

## Supporting Information for

### **Metal sulfide enhanced metal-organic framework nanoarrays for electrocatalytic oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid**

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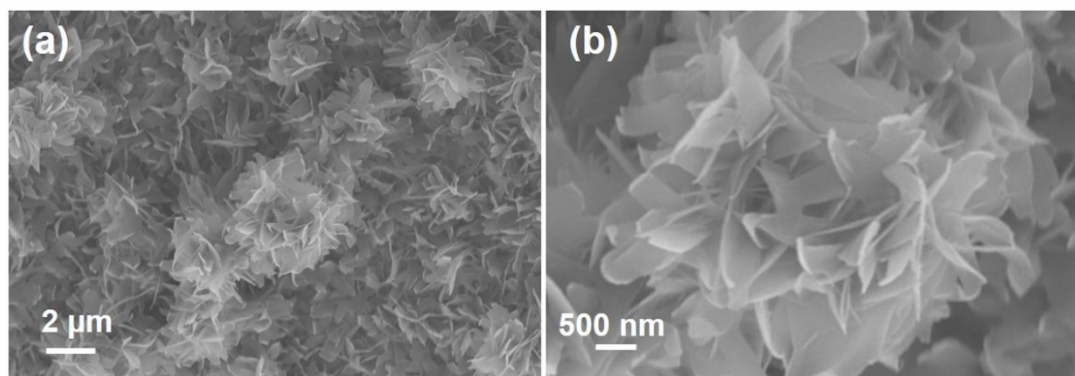


Fig. S1. SEM images of NiS-MOF.

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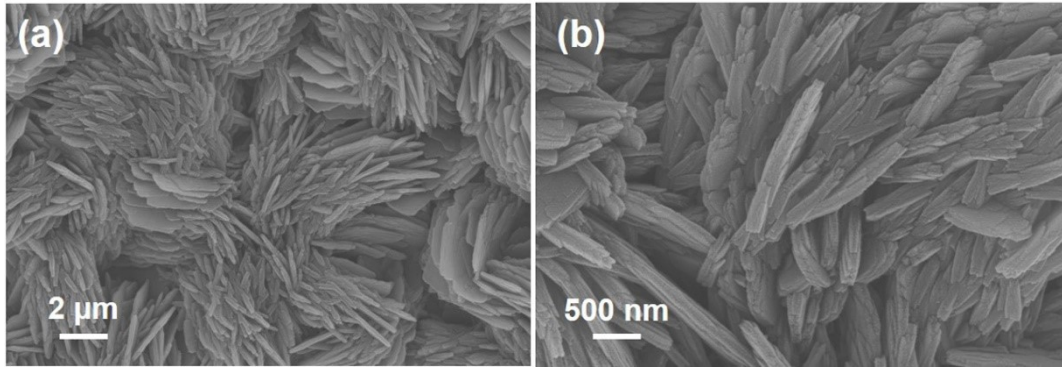


Fig.S2. SEM images of NiFeS-MOF.

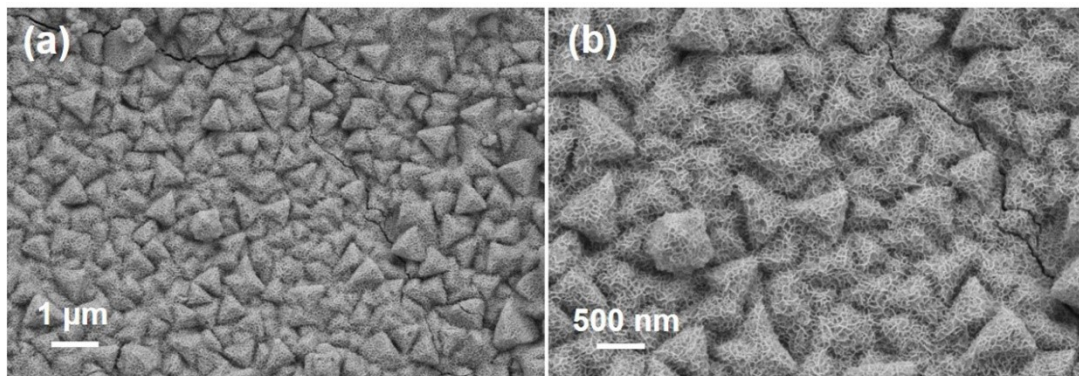


Fig.S3. SEM images of NiCoS-MOF.

