Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Self-supported $CoMoO_4$/NiFe-LDH Core-Shell nanorods grown on nickel foam for enhanced electrocatalysis of oxygen evolution

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Materials

Sodium molybdate dihydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, AR], cobalt nitrate hexahydrate [$Co(NO_3)_2\cdot 6H_2O$, AR], urea [$CO(NH_2)_2$, AR], nickel nitrate hexahydrate [$Ni(NO_3)_2\cdot 6H_2O$, AR], iron nitrate nonahydrate [$Fe(NO_3)_3\cdot 9H_2O$]. The above materials were purchased from Aladdin Reagent (Shanghai) Co., Ltd.

Synthesis of NiFe-LDH@NF

NF (2*3cm) was prepared by the above method. NiFe-LDH@NF was prepared by electrodeposition for 300 s under the above experimental conditions.

Synthesis of RuO_2 electrodes

After strong ultrasonication for 30 min, 40 mg RuO_2 was uniformly disseminated in a mixture of 50 μL Nafion solution and 1mL mixed solution of ethanol and water to make a homogeneous ink. The catalyst ink was then dropped over the cleaned NF (1*1.5 cm), which was then dried for 12 h at 60 °C in a vacuum oven, producing RuO_2/NF electrodes.

Synthesis of Powder-$CoMoO_4$/NiFe-LDH/NF and Powder-NiFe-LDH/NF

Powder of $CoMoO_4$/NiFe-LDH and NiFe-LDH were scraped from $CoMoO_4$/NiFe-LDH@NF and NiFe-LDH@NF electrodes, respectively, and then Powder-CoMoO4/NiFe-LDH/NF and Powder-NiFe-LDH/NF electrodes were prepared according to the method of RuO_2 electrodes.

Physicochemical Characterization

The morphology was obtained by scanning electron microscopy (SEM, Sirion) and transmission electron microscopy (TEM, Talos F200X). X-ray diffraction (XRD) patterns were obtained via an Ultima IV X-ray diffractometer utilizing Cu Kα1 radiation (λ =1.5406 Å) at a scanning speed of 0.02 steps per second. X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi) was utilized to obtain data on components in synthetic materials.

Electrochemical measurements

The electrochemical measurements were carried out utilizing a typical three-electrode system on a CHI-660D electrochemical workstation (CHI Instrument, Shanghai, China). The electrolyte used was 1 M KOH (pH ≈14.0), and the experiment was conducted at room temperature in an air atmosphere. The working electrode was made up of a self-supported NF electrocatalyst, while the counter electrode and reference electrode were made up of Pt and Ag/AgCl. The formula: E(vs RHE) = E(vs Ag/AgCl) + 0.097 + 0.0591 pH was utilized to change the tested potentials to reversible hydrogen electrodes (RHEs). A scan rate of 5 mV·s−1 and 90% iR-compensation were applied for linear sweep voltammetry (LSV) curves. Electrochemical impedance spectroscopy (EIS) studies were performed in the 100,000-0.01 Hz frequency range (versus Ag/AgCl). The OER was tested for stability using the chronoamperometry method for 20 h at a voltage of 1.46 V (vs. RHE). Electrochemical surface areas (ECSAs) were acquired on the basis of the following formula: ECSAs = Cdl/Cs. Here, Cdl represented the double-layer capacitance acquired from CV cycles.

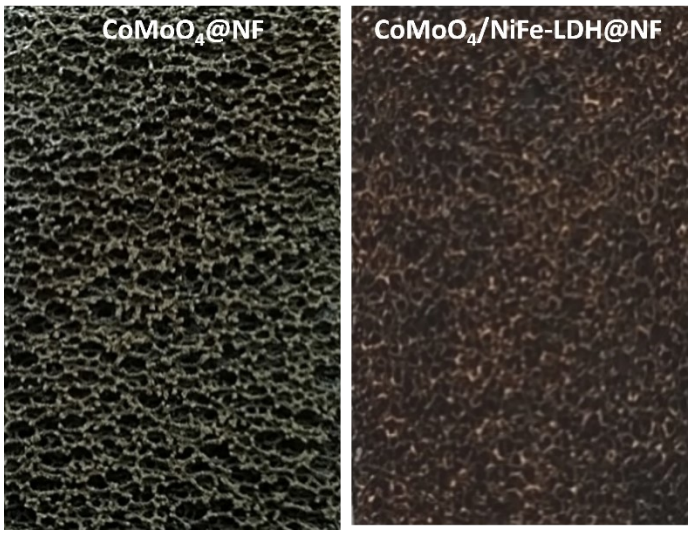

Fig. S1. The photographic images of $CoMoO_4$@NF and $CoMoO_4$/NiFe-LDH@NF.

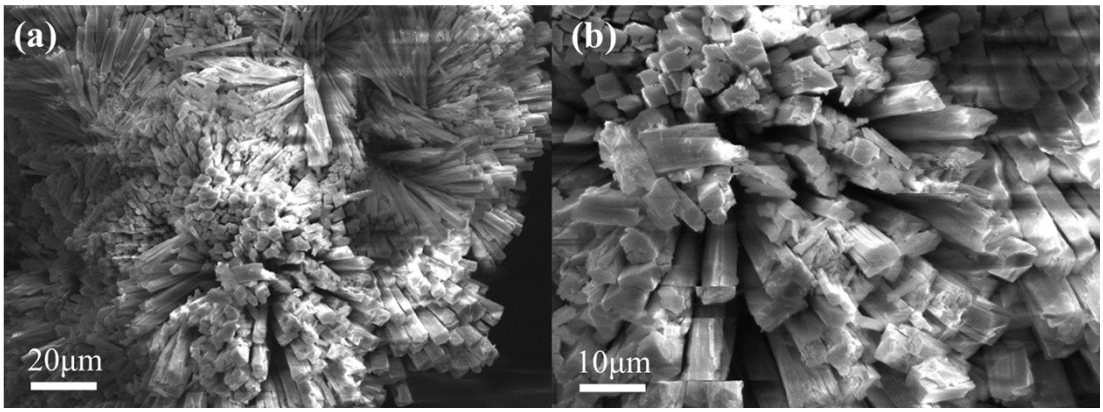

Fig. S2 (a, b). SEM images of $CoMoO_4$@NF.

