

**Modulation and engineering of MOF-derived transition metal selenides/NiFe
LDH for the application in electrocatalytic hydrogen evolution**

Jin Liang^{a,b,#,*}, Hang Luo^{a,b,#}, Tian Lei^{a,b}, Guang Yang^{a,b}

^aHunan Province Key Laboratory of Materials Surface & Interface Science and Technology, ^bCollege of Material Science and Engineering, Central South University of Forestry and Technology, Changsha 410004, P. R. China.

#These authors contributed equally to this work.

***Corresponding author: ljcfstu@163.com.**

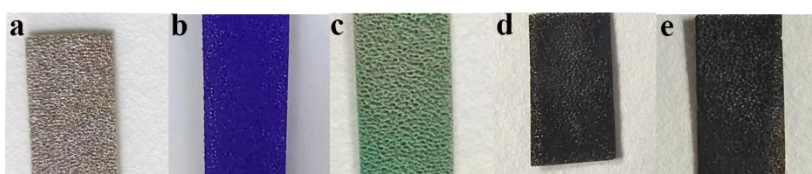


Fig. S1 The photograph of (a) NF, (b) ZIF-67/NF, (c) NiCo LDH/NF, (d) Ni-Co-Se/NF, (e) Ni-Co-Se@NiFe LDH/NF.

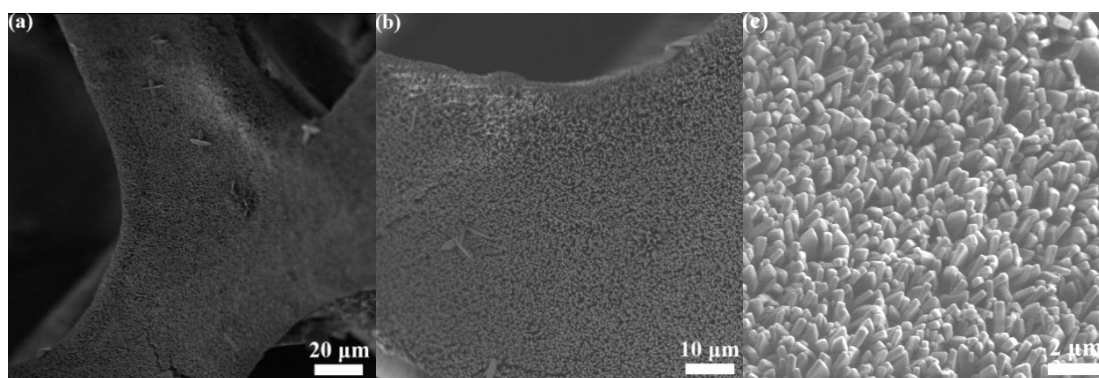


Fig. S2 SEM images of (a-c) ZIF-67/NF.