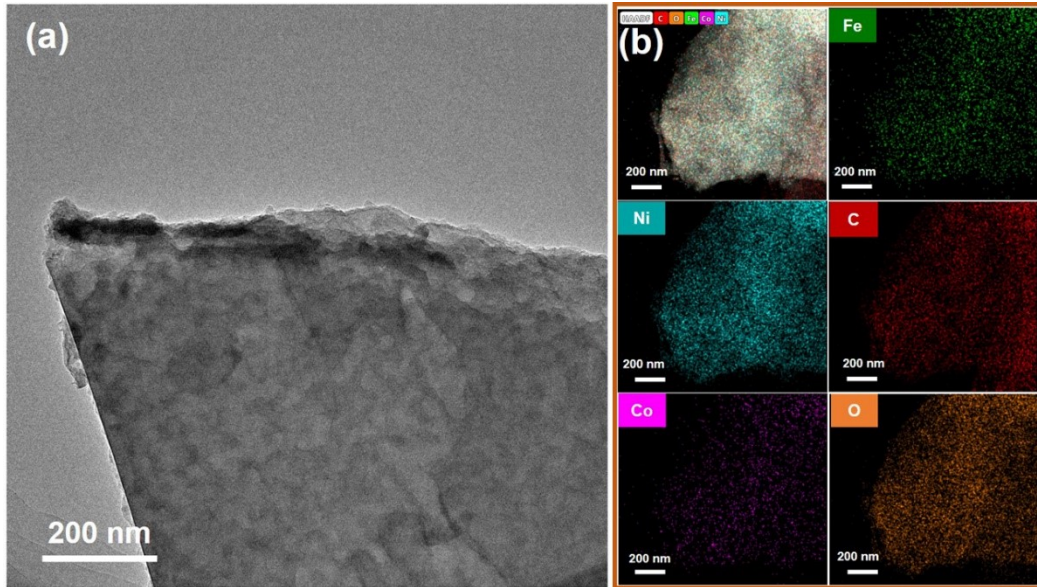


Fig. S4. NiCoFe-MOF nanosheet: (a) TEM image, (b) elemental maps.

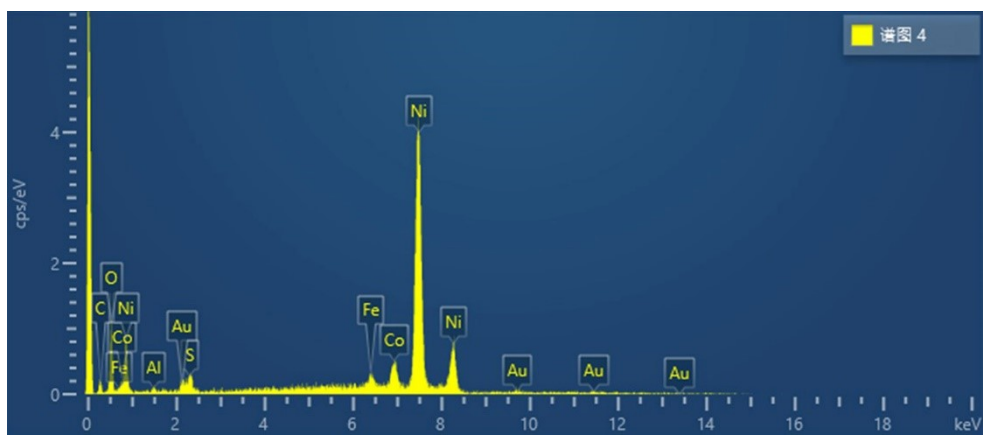


Fig. S5. SEM-EDS of NiCoFeS-MOF.