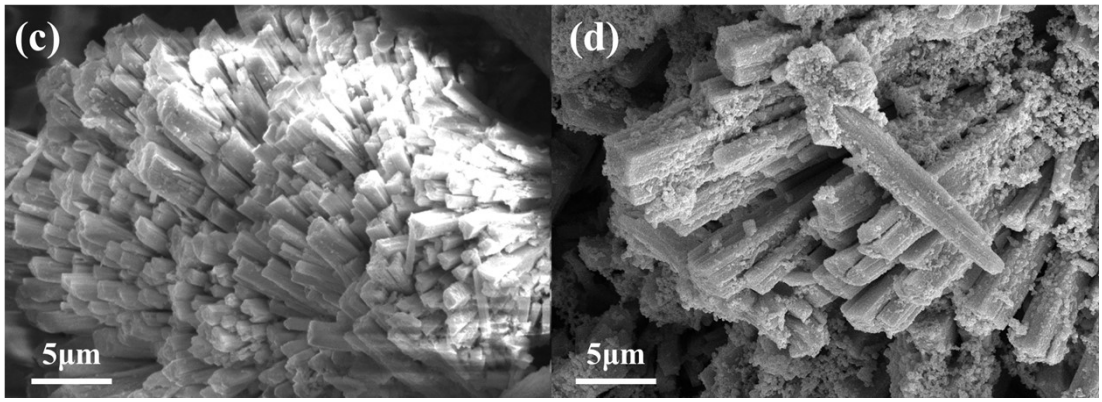

Fig. S3 (a). SEM images of $CoMoO_4$-150/NiFe-LDH@NF and (b). $CoMoO_4$-450/NiFe-LDH@NF.

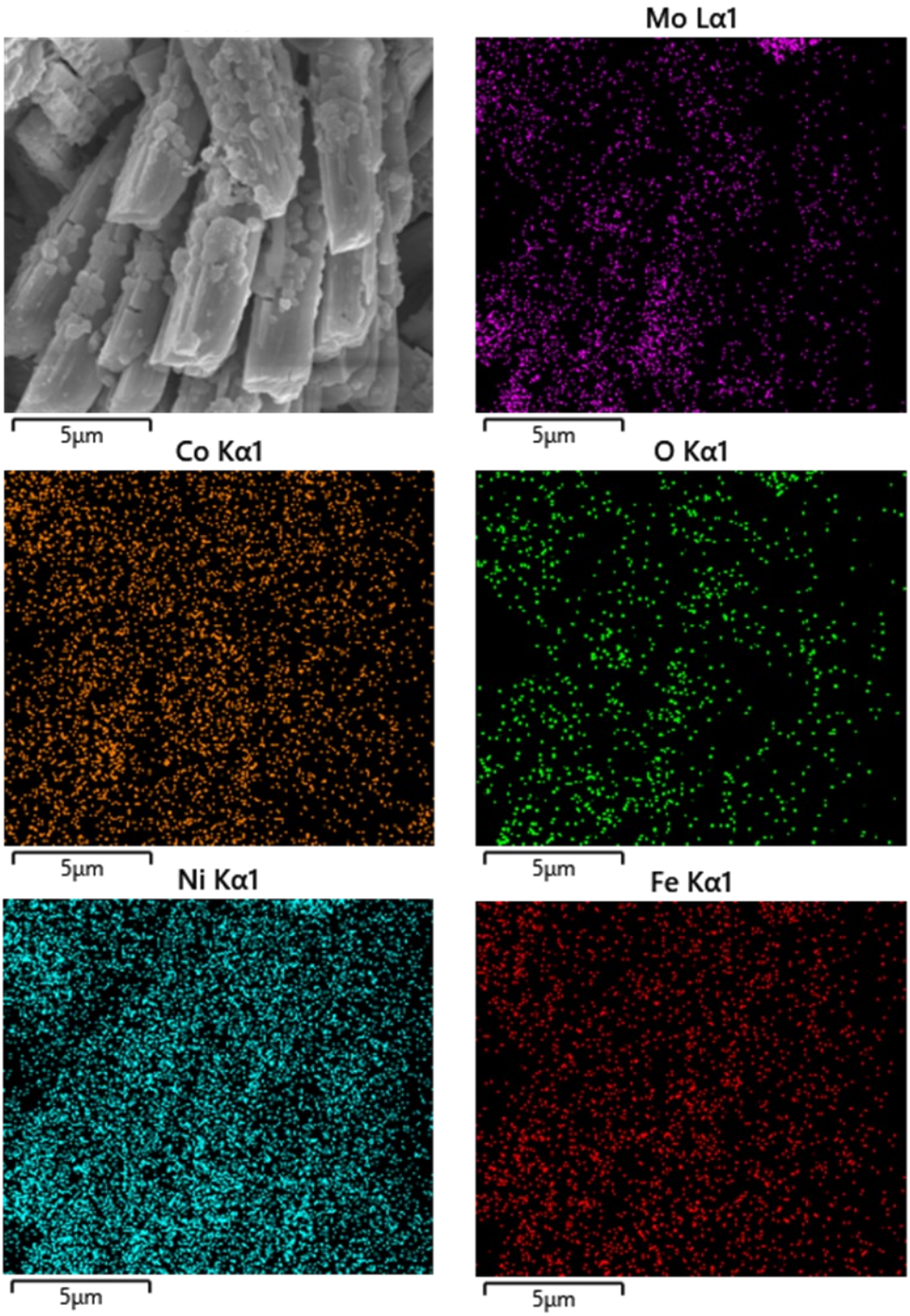

Fig. S4. EDS elemental mapping images of Co, Mo, O, Fe and Ni in $CoMoO_4$-300/NiFe-LDH@NF.