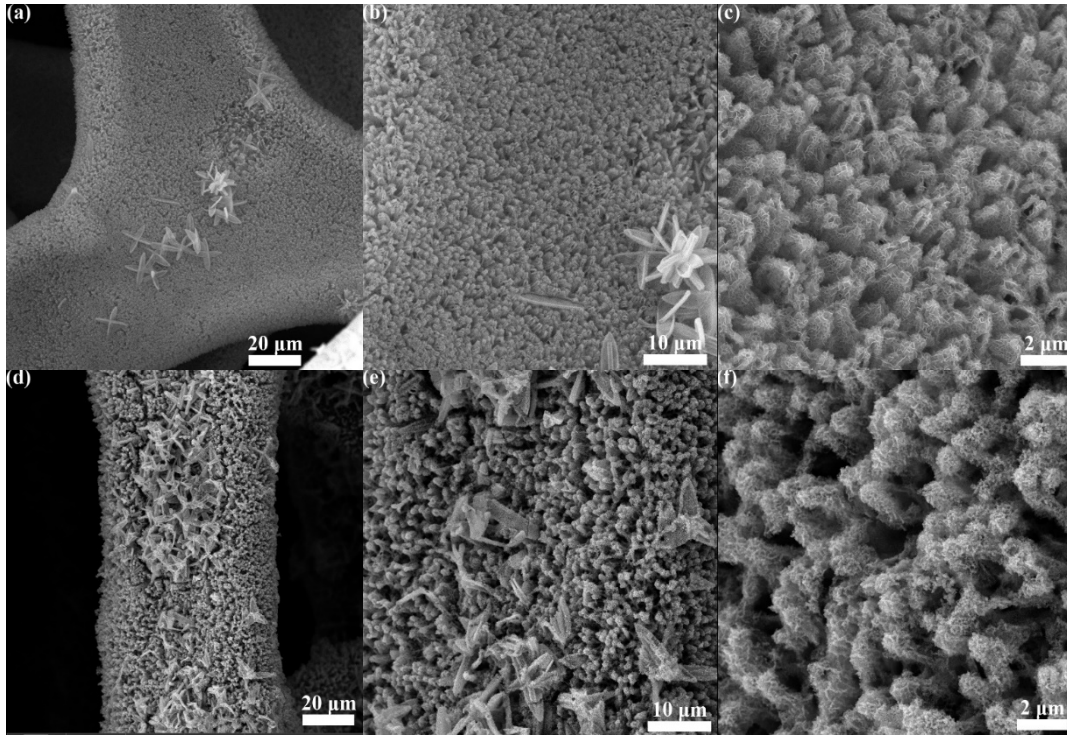


Fig. S3 SEM images of (a-c) NiCo LDH/NF, (d-f) Ni-Co-Se/NF.

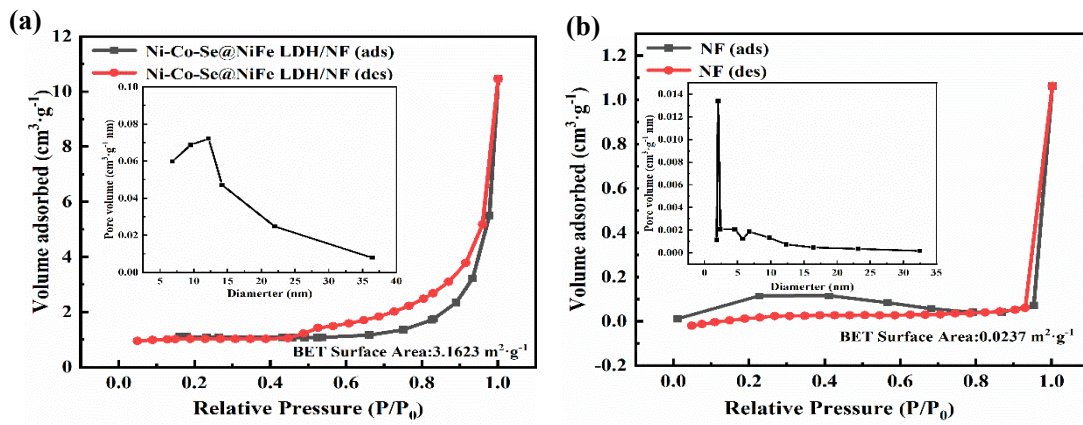


Fig. S4 Nitrogen adsorption-desorption isotherms and corresponding pore size distributions (inside) of (a) Ni-Co-Se@NiFe LDH/NF, (b) NF.