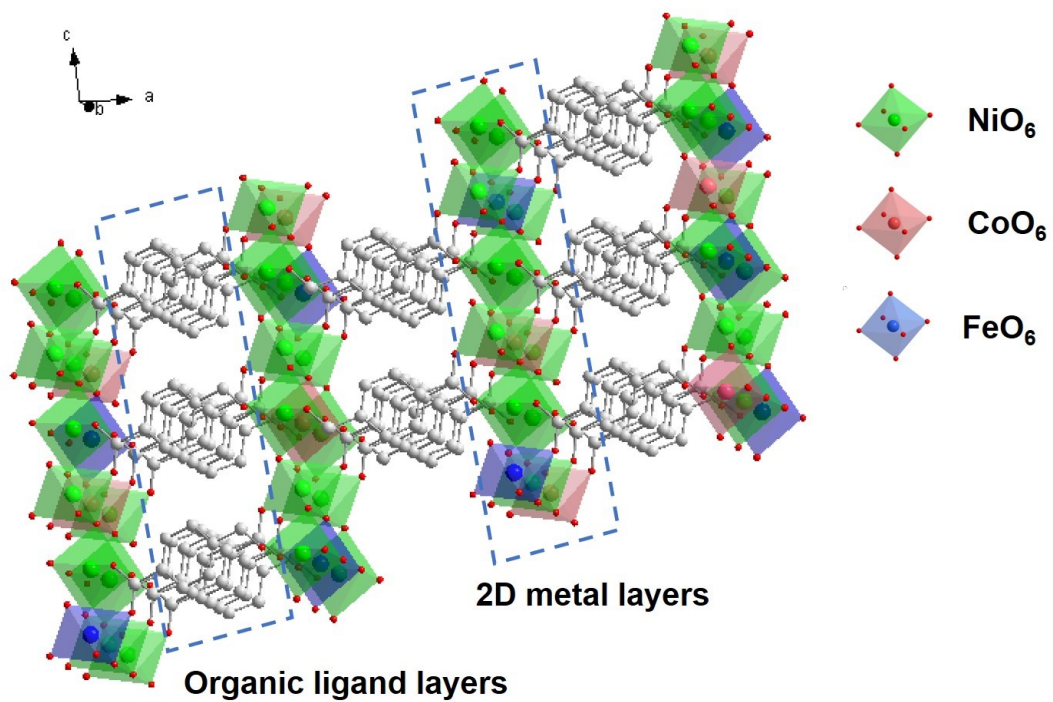


Fig. S6. Crystal structure schematic diagram of 2D NiCoFe-MOF nanosheets.

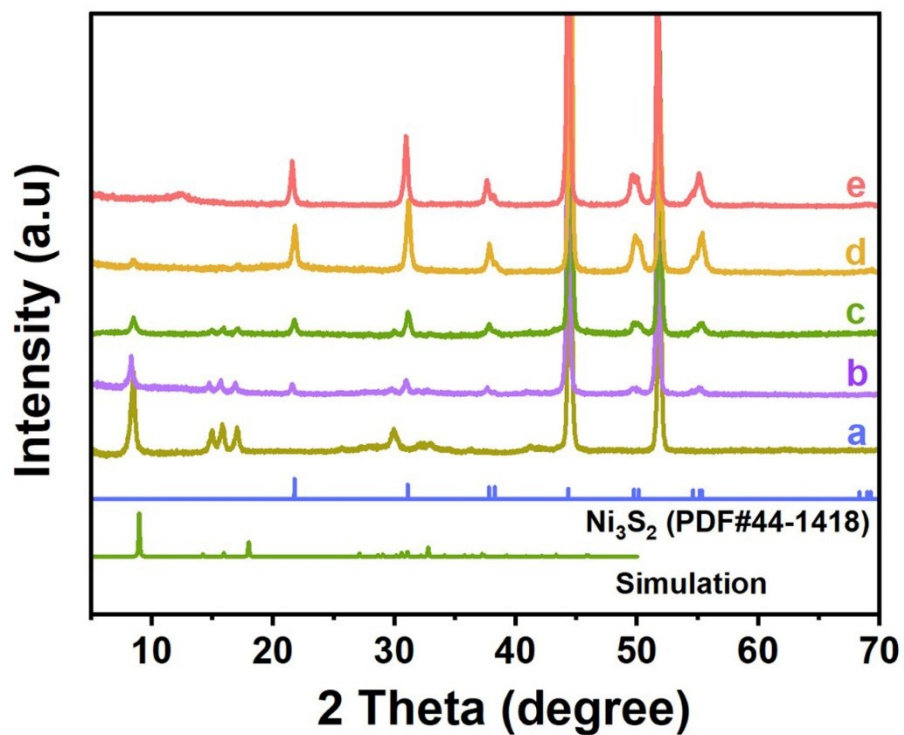


Fig. S7. XRD patterns of: (a) CoFe-Ni<sub>3</sub>S<sub>2</sub> (without TPA), (b) NiCoFe-MOF (without TAA), and NiCoFeS-MOF prepared with different doses of TAA (c) 50 mg, (d) 80 mg, and (e) 150 mg.