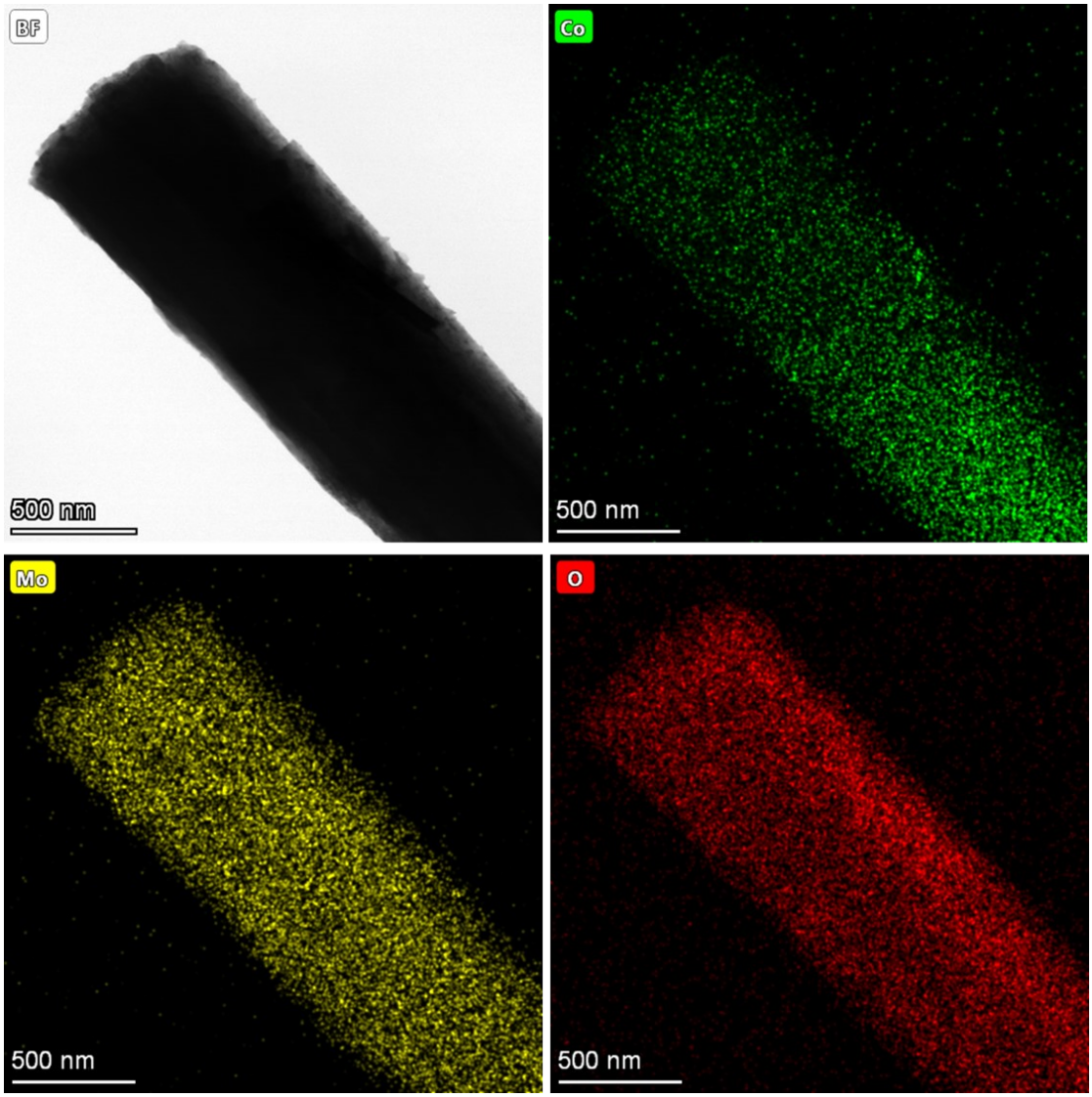

Fig. S5. HAADF-STEM and EDX elemental mapping images of Co, Mo, and O in $CoMoO_4$.

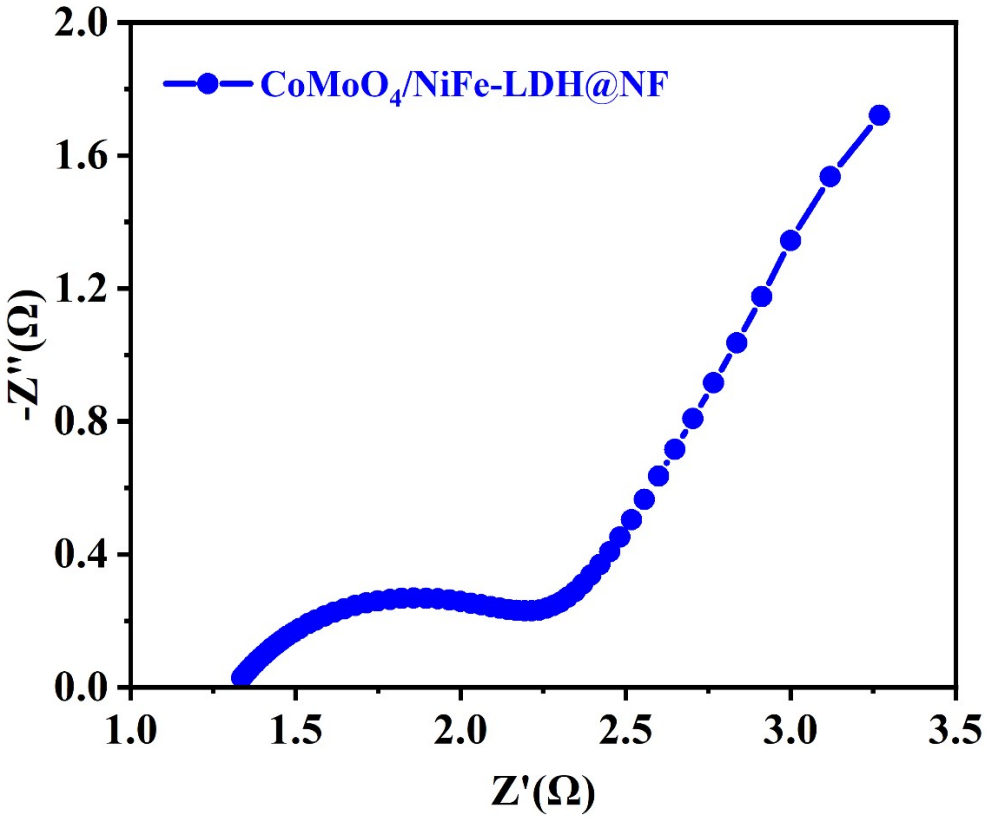

Fig. S6. EIS Nyquist plots and fitting curves of $CoMoO_4$/NiFe-LDH@NF.