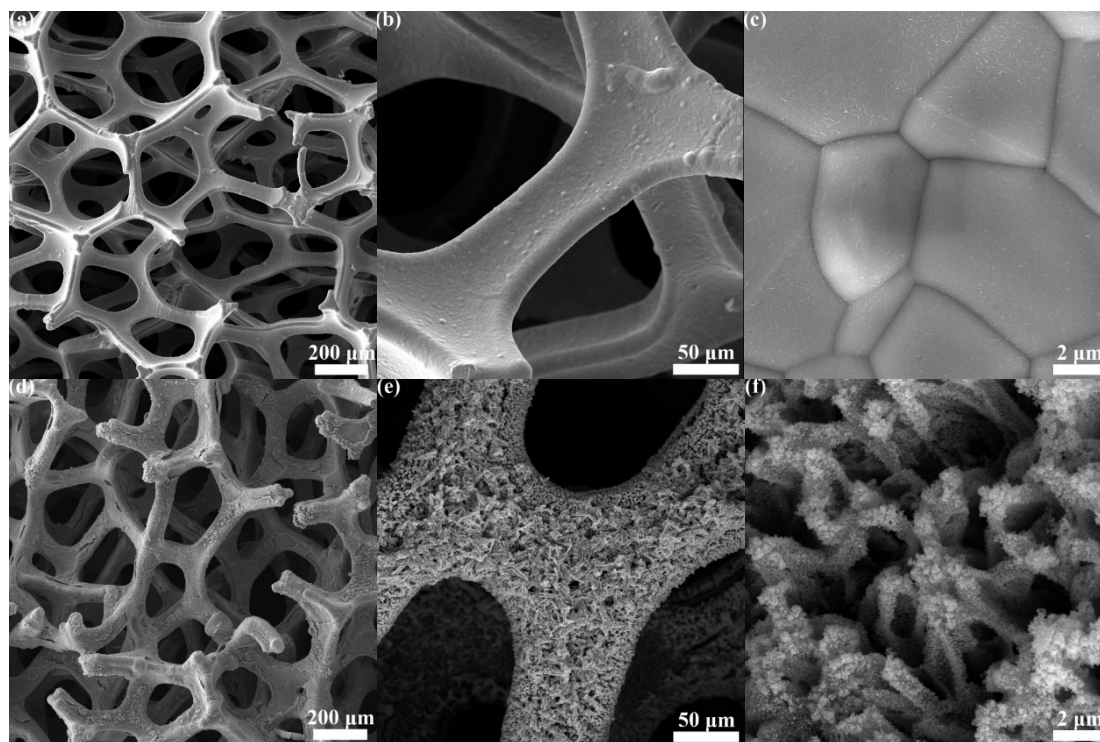


Fig. S5 SEM images of (a-c) NF, (d-f) Ni-Co-Se@NiFe LDH/NF.