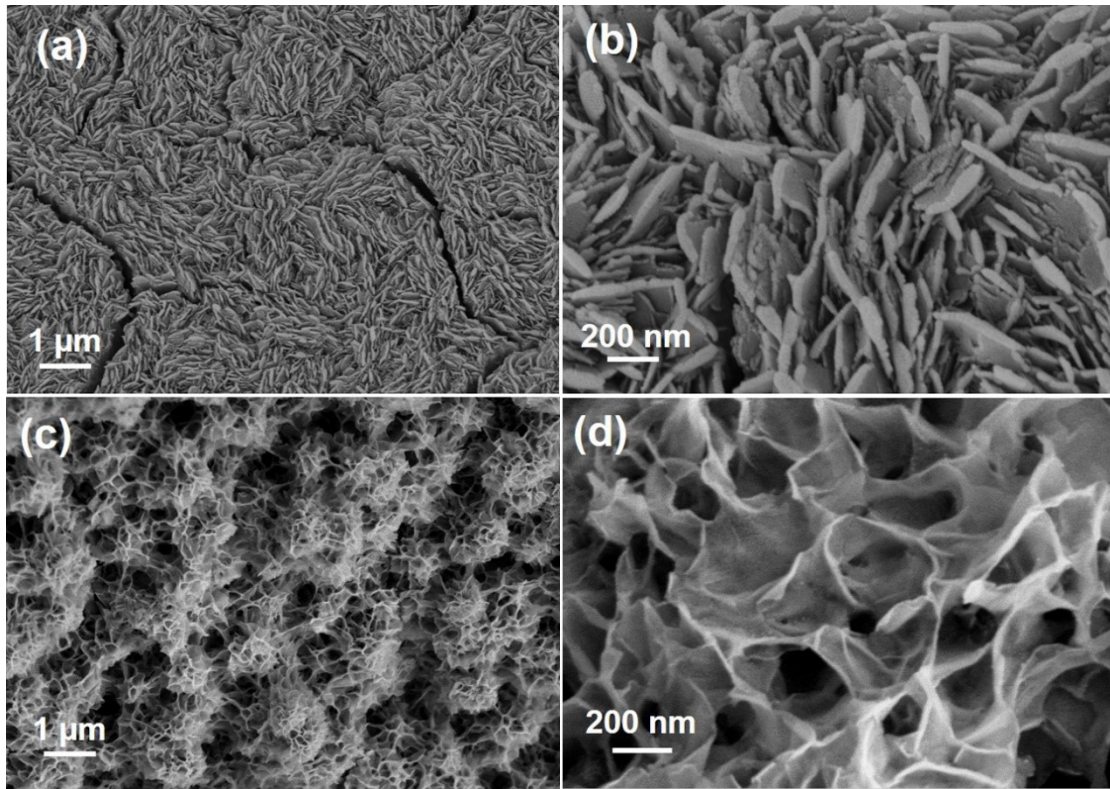


Fig. S8. SEM images of: (a) NiCoFe-MOF, (b) NiCoFe-MOF enlarged, (c) CoFe-Ni<sub>3</sub>S<sub>2</sub> (d) CoFe-Ni<sub>3</sub>S<sub>2</sub> enlarged.



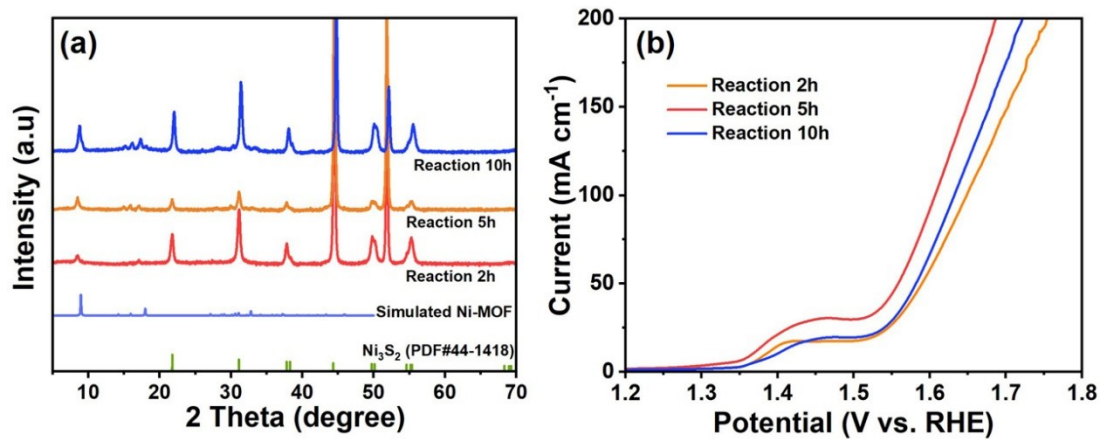


Fig. S9. Characterization of NiCoFeS-MOF material prepared at different reaction times under solvothermal conditions: (a) XRD patterns; (b) LSV curves of material in

