Supporting Information

Heterostructure Engineering of N-doped $NiMoO_4$ Two-Phase Electrocatalyst for Industrial Large-scale Synthesis of 2, 5-Furan Dicarboxylic Acid

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Experimental section

Reagents and materials: All reagents used in this study were purchased and directly used without further purification: $Ni(NO_3)_2 \cdot 6H_2O$(AR) and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$(AR) were purchased from Shanghai Titan Scientific Co., Ltd.. Nickel foam (NF) was purchased from Suzhou Cheng Er Nuo Technology Co. Ltd.

Physical characterizations: The structure of N-$NiMoO_4$/NF is determined by PXRD (Bruker D8, Cu-Kα). the spectra were recorded in the 2θ range of 5° to 60°. The morphology of Ni-Mo-S were investigated by scanning electron microscopy (SEM, Hitach S-4800) and transmission electron microscope (TEM, JEOL 2100F). X-ray electron spectroscopy (XPS) was performed on AXIS Supra by Kratos Analytical Inc. Using monochromatized Al Ka radiation as X-ray source. All spectra were calibrated

by C 1s (284.8 eV).

Product analysis:

The concentrations of HMF and oxidation products were determined by high performance liquid chromatography (HPLC) system (Waters 1525) using a 4.6 × 250 mm NuovaSil C18-WH, 5μm column with detection wavelength set at 265 nm and column temperature maintained at 30 °C. The HPLC eluent was a mixture of solvent A (5 mM ammonium formate solution) and B (methanol). For the HMF oxidation reaction, isocratic elution separation was performed using 30% A and 70% B at a flow rate of 0.6 mL min^{-1} over 15 min. HPLC samples were prepared by diluting 1.0 mL of the reaction mixture with 49.0 mL of deionized water. Quantification of HMF and oxidation products was calculated from the calibration curve. The HMF conversion, the product yield, and the FE value of FDCA were calculated using the following equations, where F is Faraday's constant.

The conversion of HMF can be calculated by the following eqn:

$$Conversion = \frac{n(reacted\ HMF)}{n(initial\ HMF)} \times 100\%$$

The selectivity and yield of the FDCA were determined by the following eqn respectively:

$$Selectivity = \frac{n(FDCA\ production)}{n(reacted\ HMF)} \times 100\%$$

$$Yield = \frac{n(FDCA\ production)}{n(initial\ HMF)} \times 100\%$$

The faradaic efficiency of the product was calculated using eqn:

$$FE\ of\ FDCA\ = \frac{mol\ of\ \ FDCA\ formed}{total\ charge\ passed/(6\ \times\ F)} \times 100\%$$

Electrochemical measurements: All electrochemical tests were carried out in a three-electrode system using a CHI760E electrochemical workstation (Shanghai Chenhua, China) without iR correction. HMFOR and OER were carried out in a typical three-electrode system with a H-type cell separated by an anion exchange membrane (N117 DuPont). Pt wire and Hg/HgO were used as counter electrode and reference electrode, the as-prepared N-$NiMoO_4$/NF (1cm ×1cm) material was used as the working electrode. The measured voltage value is converted into the electrode potential *vs* the

reversible hydrogen electrode (RHE) by the equation $E_{RHE}=E_{Hg/HgO}+0.059\times pH+0.098$ V. The electrochemical OER and HMFOR experiments were conducted in 50 mL of 1.0 M NaOH solution with and without 20 mM. Electrochemical impedance spectroscopy (EIS) measurements were recorded in the frequency range of 10^5– 0.1 Hz with an amplitude of 5 mV. The electric double layer capacitance of the prepared catalyst was determined by the CV of different scanning speeds (20, 40, 60, 80 and 100 mV s^{-1}).

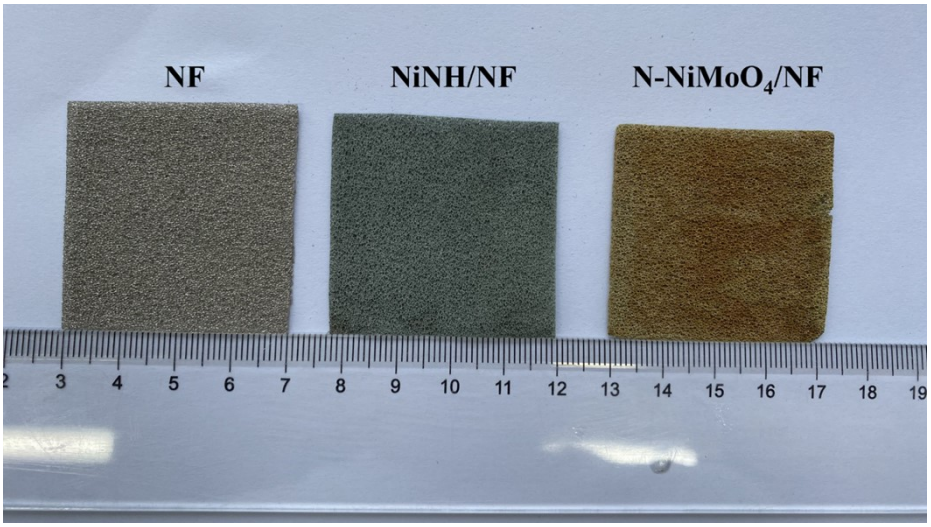

Figure S1 Photograph of bare NF (left), NiNH NF (middle), and N-$NiMoO_4$/NF (right).