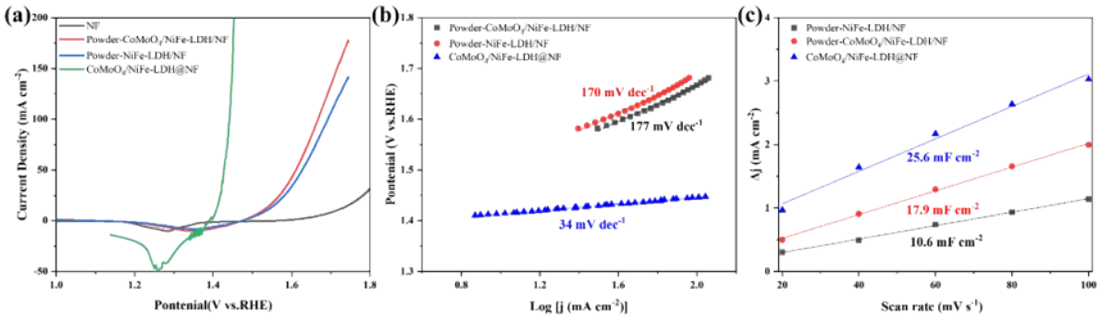

Fig. S7. (a) OER polarization curves with 90% iR compensation for NF, Powder-$CoMoO_4$/NiFe-LDH Powder-NiFe-LDH/NF, and $CoMoO_4$/NiFe-LDH@NF. (b) Tafel plots and (c). C_{dl} values of Powder-$CoMoO_4$/NiFe-LDH Powder-NiFe-LDH/NF and $CoMoO_4$/NiFe-LDH@NF.

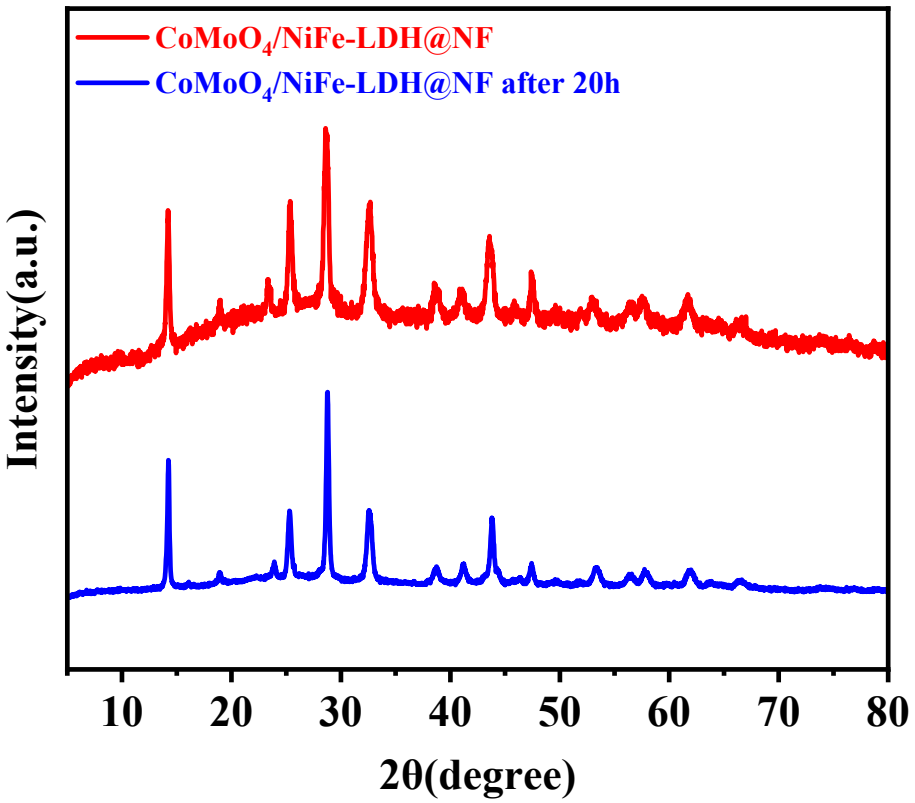

Fig. S8. XRD patterns of $CoMoO_4$/NiFe-LDH@NF and $CoMoO_4$/NiFe-LDH@NF after 20 h stability test.

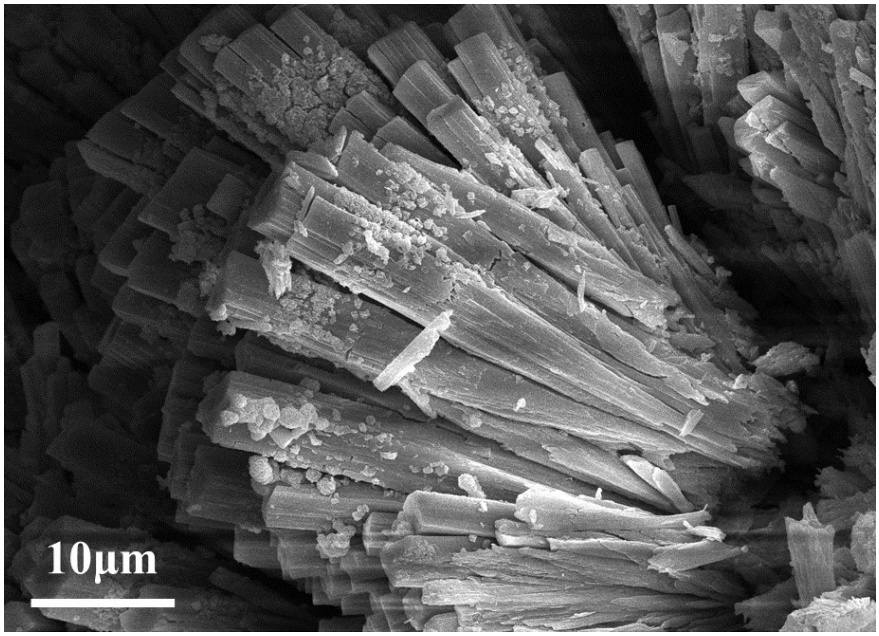

Fig. S9. SEM image of $CoMoO_4$/NiFe-LDH@NF after 20 h stability test.