1 M KOH.

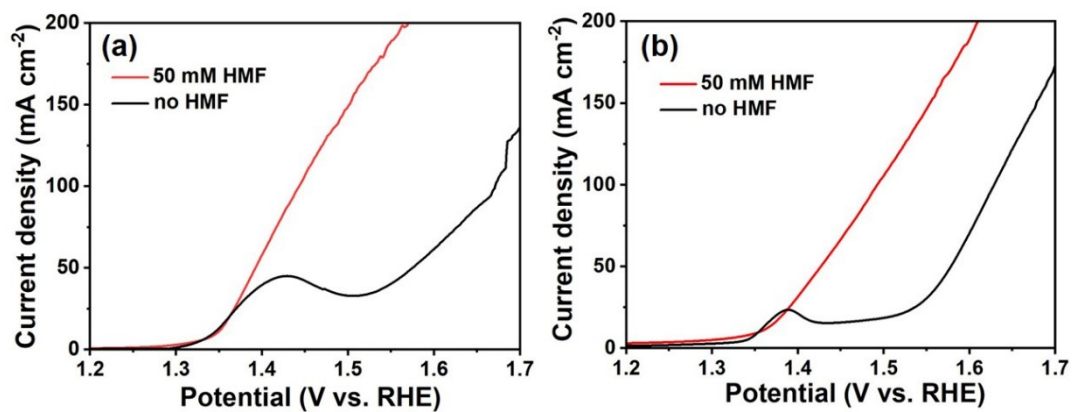


Fig.S10. LSV curves of (a) NiCoFe-MOF and (b) CoFe-Ni<sub>3</sub>S<sub>2</sub> in 1 M KOH with or without 50 mM HMF addition.

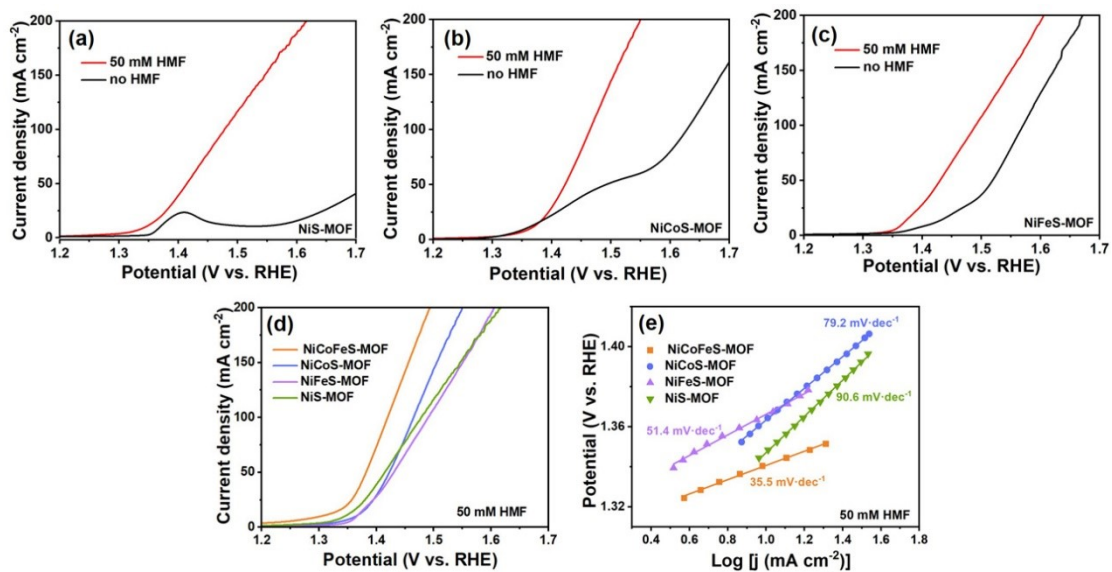


Fig. S11. LSV curves of: (a) NiS-MOF, (b) NiCoS-MOF and (c) NiFeS-MOF electrodes in 1 M KOH with or without 50 mM HMF. (e) LSV curves and (f) corresponding Tafel plots of NiCoFeS-MOF, NiS-MOF and CoFe-Ni<sub>3</sub>S<sub>2</sub> electrodes in 1 M KOH with 50 mM HMF.