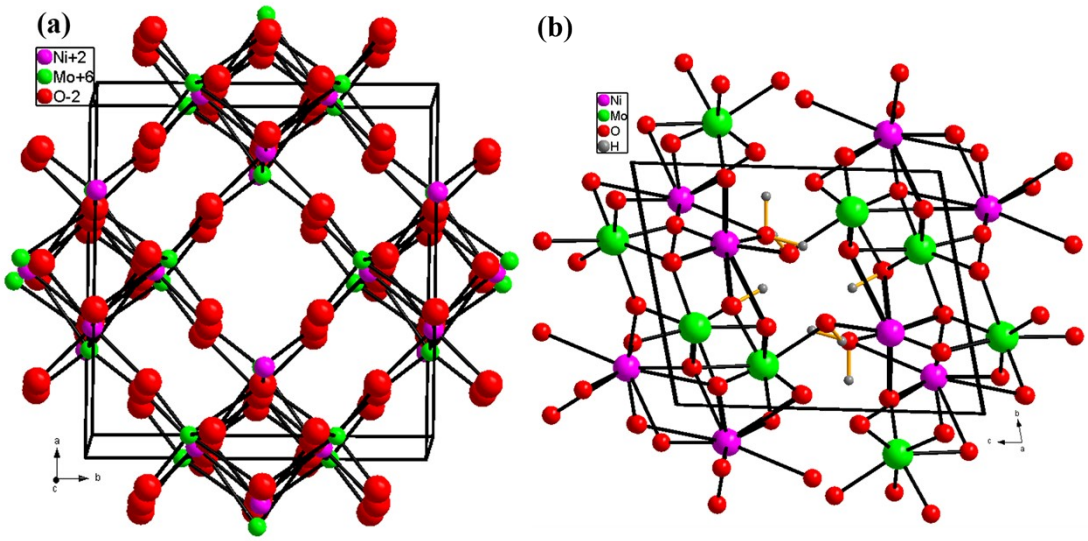

Figure S2 The crystal structure of $NiMoO_4$ (a) and $NiMoO_4 \cdot H_2O$ (b).

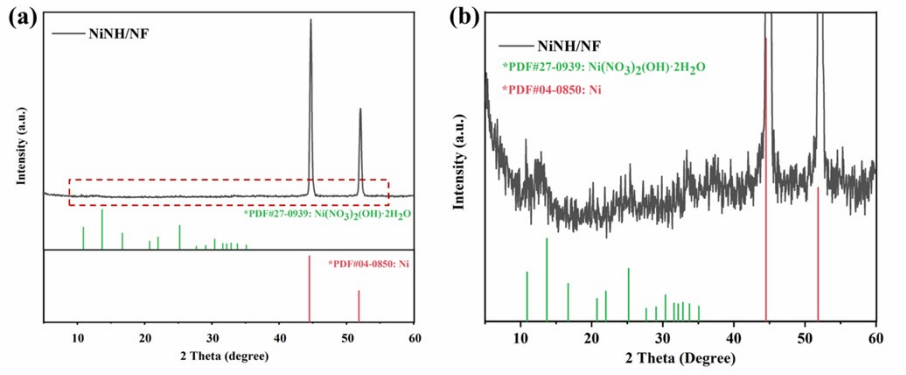

Figure S3 XRD patterns of NiNH/NF (a) and the expanded view of PXRD of NiNH/NF.

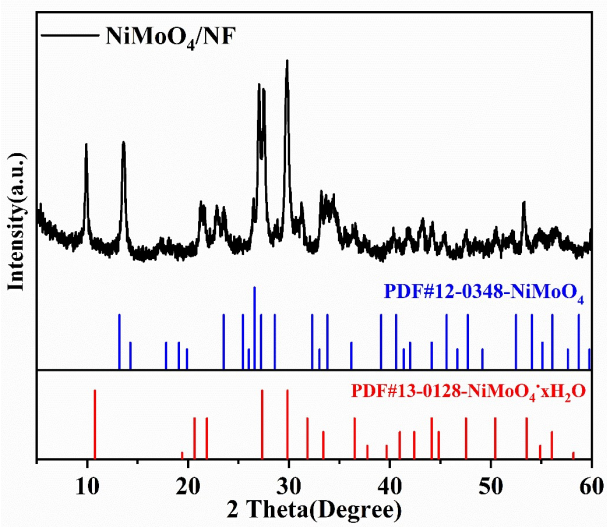

Figure S4 XRD patterns of $NiMoO_4$/NF.

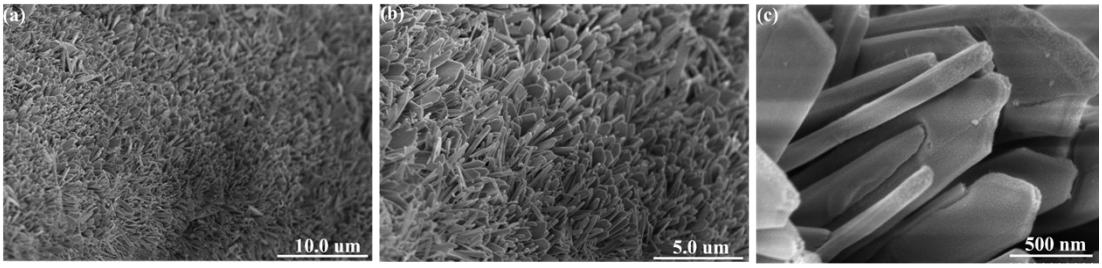

Figure S5 (a-c) SEM images of NiNH/NF.

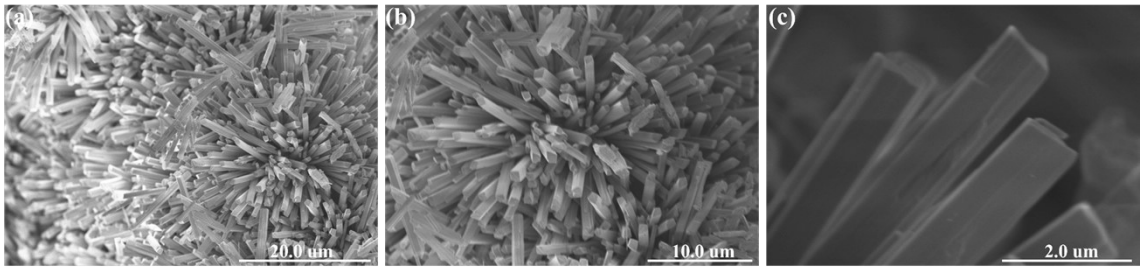

Figure S6 SEM images of $NiMoO_4$/NF.