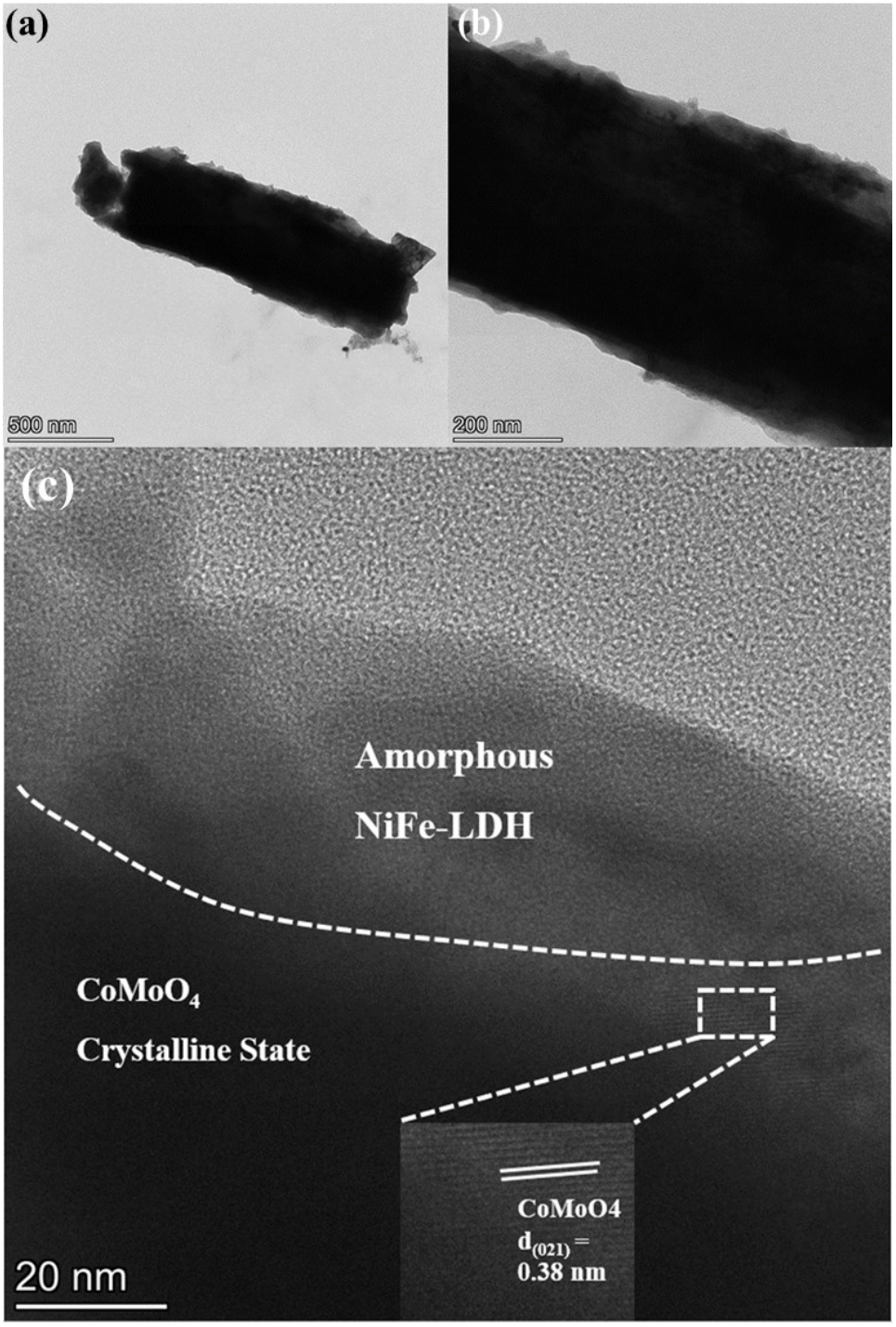

Fig. S10. (a, b) TEM and (c) HR-TEM image of $CoMoO_4$/NiFe-LDH@NF after 20 h stability test.

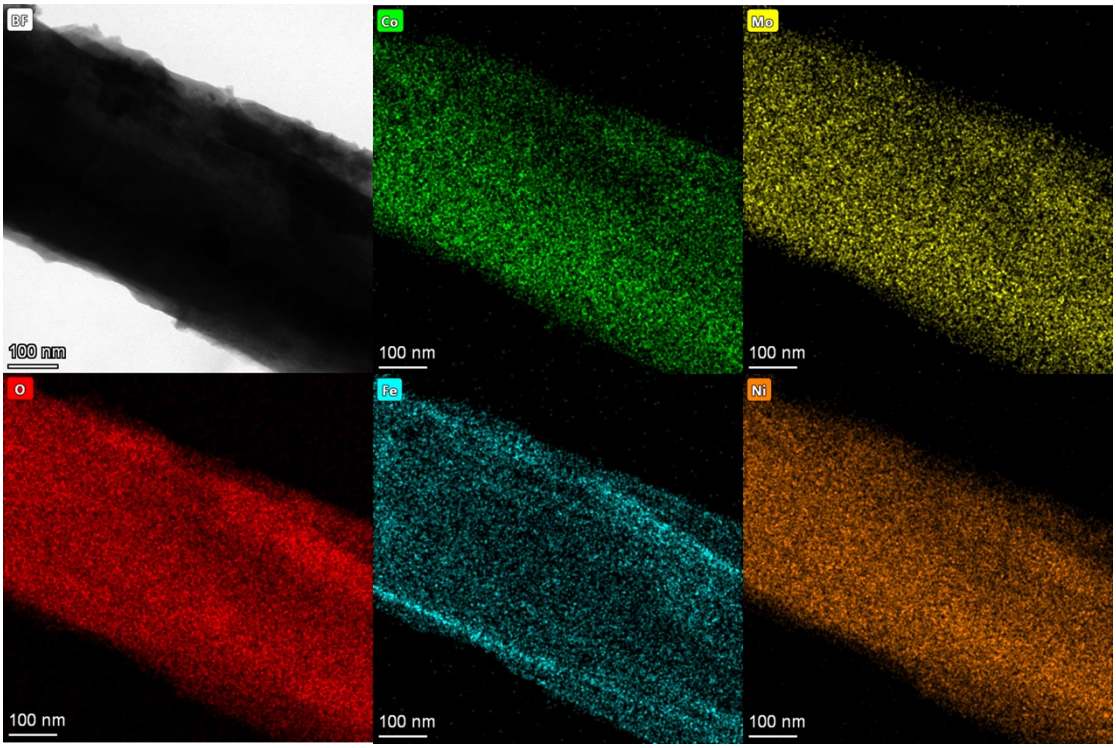

Fig. S11. HAADF-STEM and EDX elemental mapping images of Co, Mo, O, Ni and Fe in $CoMoO_4$/NiFe-LDH after 20h stability test.