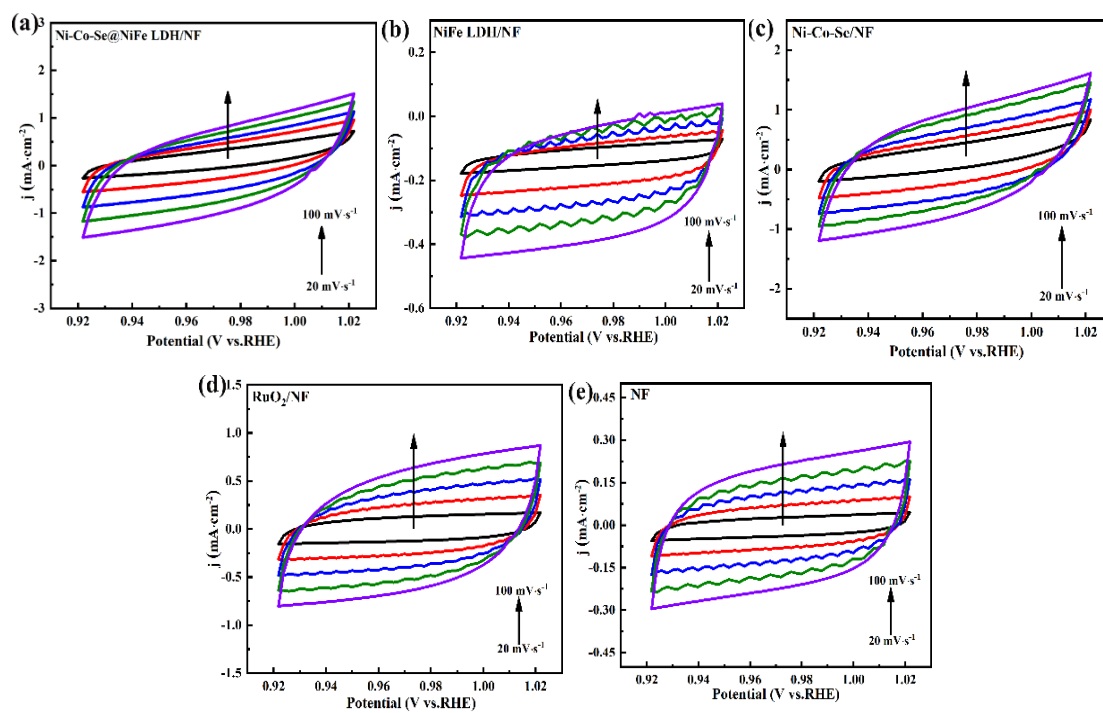


Fig. S6 CV curves of (a-e) Ni-Co-Se@NiFe LDH/NF, NiFe LDH/NF, Ni-Co-Se/NF, RuO₂/NF and NF at increasing scan rates.

ECSA can be calculated from the C_{dl} by using the specific capacitance value for a flat standard with 1 cm^2 of real surface area. For the estimates of surface area, general specific capacitances of $C_s = 0.040 \text{ mF} \cdot \text{cm}^{-2}$ based on typical reported values were used. ECSA was calculated as following:

$$A_{ECSA}^{catalyst} = \frac{C_{dl}^{catalyst} (\text{mF} \cdot \text{cm}^{-2})}{C_s (\text{mF} \cdot \text{cm}^{-2}) \text{ per } \text{cm}_{ECSA}^2}$$

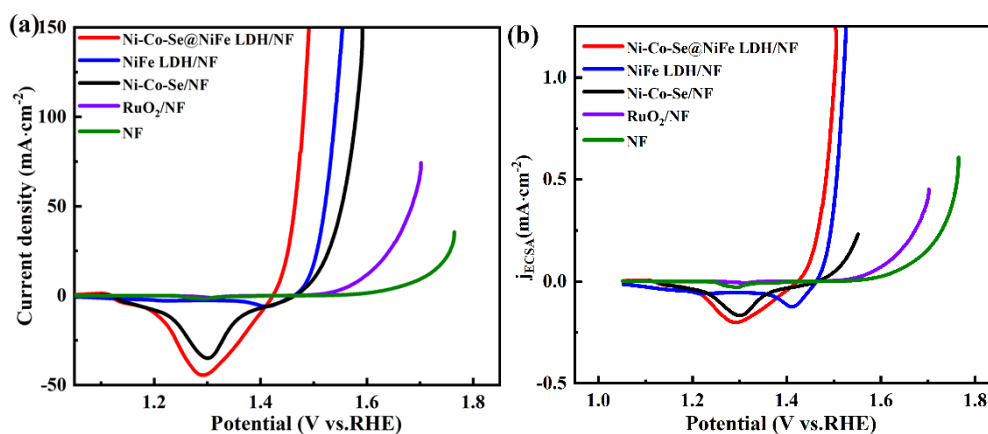


Fig. S7 OER performance of Ni-Co-Se@NiFe LDH/NF, NiFe LDH/NF, Ni-Co-Se/NF, RuO₂/NF and NF: (a) LSV curves, (b) ECSA-corrected LSV curves

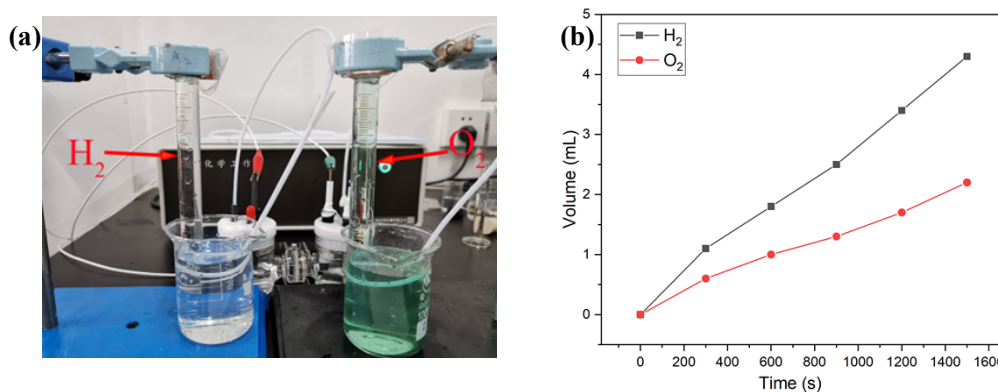


Fig. S8 (a) Gas collection of H₂ and O₂. (b) Gas volume versus time.