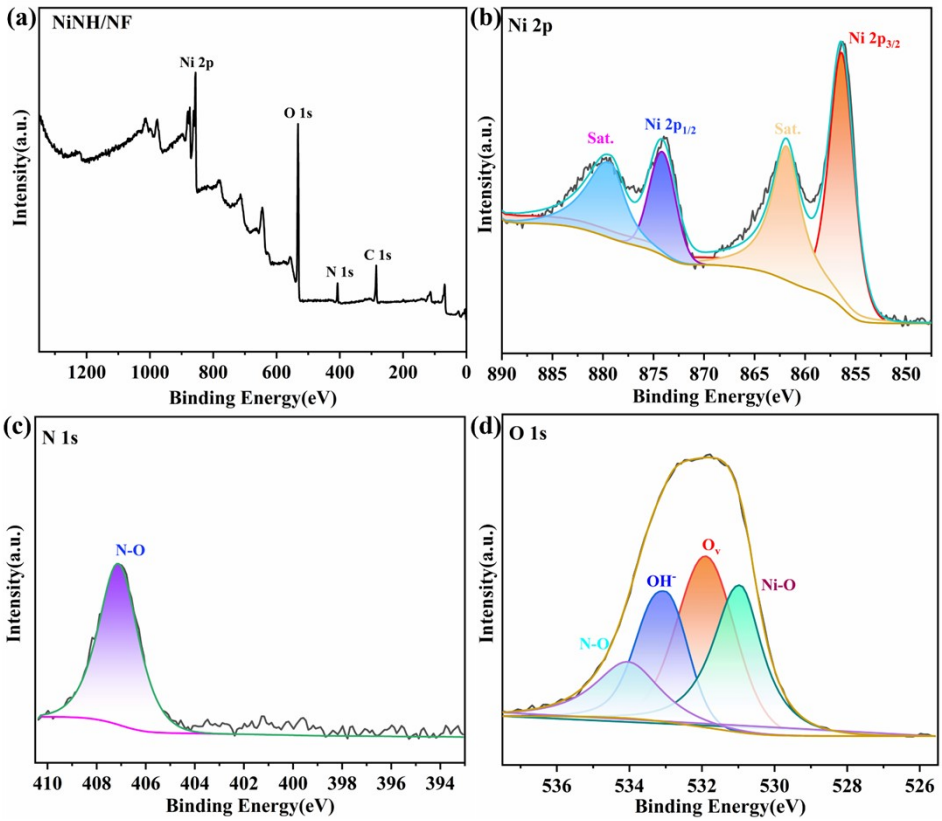

Figure. S7 XPS spectra of Survey full spectra(a), Ni 2p (b), N 1s (c) and O 1s (d) of NiNH/NF.

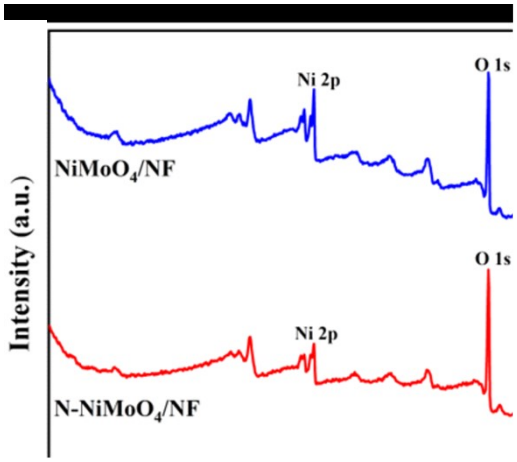

Figure. S8 High-resolution XPS spectra for $NiMoO_4$/NF and N-$NiMoO_4$/NF of survey spectra

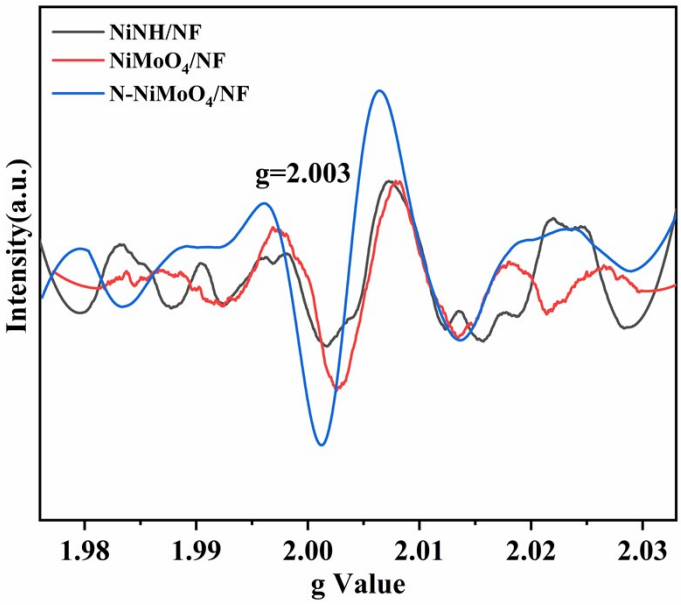

Figure. S9 EPR spectra of NiNH/NF, $NiMoO_4$/NF and N-$NiMoO_4$/NF.

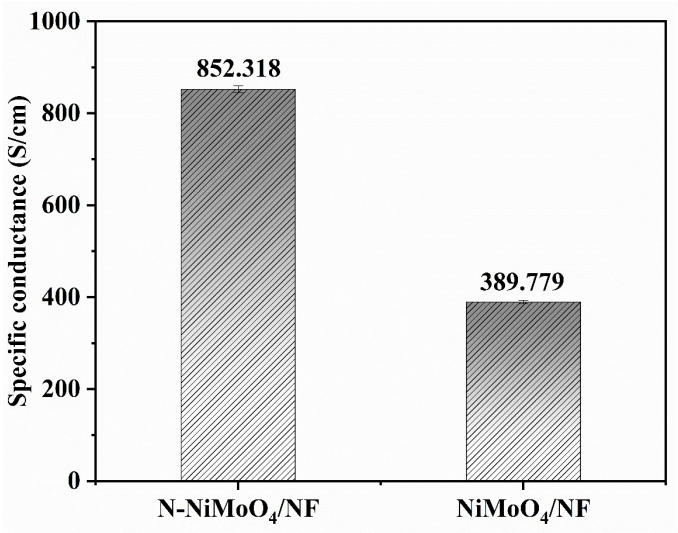

Figure. S10 Conductivity of N-$NiMoO_4$/NF and N-$NiMoO_4$/NF.