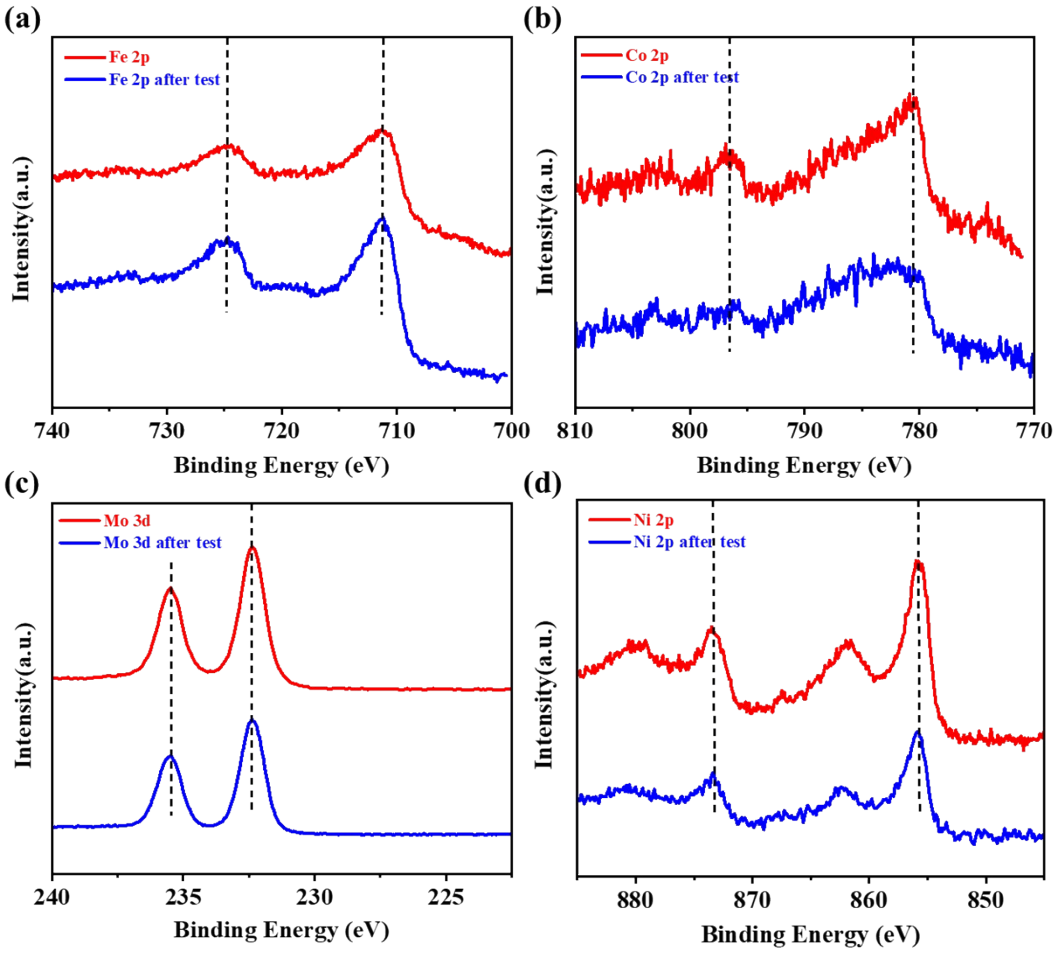

Fig. S12. (a-d) High-resolution XPS spectra of Fe, Co, Mo, and Ni after 20 h stability test.

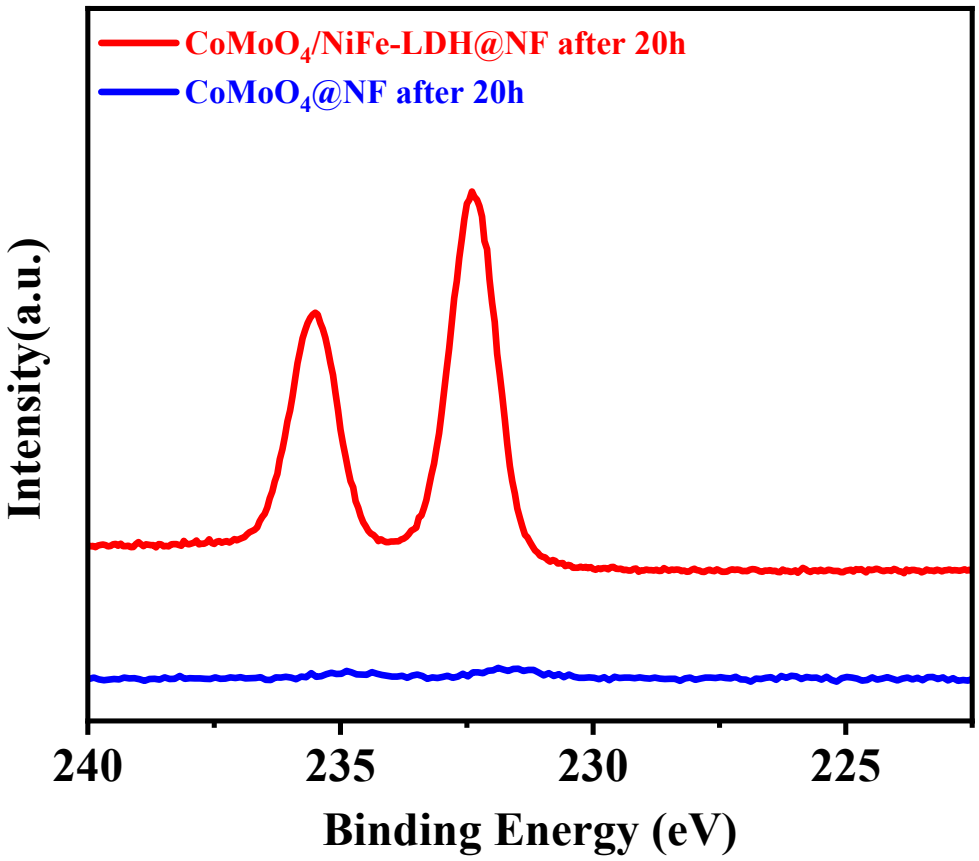

Fig. S13. High-resolution XPS spectra of Mo in the $CoMoO_4$/NiFe-LDH@NF and $CoMoO_4$/@NF after 20h stability test.