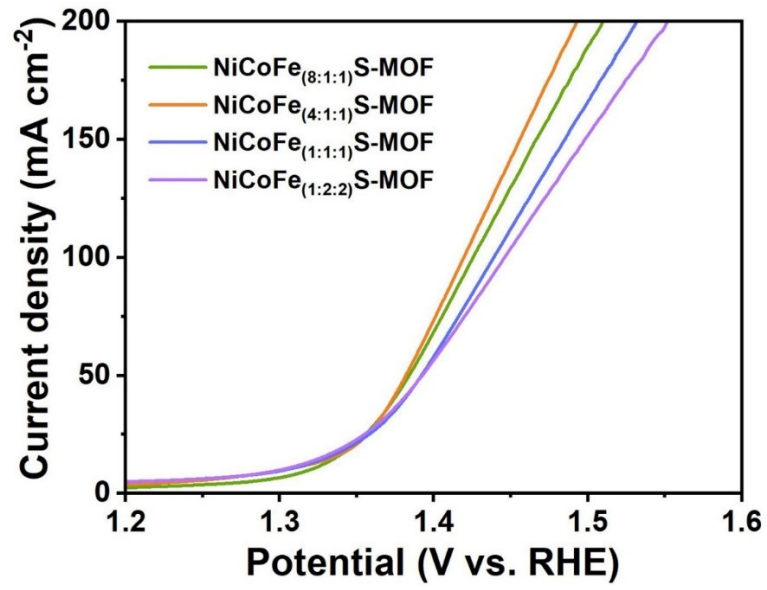


Fig. S12. LSV curves of sample catalysts prepared at different metal salt precursor ratios.

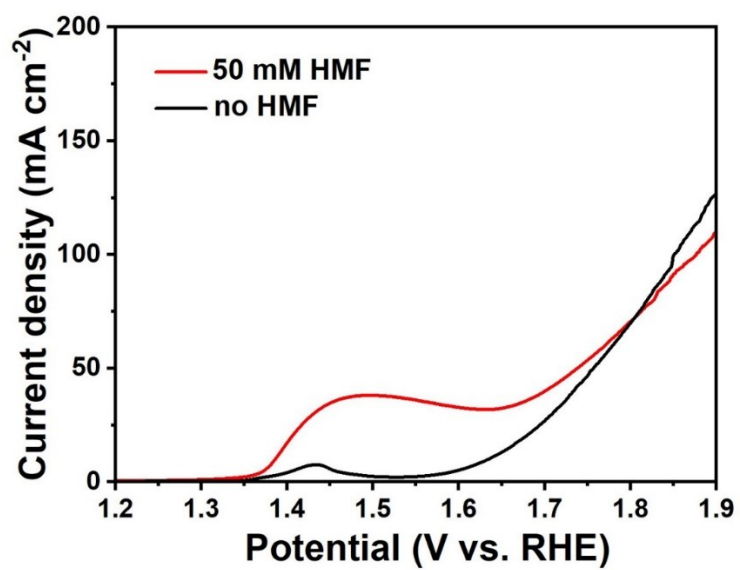


Fig. S13. Linear sweep voltammetry curves of bare nickel foam electrode in 1 M KOH with or without 50 mM HMF.

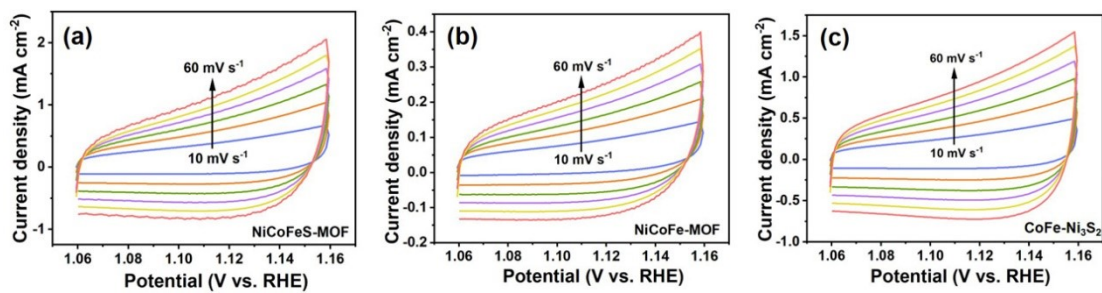


Fig. S14. Cyclic voltammetry curves for NiCoFeS-MOF, NiCoFe-MOF and CoFe-

Ni<sub>3</sub>S<sub>2</sub> electrodes at scan rates of (10, 20, 30, 40, 50, 60) mV s<sup>-1</sup>.

