Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Bimetallic sites and metalloid coordination effects: electronic structure engineering of NiCo-based sulfide for 5-hydroxymethylfurfural electrooxidation

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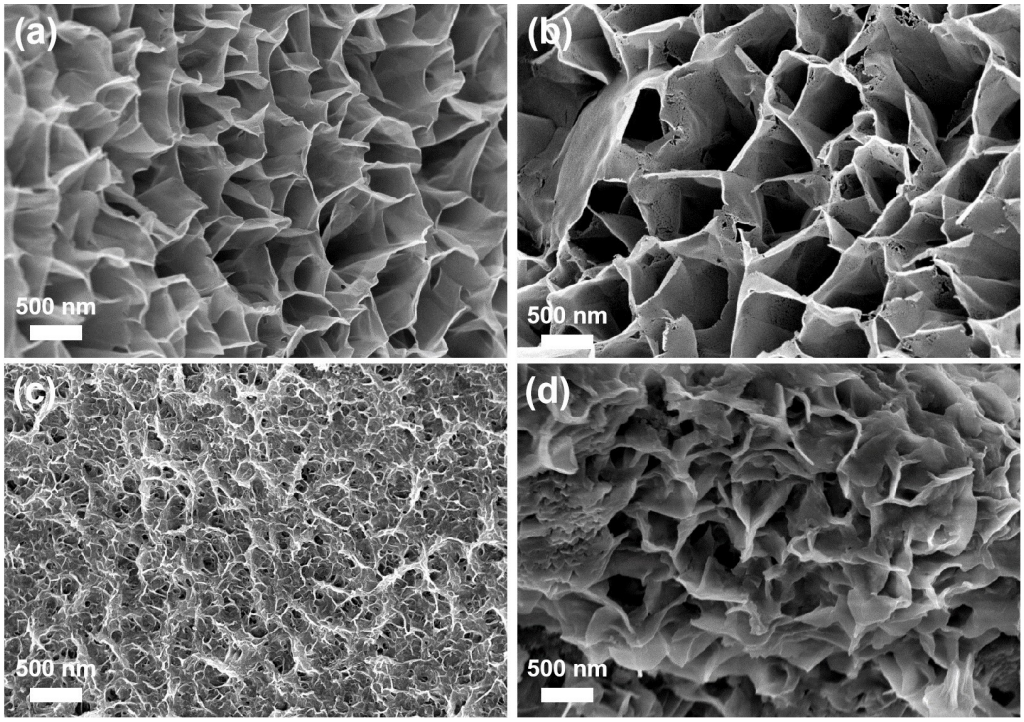

Fig. S1. SEM images of (a) NiCo-MOF, (b) NiCo-O, (c) Ni-S, and (d) Co-S samples.

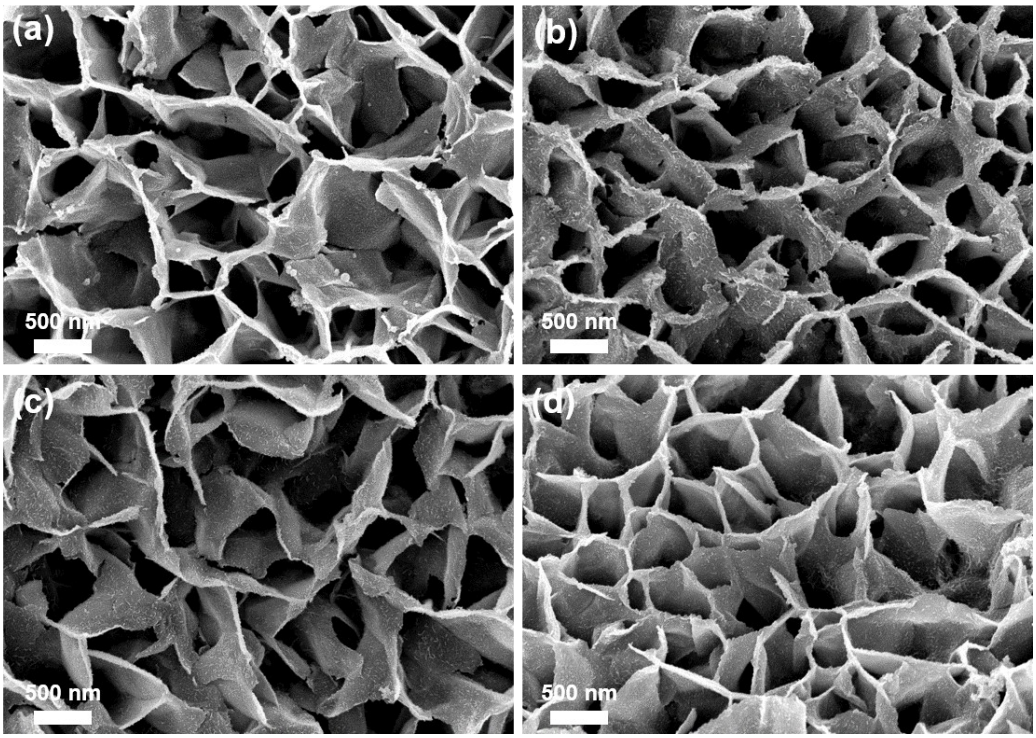

Fig. S2. SEM images of NiCo-S samples with various Ni to Co ratio (a) NiCo-S-1, (b) NiCo-S-2, (c) NiCo-S, and (d) NiCo-S-4.