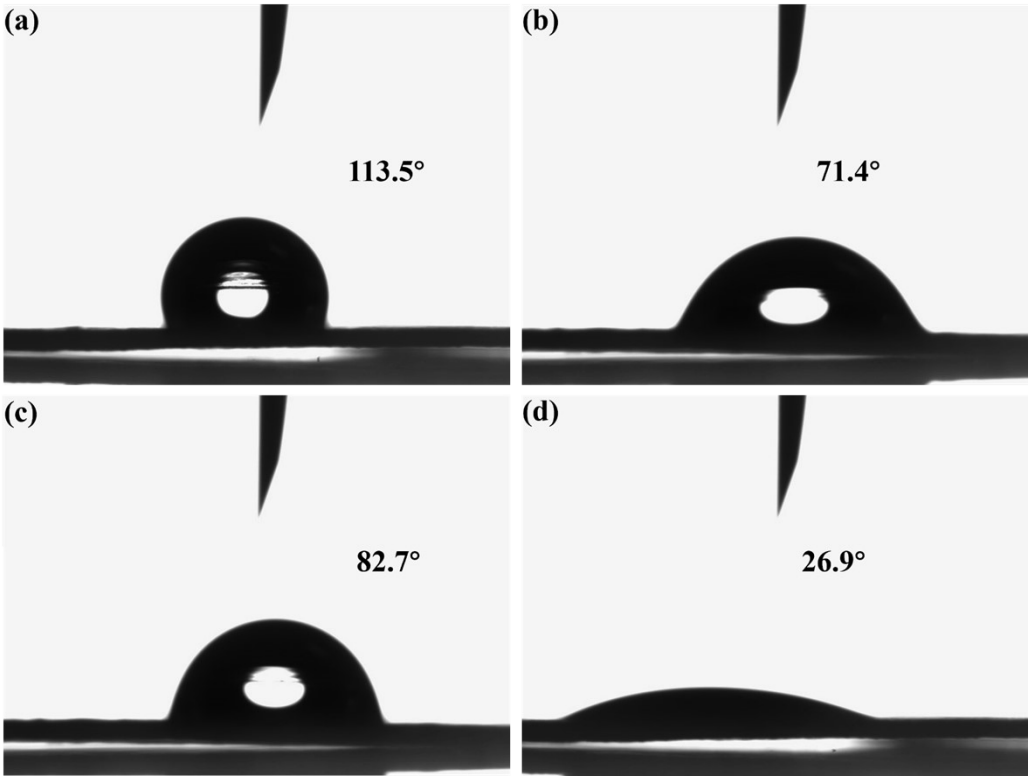

Figure. S11 Contact angle of HMF solution on (a)Ni foam, (b) $NiMoO_4$/NF, (c) NiNH/NF, and (d) N-$NiMoO_4$/NF electrode surface.