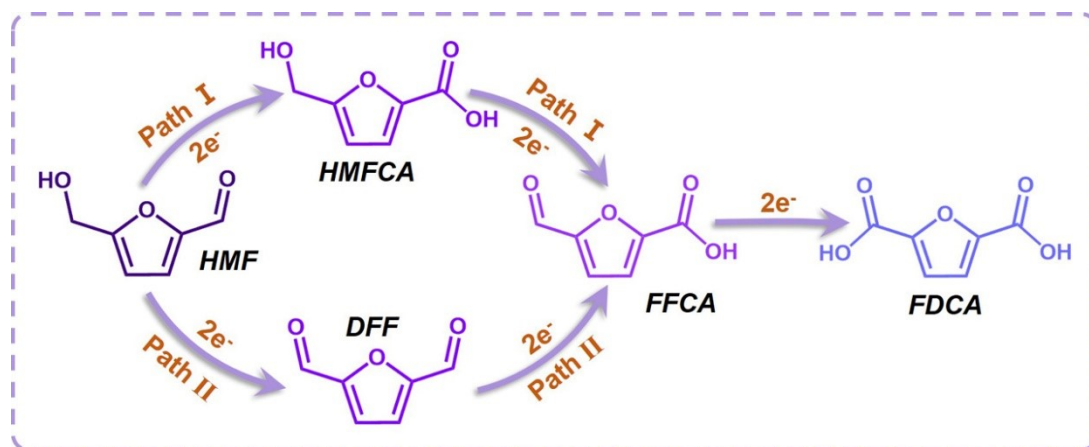


Fig. S15. Two possible pathways for oxidation of 5-hydroxymethyl-2-furfural (HMF) to 2,5-furandicarboxylic acid (FDCA).

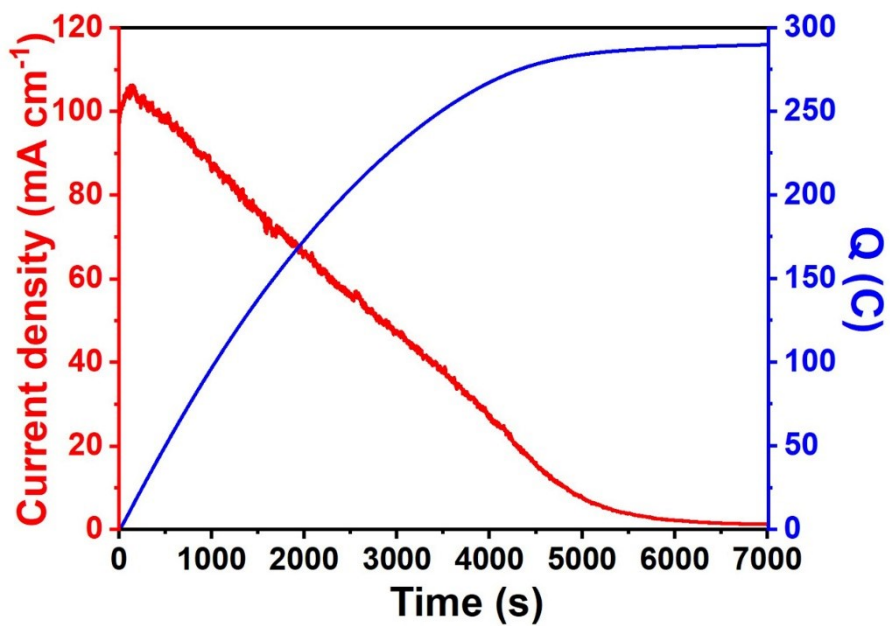


Fig. S16. Current-time and charge-time plots for NiCoFeS-MOF electrodes derived from chronoamperometry.



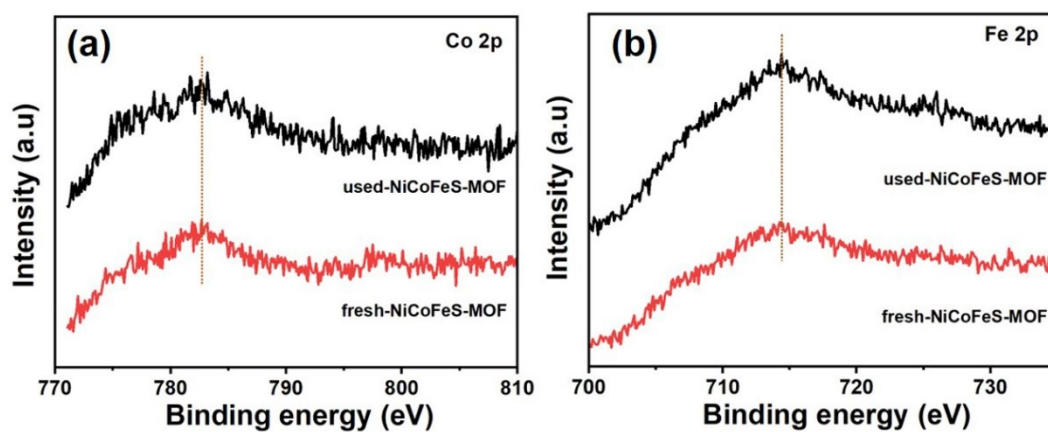
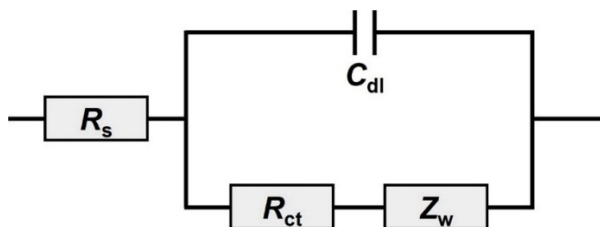


Fig. S17. XPS spectra of the fresh and used-NiCoFeS-MOF electrode after electrocatalytic oxidation of HMF, (a) Co 2p, (b) Fe 2p.