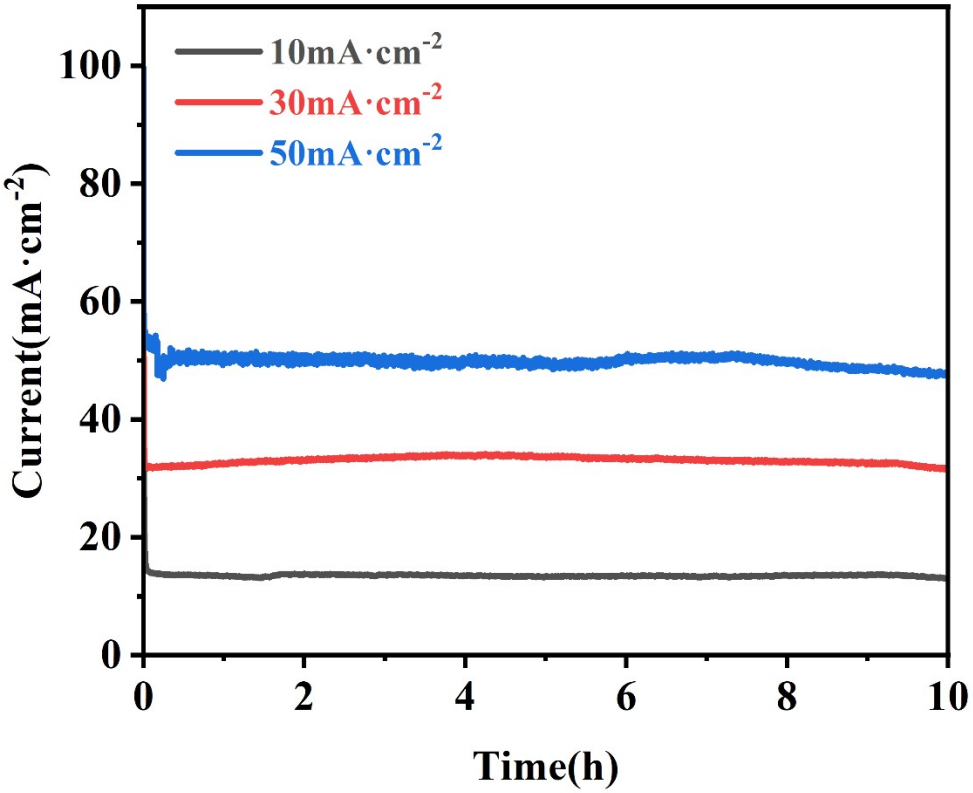

Fig. S14. I-t curves of $CoMoO_4$/NiFe-LDH@NF at different current densities.

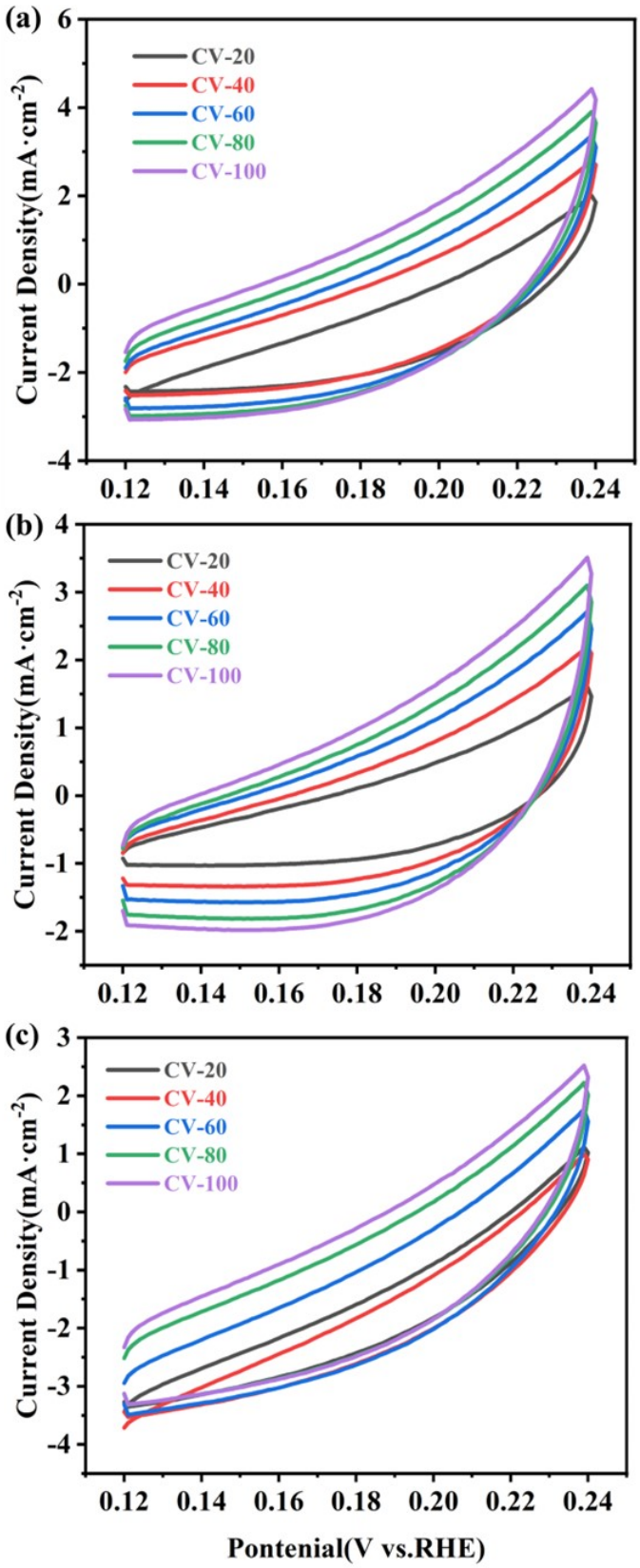

Fig. S15. CV curves of (a). $CoMoO_4$/NiFe-LDH@NF, (b). $CoMoO_4$@NF, and (c). NiFe-LDH@NF.

