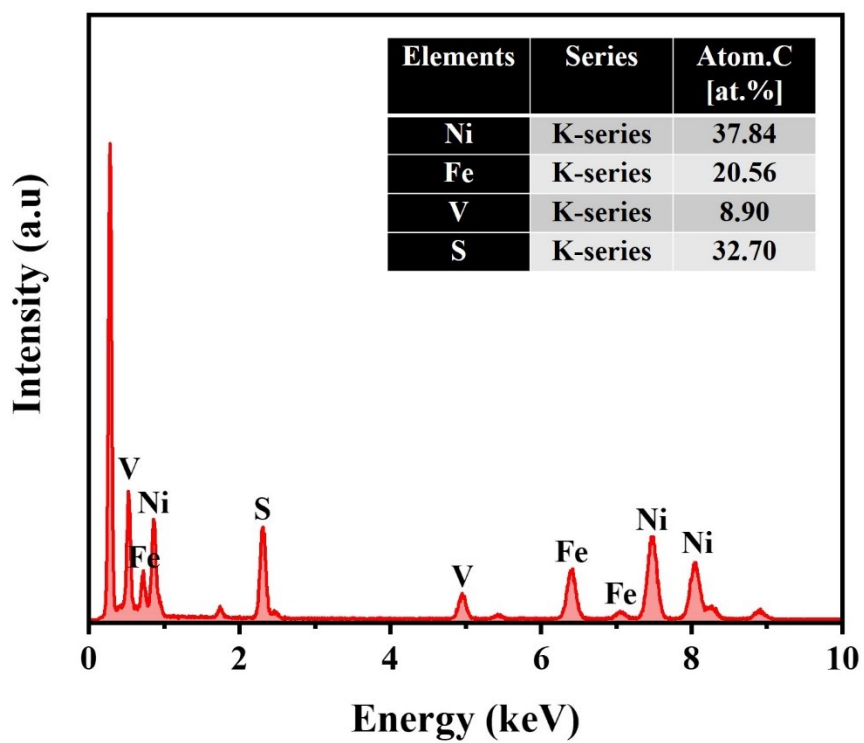


Fig. S4 EDS pattern of $(\text{Ni, Fe, V})_3\text{S}_4\text{-NiS}$.

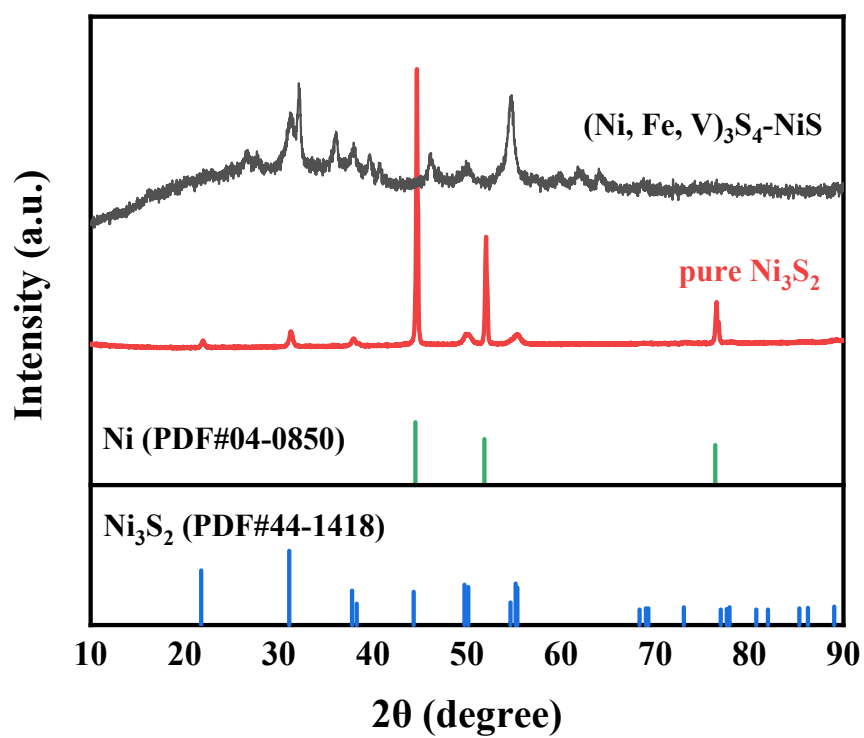


Fig. S5 XRD pattern of (Ni, Fe, V)₃S₄-NiS and pure Ni₃S₂.