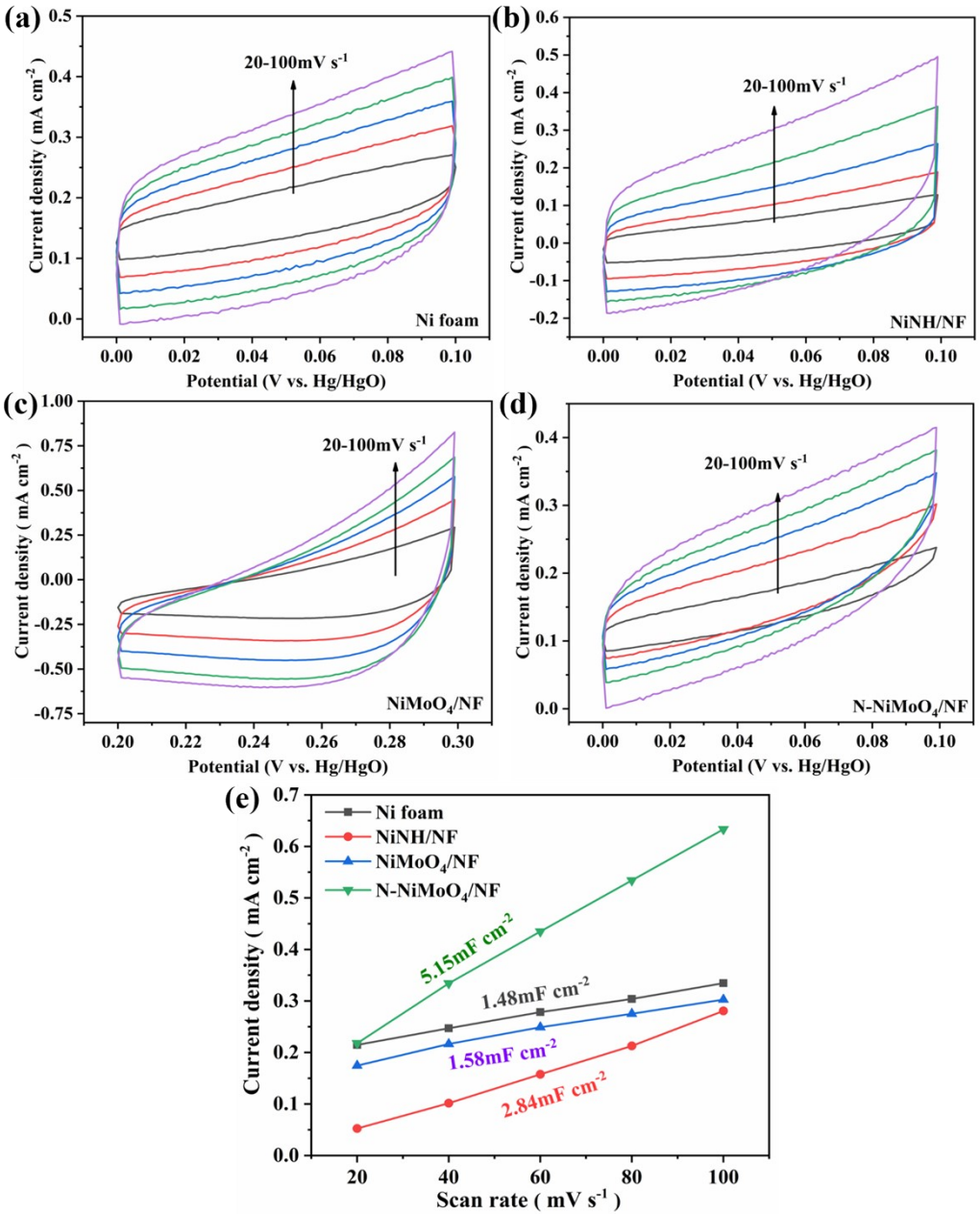

Figure. S12 Cyclic voltammetry of (a) Ni foam，(b) NiNH/NF，(c) $NiMoO_4$/NF，(d) N-$NiMoO_4$/NF at the scanning rate of 20-100 mV s^{-1}, (e) the relationship between current density and scanning rate

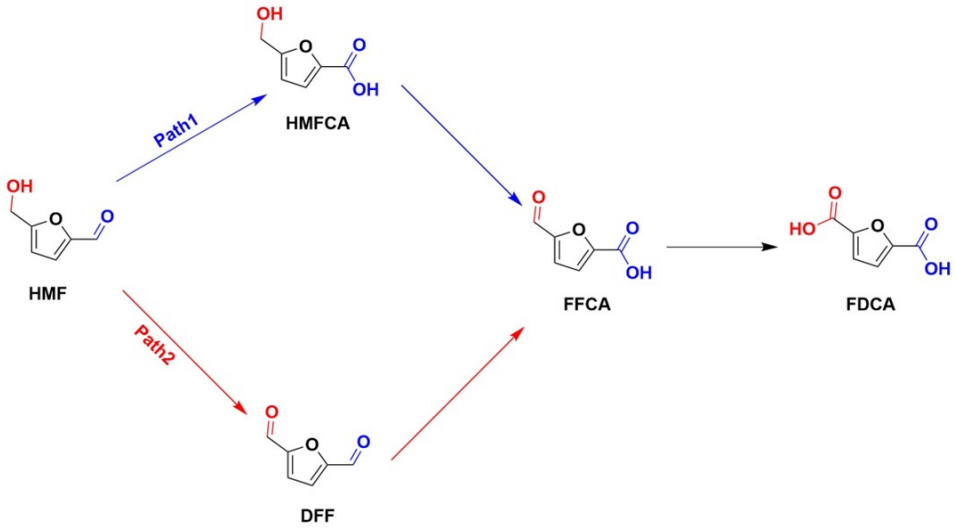

Figure S13 Two possible pathways of converting HMF to FDCA.

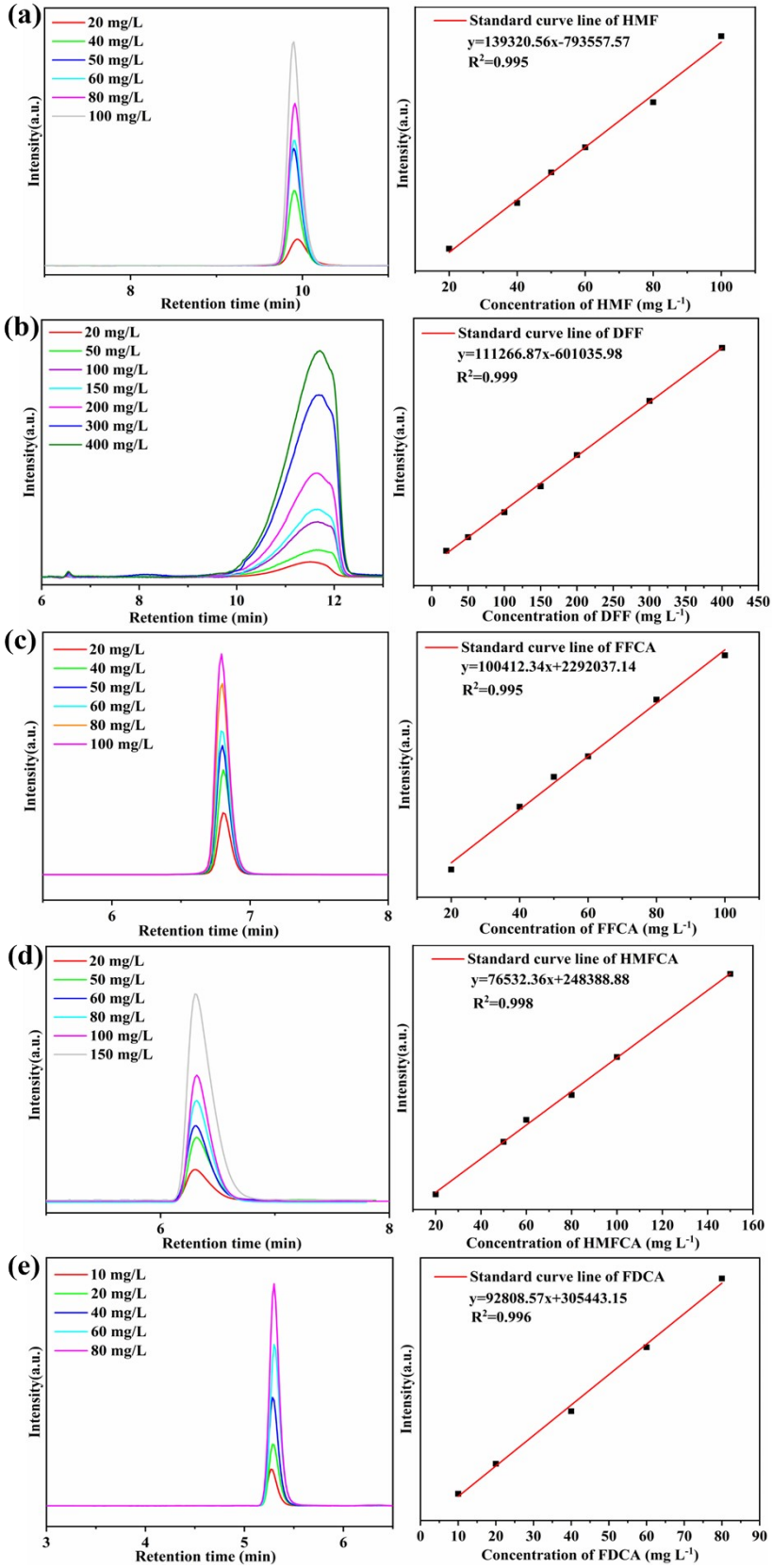

Figure. S14 HPLC chromatogram of standard samples at different concentrations and standard curve: (a) HMF, (b) DFF, (c) FFCA, (d) HMFCA, and (e) FDCA.