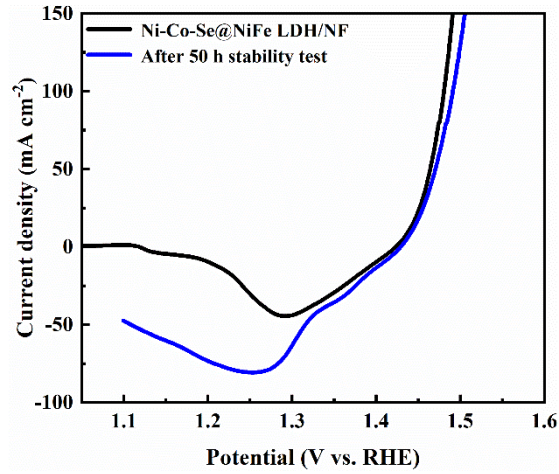


Fig. S9 LSV curves of Ni-Co-Se@NiFe LDH/NF before and after 50 h OER stability test.

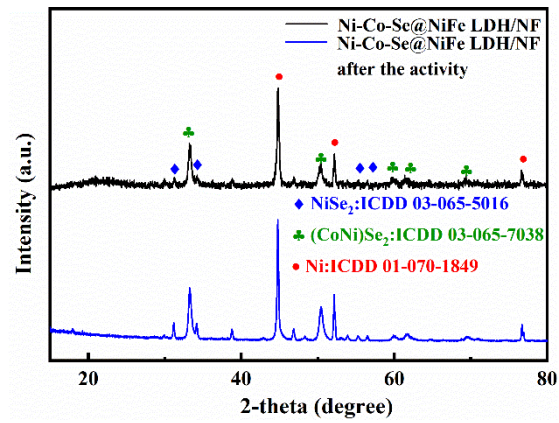


Fig. S10 X-ray diffraction pattern depicting the Ni-Co-Se@NiFe LDH/NF before and after activity test

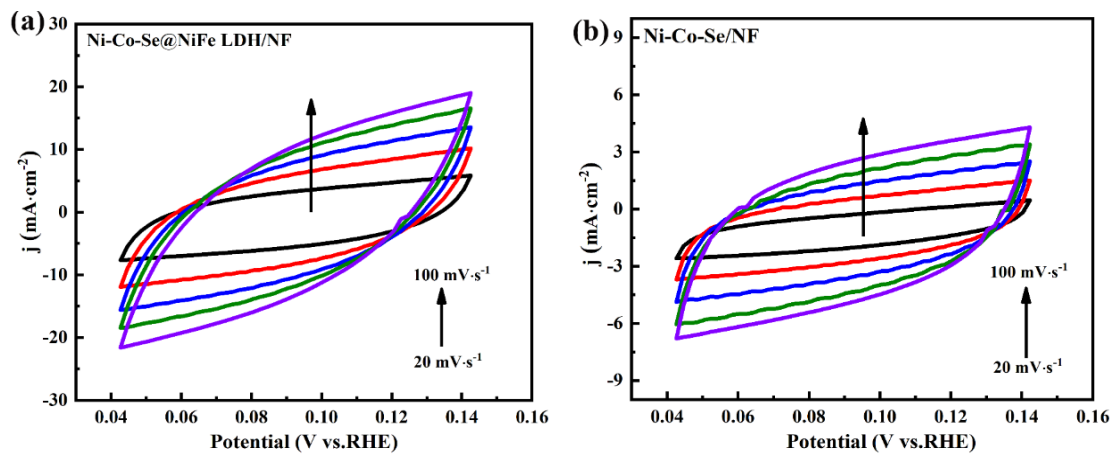


Fig. S11 CV curves of (a) Ni-Co-Se@NiFe LDH/NF, (b) Ni-Co-Se/NF at different scan rates.