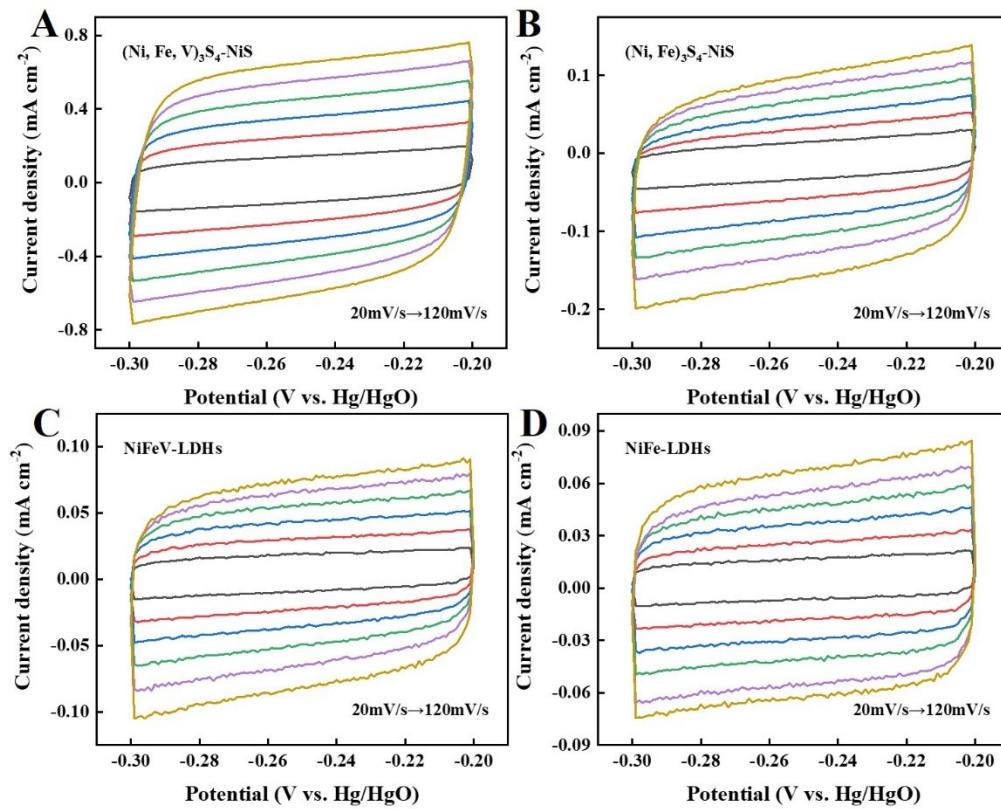


Fig. S6 Cyclic voltammetry curves of (Ni, Fe, V)₃S₄-NiS (A), (Ni, Fe)₃S₄-NiS (B), NiFeV-LDHs (C) and NiFe-LDHs (D) at various scan rates in the region of 0.2-0.3 V vs. Hg/HgO.