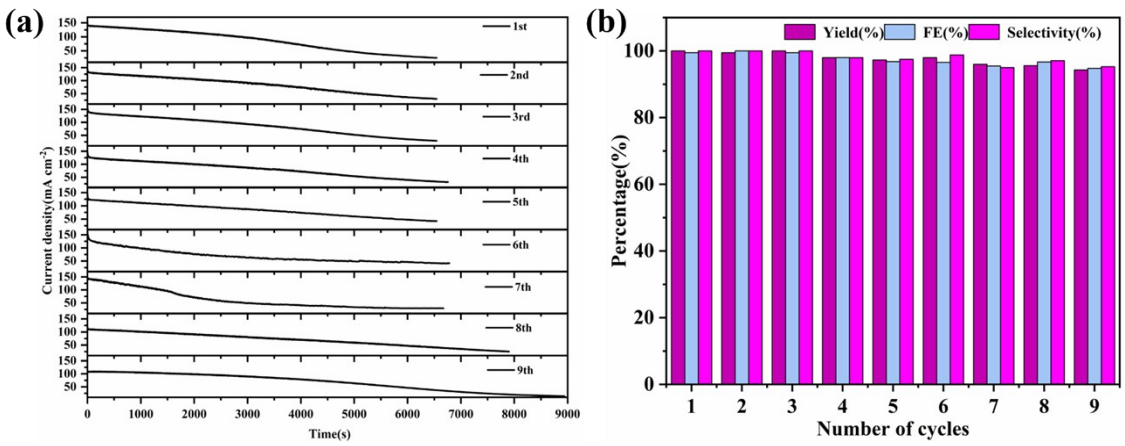

Figure S15 N-$NiMoO_4$/NF i-t curve lasting 9 cycles at 1.52 V (vs. RHE), (b) the yield, FE and selectivity at different cycle times.

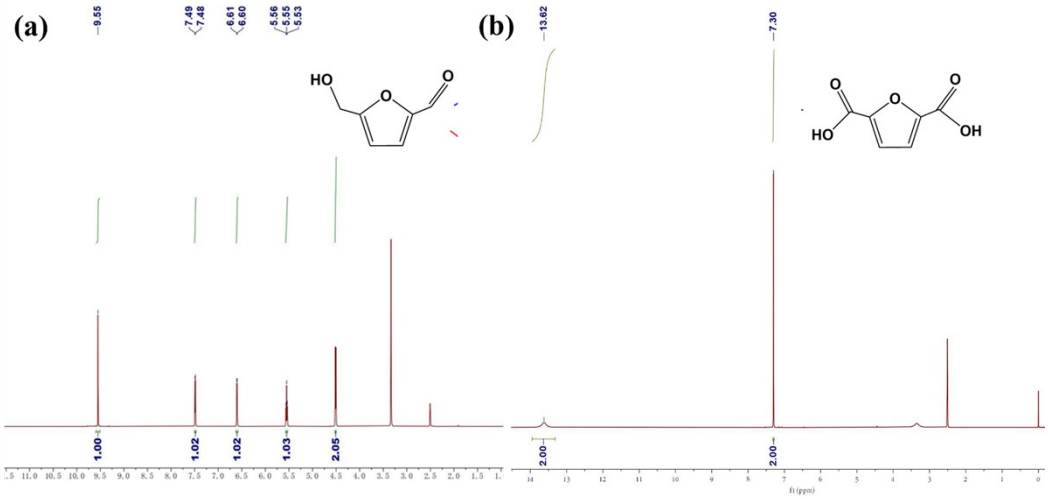

Figure S16 (a) ^1H NMR spectra of HMF raw material, (c) ^1H NMR spectra of acid-precipitated solid products.

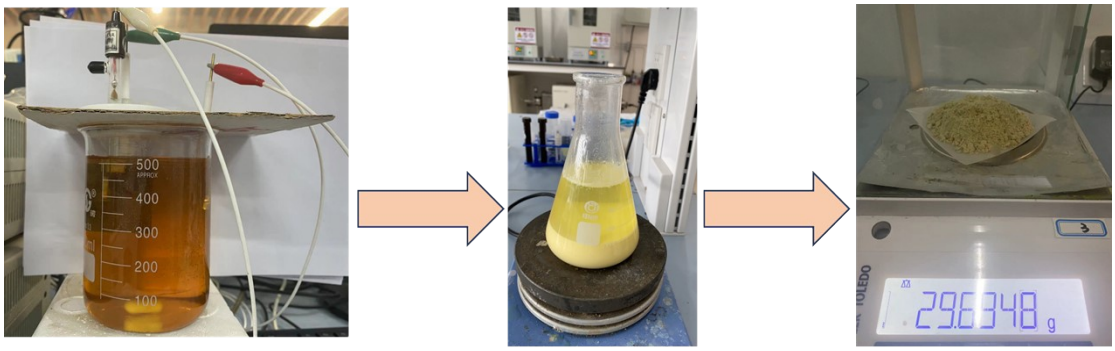

Figure S17 Enlarge the actual picture of the experiment.