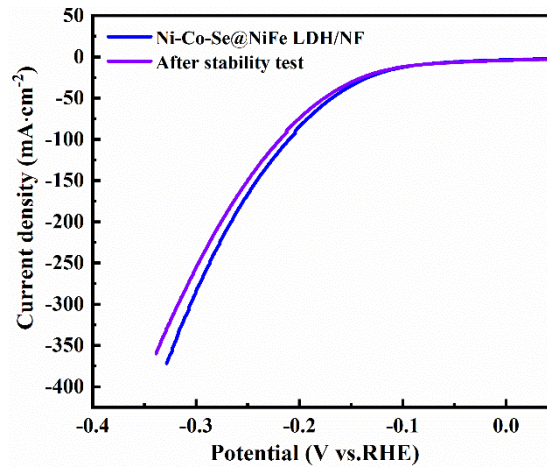


Fig. S12 LSV curves of Ni-Co-Se@NiFe LDH/NF before and after 50 h HER stability test.

Table S1 Map Sum Spectrum

Element	At. %
Ni	50.2
Se	34.4
O	11.0
Co	4.2
Fe	0.2

Table S2 Summary of EIS fitting results for OER

Catalysts	R_s (Ω)	R_{ct} (Ω)
Ni-Co-Se@NiFe LDH/NF	0.95	0.19
NiFe-LDH/NF	1.57	0.56
Ni-Co-Se/NF	1.29	1.56
RuO ₂ /NF	1.43	8.83
NF	1.12	58.88

Table S3 Summary of LDH-based non-noble metal electrocatalysts for OER

Catalysts	Overpotential (mV)	Electrolyte	Tafel slope (mV·dec ⁻¹)	Reference
This work	209@10 mA·cm ⁻²	1.0 M KOH	38.6	/
	234@50 mA·cm ⁻²			
Co ₃ O ₄ @NiFe-LDH/NF	215@10 mA·cm ⁻²	1.0 M KOH	40.4	1
s-EPS@FeNi LDH	220@10 mA·cm ⁻²	1.0 M KOH	34.34	2
NiFe LDH@SnO ₂ /NF	234@10 mA·cm ⁻²	1.0 M KOH	37	3
Cr-FeNi LDH/MXene	232@10 mA·cm ⁻²	1.0 M KOH	54.4	4
NiFe-LDH/Ni ₃ S ₄	223@10 mA·cm ⁻²	1.0 M KOH	49	5
FeCo ₂ O ₄ @NiMn LDH	232@10 mA·cm ⁻²	1.0 M KOH	31.85	6
NiFe-LDH@γ-MnOOH/NF	226@10 mA·cm ⁻²	1.0 M KOH	88	7
NiCu-LDH@CoS/g-C ₃ N ₄	290@10 mA·cm ⁻²	1.0 M KOH	75	8
SSFF@NiFe LDH	180@10 mA·cm ⁻²	1.0 M KOH	31.6	9

Table S4 Summary of EIS fitting results for HER

Catalysts	R_s (Ω)	R_{ct} (Ω)
Ni-Co-Se@NiFe LDH/NF	1.17	0.39
NiFe-LDH/NF	1.16	4.92
Ni-Co-Se/NF	1.29	1.32
Pt-C/NF	1.73	0.48
NF	1.49	4.63