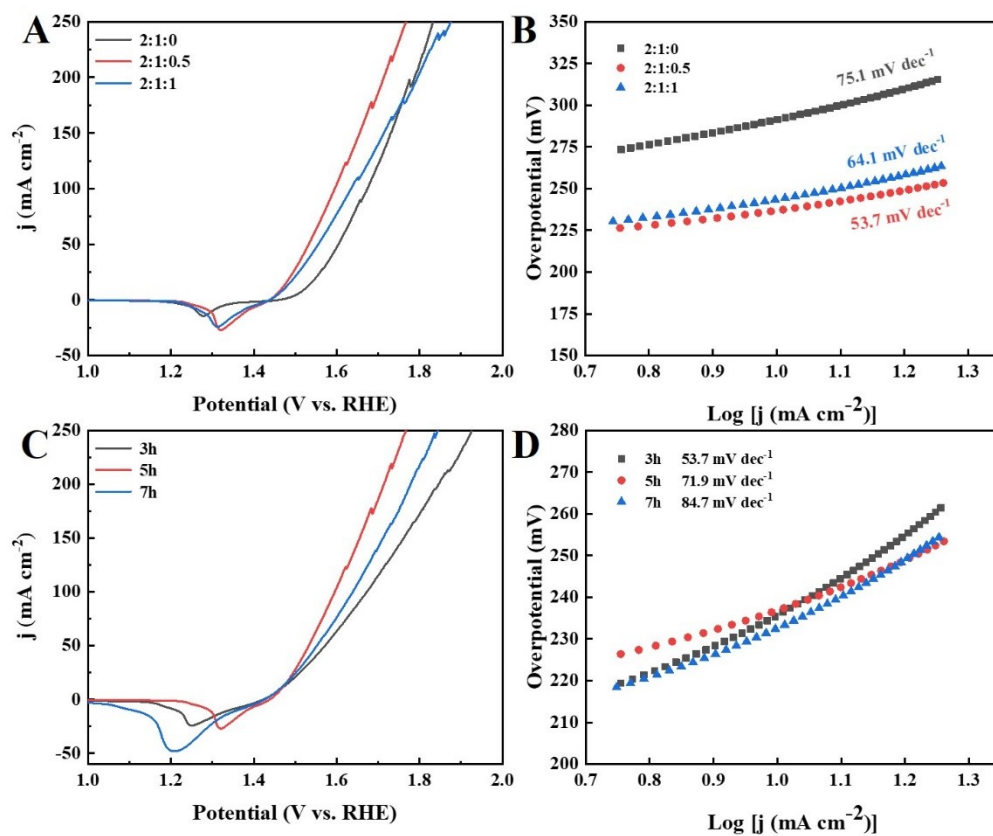


Fig. S7 (A) Polarization curves of samples with different vulcanization ratios of Ni:Fe:V, (B) The corresponding Tafel plots of the catalysts, (C) Polarization curves of samples with different vulcanization times and (D) The corresponding Tafel plots of the catalysts.

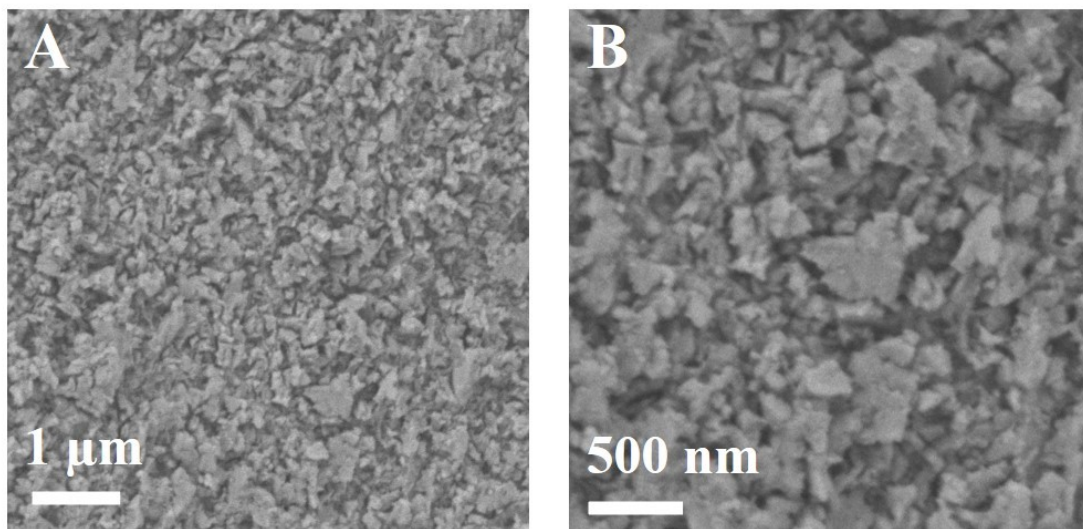


Fig. S8 SEM images of $(\text{Ni, Fe, V})_3\text{S}_4\text{-NiS}$ prepared by overvulcanization.