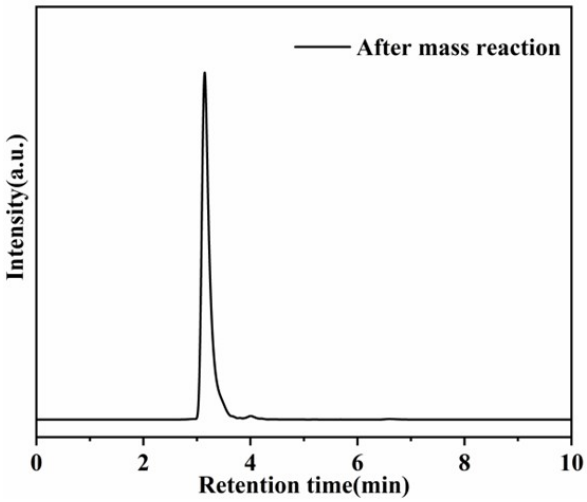

Figure S18 HPLC diagram after magnification experiment.

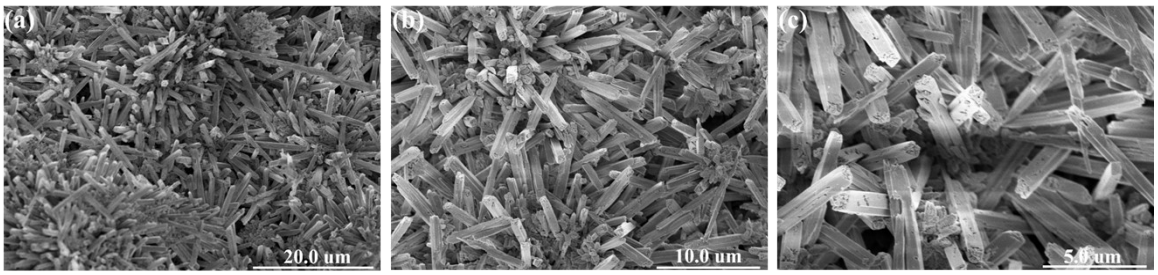

Figure S19 SEM images for N-$NiMoO_4$/NF after 3 i-t cycle tests.

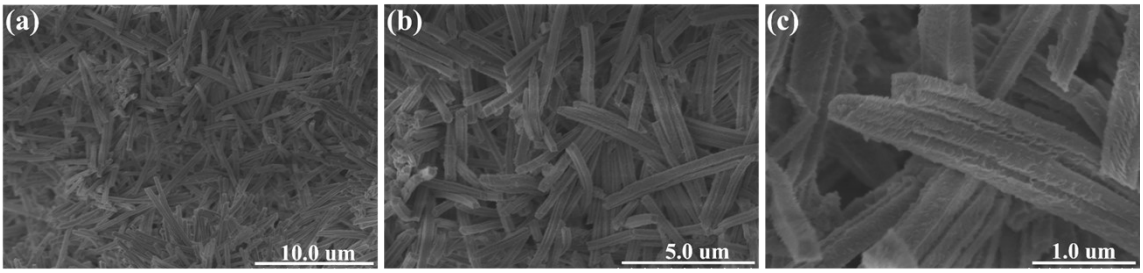

Figure S20 SEM images for N-$NiMoO_4$/NF after 9 i-t cycle tests.

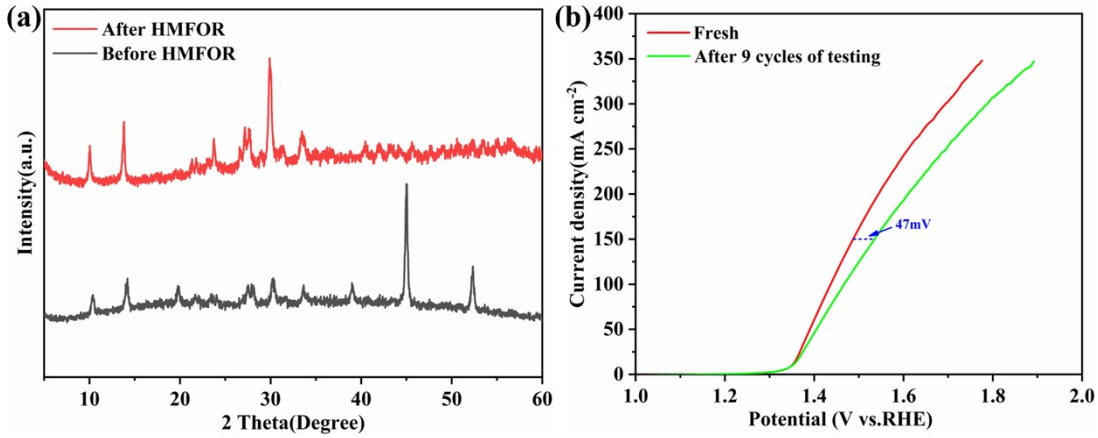

Figure S21 (a) XRD pattern for N-$NiMoO_4$/NF after 9 i-t cycle tests, (b) LSV curves before and after cyclic test of N-$NiMoO_4$/NF.