Table. S1. Fe content change of 1. $CoMoO_4$-150/NiFe-LDH@NF, 2. $CoMoO_4$-300/NiFe-LDH@NF, 3. $CoMoO_4$-450/NiFe-LDH@NF, and 4. $CoMoO_4$-600/NiFe-LDH@NF

Element	1. Atomic percentage	2. Atomic percentage	3. Atomic percentage	4. Atomic percentage
O	65.89	63.78	61.94	59.86
Fe	0.86	1.23	1.75	2.37
Co	6.94	7.56	8.19	9.03
Ni	11.32	13.43	15.02	15.81
Mo	14.99	14.00	13.10	12.93

Table. S2. OER activity comparison of different electrocatalysts.

Catalysts	Current density (mA cm^{-2})	Overpotential (mV)	Ref.
$CoMoO_4$/NiFe-LDH@NF	**10**	**180**	**This work**
NiFe-LDH/$NiCo_2O_4$	50	290	1
NiFe-LDH@CoS_x	10	206	2
NF@NiFe-LDH-1.5-4	100	190	3
NiFe-60/Co_3O_4@NF	100	221	4
Co_9S_8@NiFe-LDH	50	287	5
NiFe-LDHs/$Ni(OH)_2$	50	292	6
NiFe-LDH-Ti_4O_7	10	200	7
$FeNi_2S_4$@NiFe-LDH	100	238	8
V-NiFe LDH@Ni_3S_2	10	178	9
NiMoP@NiFe-LDH	150	299	10

S-$NiMoO_4$@NiFe-LDH/NF	100	273	11
MIL-101@NiFe-LDH	10	215	12
NiFe-LDH@$Co(OH)_2$	10	130	13
v-NiFe LDH microtubes	10	195	14
$Fe_{0.5}Co_{0.5}MoO_{4-x}S_x$	10	263	15
$CoMoO_4$@$CoNiO_2$	10	180	16
$CoMoO_4$ nanotubes	10	315	17
A-$CoMoO_4$	10	264	18
$Co_3Mo/CoMoO_x$	10	256	19
F-$CoMoO_{4-x-2}$@GF	10	256	20

Notes and references

1. Z. Wang, S. Zeng, W. Liu, X. Wang, Q. Li, Z. Zhao and F. Geng, *ACS Appl. Mater. Interfaces*, 2017, **9**, 1488-1495.
2. 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.
3. X. Li, C. Liu, Z. Fang, L. Xu, C. Lu and W. Hou, *Small*, 2022, **18**, 2104354.
4. J. Lv, L. Wang, R. Li, K. Zhang, D. Zhao, Y. Li, X. Li, X. Huang and G. Wang, *ACS Catal.*, 2021, **11**, 14338-14351.
5. X.-T. Gao, Z. Yu, K.-X. Zheng, J.-M. Yin, Y. Zheng, X.-M. Zhu and Y.-W. Dong, *Mater. Lett.*, 2022, **319**, 132302.
6. W. Mu, D. Bao and C. Chang, *Int. J. Hydrog. Energy*, 2022, **35**, 15603.
7. K. B. Ibrahim, W. N. Su, M. C. Tsai, A. W. Kahsay, S. A. Chala, M. K. Birhanu, J. F. Lee and B. J. Hwang, *Mater. Today Chem.*, 2022, **24**, 100824.
8. F.-L. Wang, X. Yu Zhang, J.-C. Zhou, Z.-N. Shi, B. Dong, J.-Y. Xie, Y.-W. Dong, J.-F. Yu and Y.-M. Chai, *Inorg. Chem. Front.*, 2022, **9**, 2068.
9. J. Bai, T. Zhou, Y. Gao, M. Zhang, X. Jing and Y. Gong, *Dalton. Trans.*, 2022, **51**, 4853-4861.
10. L. Xiao, W. Bao, J. Zhang, C. Yang, T. Ai, Y. Li, X. Wei, P. Jiang and L. Kou, *Int. J. Hydrog. Energy*, 2022, **47**, 9230-9238.
11. H. Wang, L. Chen, L. Tan, X. Liu, Y. Wen, W. Hou and T. Zhan, *J. Colloid Interface Sci.*, 2022, **613**, 349-358.
12. J. Huang, K. Li, L. Wang, H. She and Q. Wang, *Chin. Chem. Lett.*, 2021, **8**, 3787-7791.
13. Y. Yang, Q. Zhou, L. Jiao, Q. Yin, Z. Li, Z. Zhang and Z. Hu, *Ionics*, 2021, **28**, 341-351.
14. S. Liu, H. Zhang, E. Hu, T. Zhu, C. Zhou, Y. Huang, M. Ling, X. Gao and Z. Lin, *J. Mater. Chem. A*, 2021, **9**, 23697-23702.
15. B. Fei, Z. Chen, Y. Ha, R. Wang, H. Yang, H. Xu and R. Wu, *Chem. Eng. J.*, 2020, **394**, 124926.
16. X. Du, G. Ma and X. Zhang, *Dalton Trans.*, 2019, **48**, 10116-10121.
17. R. Wang, F. Li, J. Ji and F. Wang, *Appl. Surf. Sci.*, 2022, **579**, 152128.
18. L. Ge, W. Lai, Y. Deng, J. Bao, B. Ouyang and H. Li, *Inorg. Chem.*, 2022, **61**, 2619-2627.
19. Y. Liu, Y. Xing, S. Xu, Y. Lu, S. Sun and D. Jiang, *Chem. Eng. J.*, 2022, **431**, 133240.
20. W. Xie, J. Huang, L. Huang, S. Geng, S. Song, P. Tsiakaras and Y. Wang, *Appl. Catal. B*, 2022, **303**, 120871.