Table S5 Summary of non-noble metal electrocatalysts for HER

Catalysts	Overpotential (mV)	Electrolyte	Tafel slope (mV·dec ⁻¹)	Reference
This work	78@10 mA·cm ⁻²	1.0 M KOH	88.7	/
NiCoP@NiFe LDH/NF	119@10 mA·cm ⁻²	1.0 M KOH	149.42	10
NiCoP-Ni ₃ S ₂ -MoS ₂	140@10 mA·cm ⁻²	1.0 M KOH	91.3	11
NiFe LDH@CoS _x /NF	136@10 mA·cm ⁻²	1.0 M KOH	/	12
NiCo-LDH@CdS-N	133@20 mA·cm ⁻²	1.0 M KOH	76	13
Ni ₃ Se ₂ @NiFe- LDH/NF	68@10 mA·cm ⁻²	1.0 M KOH	106.2	14
Co-Ni-P@Ce ₂ O/NF	120@20 mA·cm ⁻²	1.0 M KOH	176.7	15
Zn-Co-Ni-P/NF	94@10 mA·cm ⁻²	1.0 M KOH	39.4	16
CoSe/MoSe ₂	110@10 mA·cm ⁻²	1.0 M KOH	54.24	17
NcSe@MGA	78@10 mA·cm ⁻²	1.0 M KOH	55	18

Table S6 Summary of EIS fitting results for overall water splitting

Catalysts	R_s (Ω)	R_{ct} (Ω)
Ni-Co-Se@NiFe LDH/NF Ni-Co- Se@NiFe LDH/NF	2.113	88.83
RuO ₂ /NF Pt-C/NF	2.599	852.8
NF NF	2.482	1144

References

1. L. Meng, H. Xuan, J. wang, X. Liang, Y. Li, J. Yang and P. Han, *J. Alloys Compd.*, 2022, **919**, 165877.
2. G. Li, C. Liu, Y. Yang, X. Pan, T. Wu, F. Zeng, E. Ma, Q. Qu and L. Li, *Chem. Eng. J.*, 2023, **455**, 140893.
3. C. Wan, J. Jin, X. Wei, S. Chen, Y. Zhang, T. Zhu and H. Qu, *Journal of Materials Science & Technology*, 2022, **124**, 102-108.
4. L. Yan, Z. Du, X. Lai, J. Lan, X. Liu, J. Liao, Y. Feng and H. Li, *Int. J. Hydrogen Energy*, 2023, **48**, 1892-1903.
5. Y. Yao, E. Hu, Y. Chen, Y. Cui, Z. Wang and G. Qian, *J. Solid State Chem.*, 2022,

315, 123542.

6. G. Gao, K. Wang and X. Wang, *J. Alloys Compd.*, 2023, **937**, 168478.
7. S.-B. Wang, Y.-S. Xia, Z.-F. Xin and L.-X. Xu, *Catal. Commun.*, 2023, **173**, 106564.
8. K. Kumar Mandari, N. Son and M. Kang, *Appl. Surf. Sci.*, 2022, **593**, 153453.
9. Y. Liu, Z. Song, Z. Li, M. Han, Y. Cheng and Z. Zheng, *Catal. Commun.*, 2022, **164**, 106425.
10. H. Zhang, X. Du, X. Zhang and Y. Wang, *J. Alloys Compd.*, 2023, **937**, 168412.
11. Q. Wang, X. Du and X. Zhang, *Int. J. Hydrogen Energy*, 2023, **48**, 9260-9272.
12. Y. Yang, Y. Xie, Z. Yu, S. Guo, M. Yuan, H. Yao, Z. Liang, Y. R. Lu, T.-S. Chan, C. Li, H. Dong and S. Ma, *Chem. Eng. J.*, 2021, **419**, 129512.
13. A. Pirkarami, S. Rasouli and E. Ghasemi, *J. Energy Chem.*, 2021, **57**, 118-130.
14. J. Hu, S. Zhu, Y. Liang, S. Wu, Z. Li, S. Luo and Z. Cui, *J. Colloid Interface Sci.*, 2021, **587**, 79-89.
15. G. Ma, X. Du and X. Zhang, *J. Alloys Compd.*, 2021, **864**, 158486.
16. Y. Ding, X. Du and X. Zhang, *Appl. Surf. Sci.*, 2021, **543**, 148818.
17. M. Hassan, M. M. Baig, K. H. Shah, A. Hussain, S. A. Hassan and A. Ali, *J. Phys. Chem. Solids*, 2022, **167**, 110780.
18. K. Chaudhary, S. Zulfiqar, H. H. Somaily, M. Aadil, M. F. Warsi and M. Shahid, *Electrochim. Acta*, 2022, **431**, 141103.