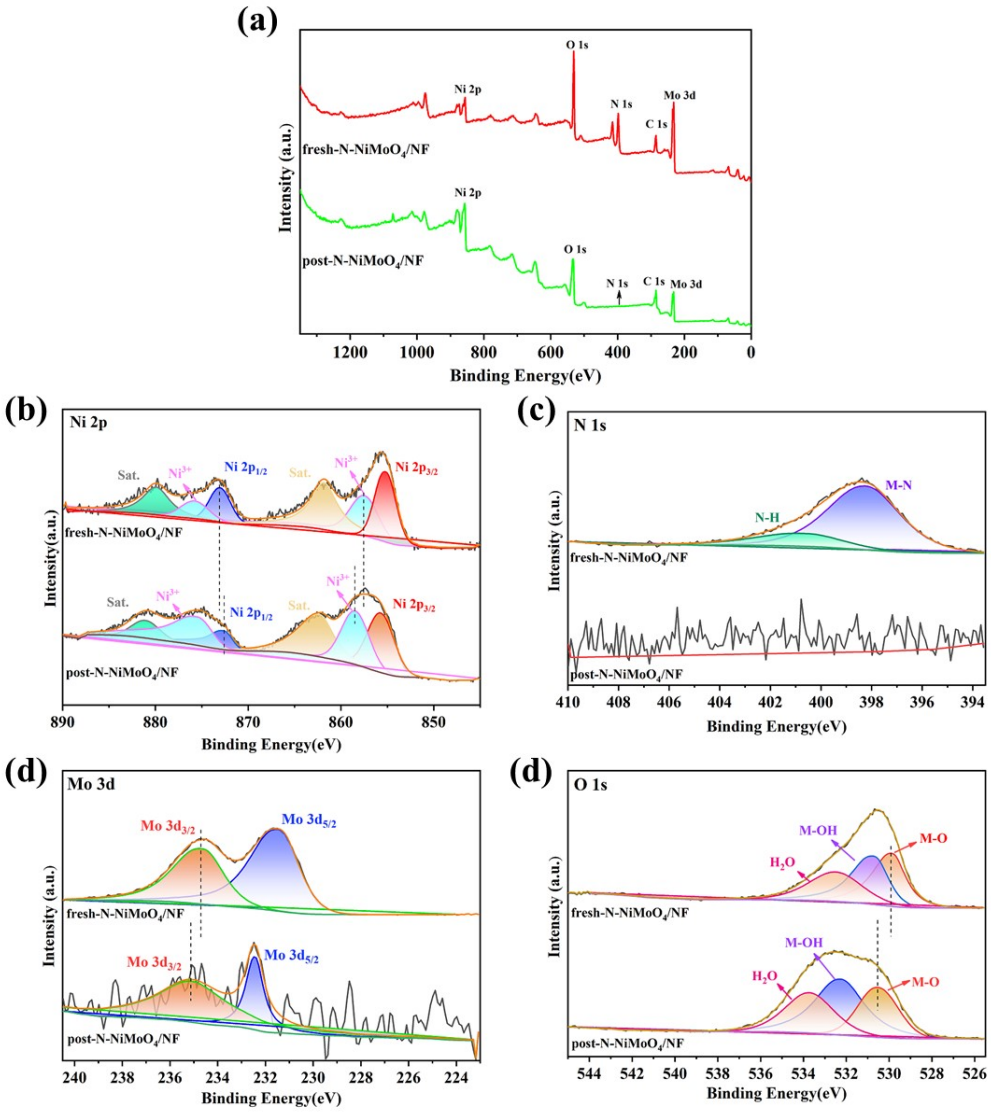

Figure S22 High-resolution XPS spectra for (a) survey full spectra, (b) Ni 2p, (c) N 1s, (d) Mo 3d (e) O 1s before and after HMFOR.

Table S1 Lattice parameters of $NiMoO_4$ and $NiMoO_4.H_2O$

Samples	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	*V* (Å^3)	*Space Group*
$NiMoO_4$	9.566	8.734	7.649	90.00	114.22	90.00	582.82	$C_{2/m}$
$NiMoO_4.H_2O$	4.4700	6.9500	8.4100	76.60	84.20	74.50	244.71	P_1

Table S2 Impedance fitting results of as-prepared N-$NiMoO_4$/NF, $NiMoO_4$/NF, NiNH/NF and Ni foam.

catalyst	R_s/Ω cm^{-2}	R_{ct}/Ω cm^{-2}
N-$NiMoO_4$/NF	1.16	3.30
$NiMoO_4$/NF	1.65	5.20
NiNH/NF	2.12	6.07
Ni foam	2.59	10.87

Table S3 The electrocatalytic performance comparison of prepared N-$NiMoO_4$/NF with reported HMFOR electrocatalysts.

Electrocatalysts	Potential(V vs.RHE)	HMF (mM)	Conversion (%)	FDCA yield (%)	FE (%)	Ref.
N-$NiMoO_4$	1.473	10	100	97	97	*Catal. Sci. Technol.* 2021, 11, 7326-7330.
Co_3O_4	1.65	10	100	93.2	92.9	Appl. Catal. B Environ. 2022, 307, 121209.
NiOOH/$Cu(OH)_2$	1.50	5	100	93.8	93.8	*ACS Catal.* 2022, 12, 4078-4091.
Ni/NiO heterostructures	1.45	50	95	91	95	*Catal. Sci. Technol.* 2021, 11, 2480-2490.
$Ni(OH)_2$-1PO_x	1.464	10	＞99	94.2	93.5	*ACS Sustainable Chem. Eng.* 2022, 10, 5538-5547.
NiB	1.45	10	＞99	98.5	100	*Angew. Chem. Int. Ed.* 2018, 57, 11460.
NCF (Cu foam)	1.62	5	99.9	96.4	95.3	*ACS Catal.* 2018, 8, 1197-1206.
Co_3O_4/CF	1.40	10	1.0 M KOH	92.9	93.2	*Appl. Catal B-Environ.* **2022**, *307*, 121209.
NiS_x/β-$Ni(OH)_2$	1.45	10	1.0 M KOH	98.3	97.7	Adv. Mater. **2023**, *35*, 2211177
Ni_3N@C	1.45	10	1.0 M KOH	99	98.0	*Angew. Chem.* **2019**, *131*, 16042
$Co_{0.4}$NiS@NF	1.45	10	1.0 M KOH	98.5	96.3	*Adv. Sci.* **2022**, *9*, 2200957

Co-NiO/CC	1.47	10	1.0 M KOH	94.6	94.8	*Chem. Eng. J.*. **2022**, *433*, 133842
NiOOH-VN/NF	1.402	10	1.0 M KOH	95.0	94.7	*Chem. Eng. J.*. **2022**, *433*, 133842
Ni_3S_2-MoS_2	1.45	10	1.0 M KOH	93.0	93.0	*Small* **2022**, *18*, 2201306
NiRu@PCNS	1.45	10	1.0 M KOH	NA	98.2	*Chem. Eng*. **2023**, *11*, 13441
Co_4N/NC@CC	1.40	10	1.0 M KOH	90.3	92.4	*ACS Catal.* **2022**, *12*, 4242
NiSe@NiO_x	1.423	10	1.0 M KOH	95.0	93.0	*Appl. Catal B-Environ.* **2020**, *261*, 118235
$Al(OH)_3$/$Co(OH)_2$	1.5	10	100	99.1	99.4	*Adv. Mater.* 2023, 35, 2301549
N-$NiMoO_4$/NF	1.52	20	100	99.8	99.8	**This work**