Table S1. Oxygen evolution reaction (OER) performance of NiCoFeS-MOF electrocatalyst and literature electrocatalysts.

Catalyst	Electrolyte	Current density (mA · cm <sup>-2</sup> )	Overpotential (mV)	Ref.
NiCoFeS-MOF	1.0 M KOH	50	320	This work
NiS/Fe <sub>3</sub> O <sub>4</sub> HNPs@CN	1.0 M KOH	10	243	1
NiS/NF	1.0 M KOH	10	335	2
Co <sub>9</sub> S <sub>8</sub> @MoS <sub>2</sub> -0.5	1.0 M KOH	10	340	3
NiFeZn-MOF	1.0 M NaOH	50	350	4
Co <sub>9</sub> S <sub>8</sub> /NSCP	0.1 M KOH	10	370	5
Co/Co <sub>9</sub> S <sub>8</sub> @NSOC-800	1.0 M KOH	10	373	6
Ni <sub>3</sub> Fe-Co <sub>9</sub> S <sub>8</sub> /rGO	0.1 M KOH	10	390	7
NiS@N/S-C	1.0 M KOH	10	417	8

Table S2. Simulation parameters of equivalent circuit components showing fitted values for solution resistance ( $R_s$ ), charge transfer resistance ( $R_{ct}$ ), double-layer capacitance ( $C_{dl}$ ) and Warburg impedance ( $Z_w$ ) determined with ZSimpWin software



Samples	$R_{ct}$ ( $\Omega$ )	$R_s$ ( $\Omega$ )	$C_{dl}$ (F)	$Z_w$
NiCoFeS-MOF	0.52	1.27	0.37	2.26
NiCoFe-MOF	0.77	1.02	0.31	1.79
CoFe-Ni <sub>3</sub> S <sub>2</sub>	1.60	1.50	0.15	1.40

Table S3. Electrocatalytic oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) for non-platinum group electrodes

Electrode	Electrolyte	Applied potential (vs. RHE)	HMF conversion (%)	FDCA yield (%)	FE (%)	Ref.
NiCoFeS-MOF	1 M KOH + 50 mM HMF	1.39 V	100	99	99	This work
MnO <sub>x</sub>	pH 1 H <sub>2</sub> SO <sub>4</sub> + 20 mM HMF	2.0 V	>99.9 (60 °C)	53.8	-	9
NiO-CMK-1	0.2 M KOH + 20 mM HMF	1.73 V	65	51.4	-	10
NiFe-LDHs	1 M NaOH + 5 mM HMF	1.55 V	95.5 (55 °C)	84.9	~90	11
P-HEOs	1 M KOH + 10 mM HMF	1.50 V	99	97.4	96.6	12
NiCo <sub>2</sub> O <sub>4</sub>	1 M KOH + 5 mM HMF	1.5 V	99.6	90.4	-	13
d-NiFe LDH/CP	1 M KOH + 10 mM HMF	1.48 V	97.35	96.8	84.47	14
NiS <sub>x</sub> /Ni <sub>2</sub> P	1 M KOH + 10 mM HMF	1.46 V	~100	~98.5	-	15
om-Co <sub>3</sub> O <sub>4</sub> /NF	1 M KOH +	1.457 V	100	> 99.8%	~100	16

	10 mM HMF					
NiSe@NiO <sub>x</sub>	1 M KOH + 10 mM HMF	1.423 V	~100	~99	~99	17
Ni <sub>3</sub> S <sub>2</sub> /NF	1 M KOH + 10 mM HMF	1.423 V	-	-	96 ~ 99	18
CoFe PBA	1 M KOH + 10 mM HMF	1.42 V	-	94	94	19
t-Ni <sub>1</sub> Co <sub>1</sub> -MOF	1 M KOH + 10 mM HMF	1.4 V	98	~100	~100	20
Cu <sub>x</sub> S@NiCo-LDH	1 M KOH + 10 mM HMF	1.32 V	-	~99	~99	21

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## Reference

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