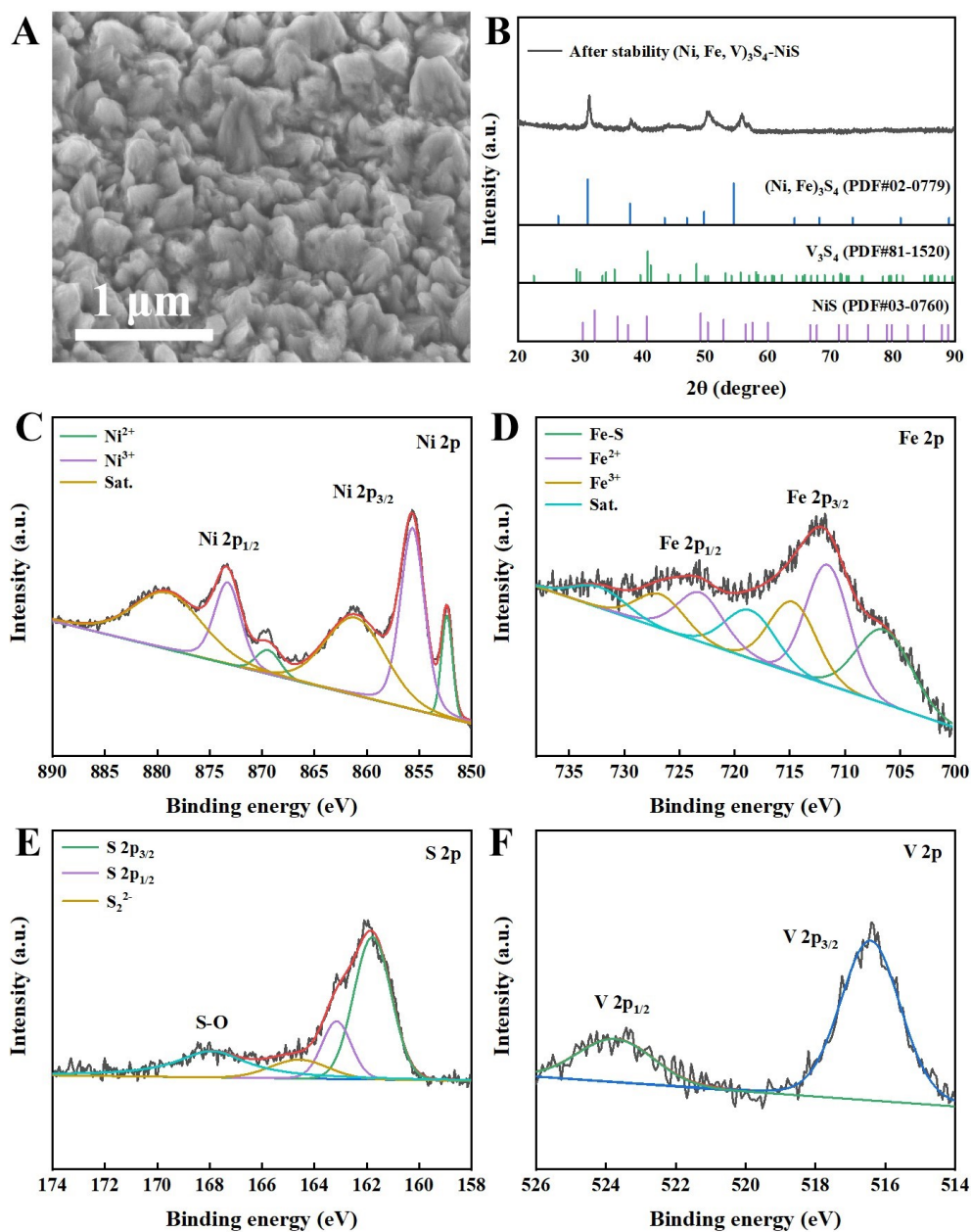


Fig. S9 Characterization of $(\text{Ni, Fe, V})_3\text{S}_4\text{-NiS}$ catalysts after stabilization: (A) SEM, (B) XRD and (C-F) XPS.

Table. S1 Comparison of the electrocatalytic OER performance of the (Ni, Fe, V)₃S₄-NiS with other non-noble-metal catalysts recently reported in alkaline solutions.

Catalyst	Electrolyte	η_{10} (mV)	Ref.
(Ni, Fe, V) ₃ S ₄ -NiS	1M KOH	236	This work
NiCo ₂ S ₄ @NiFe LDH	1M KOH	287	[1]
FeCoNi-LDH	1M KOH	299	[2]
CoS-Co(OH) ₂ @aMoS _{2+x}	1M KOH	380	[3]
Mo _(1-x) W _x S ₂	1M KOH	285	[4]
CdS/Ni ₃ S ₂	1M KOH	280	[5]
Ni ₃ S ₄ /NF	1M KOH	266	[6]
NiSe ₂ -CoSe ₂ /CFC	1M KOH	286	[7]
FeNi ₂ S ₄ NPs/rGO	1M KOH	250	[8]
pc-Ni ₃ S ₂ @CNF	1M KOH	270	[9]
NiS ₂ @NS	1M KOH	290	[10]
NM50-Ni ₃ S ₄	1M KOH	257	[11]
NiCu-LDH	1M KOH	290	[12]
Co ₃ O ₄ /Co-Fe	1M KOH	297	[13]
Ni ₆₅ Fe ₃₅ (OOH)	1M KOH	316	[14]
Co ₂ Fe-P	1M KOH	303	[15]
CoMnV-LDH	1M KOH	270	[16]

[1] X. Feng, Q. Jiao, W. Chen, Y. Dang, Z. Dai, S. Suib, J. Zhang, Y. Zhao, H. Li and C. Feng, *Appl Catal B-Environ*, 2021, 286, 119869.

[2] F. Li, Z. Sun, H. Jiang, Z. Ma, Q. Wang and F. Qu, *Energy Fuels*, 2020, 34, 11628-36.

[3] T. Yoon and K. S. Kim, *Adv Funct Mater*, 2016, 26, 7386.

[4] M. Zheng, J. Du, B. Hou and C. Xu, *ACS Appl. Mater. Interfaces*, 2017, 9, 26066–76.

[5] S. Qu, J. Huang, J. Yu, G. Chen, W. Hu, M. Yin, R. Zhang, S. Chu and C. Li,

- ACS Appl. Mater. Interfaces, 2017, 9, 29660–8.
- [6] N. Li, L. Ai, J. Jiang and S. Liu, *J Colloid Interf Sci*, 2020, 564, 418–27.
- [7] X. Zheng, X. Han, Y. Cao, Y. Zhang, D. Nordlund, J. Wang, S. Chou, H. Liu, L. Li, C. Zhong, Y. Deng and W. Hu, *Adv Mater*, 2020, 32, 2000607.
- [8] J. Jiang, Y. Zhang, X. Zhu, S. Lu, L. Long and J. Chen, *Nano Energy*, 2021, 81, 105619.
- [9] A. Tahir, T. Haq, F. Aftab, M. Zaheer, H. Duran, K. Kirchhoff, I. Lieberwirth and S. N. Arshad, *ACS Appl. Nano Mater.*, 2023, 6, 2336–45.
- [10] Y. Wang, M. Qiao, Y. Li, and S. Wang, *Small*, 2018, 14, 1800136.
- [11] K. Wan, J. Luo, C. Zhou, T. Zhang, J. Arbiol, B. Mao, X. Zhang and J. Fransaer, *Adv Funct Mater*, 2019, 29, 1900315.
- [12] Y. Zheng, J. Qiao, J. Yuan, J. Shen, A. Wang, P. Gong, X. Weng and L. Niu, *Electrochim Acta*, 2018, 282, 735–42.
- [13] X. Wang, L. Yu, B. Guan, S. Song and X. Lou, *Adv Mater*, 2018, 30, 1801211.
- [14] M. Görlin, J. Halldin Stenlid, S. Koroidov, M. Börner, M. Shipilin, A. Kalinko, V. Murzin, O. Safonova, M. Nachtegaal, A. Uheida, J. Dutta, M. Bauer, A. Nilsson and O. Diaz-Morales, *Nat commun*, 2020, 11, 6181.
- [15] L. Li, Y. Lu, X. Liu, X. Wang and S. Zhou, *J Alloy Compd*, 2022, 895, 162549.
- [16] J. Bao, Z. Wang, J. Xie, L. Xu, F. Lei, M. Guan, Y. Zhao, Y. Huang and H. Li, *Chem Commun*, 2019, 55, 3521–3524.