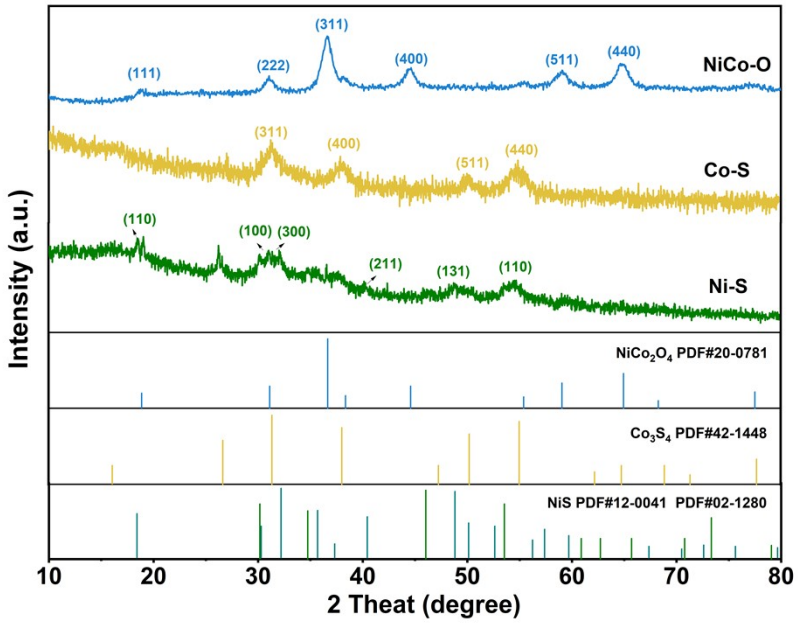

Fig. S3. XRD patterns of NiCo-O, Ni-S and Co-S powder sample.

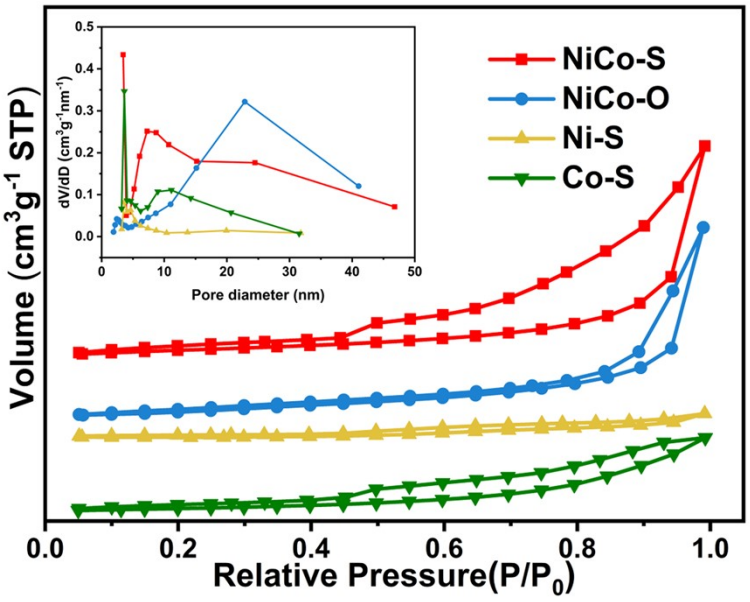

Fig. S4. N_2 adsorption–desorption isotherms of the four samples, the inset shows the corresponding pore size distribution.

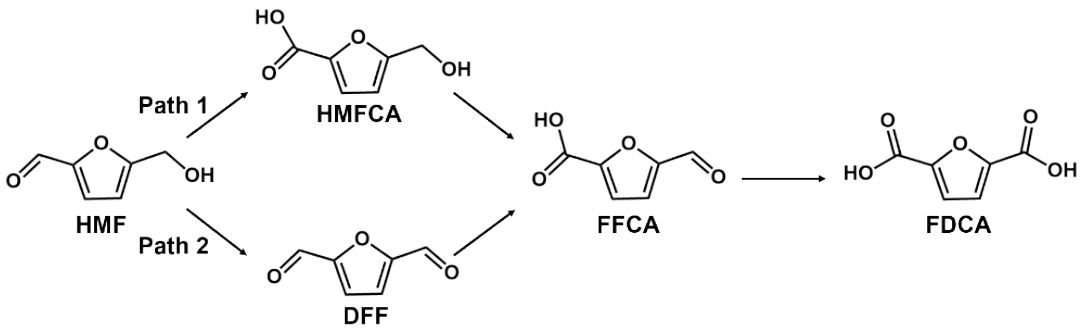

Fig. S5. Two pathways of the oxidation of HMF to FDCA.

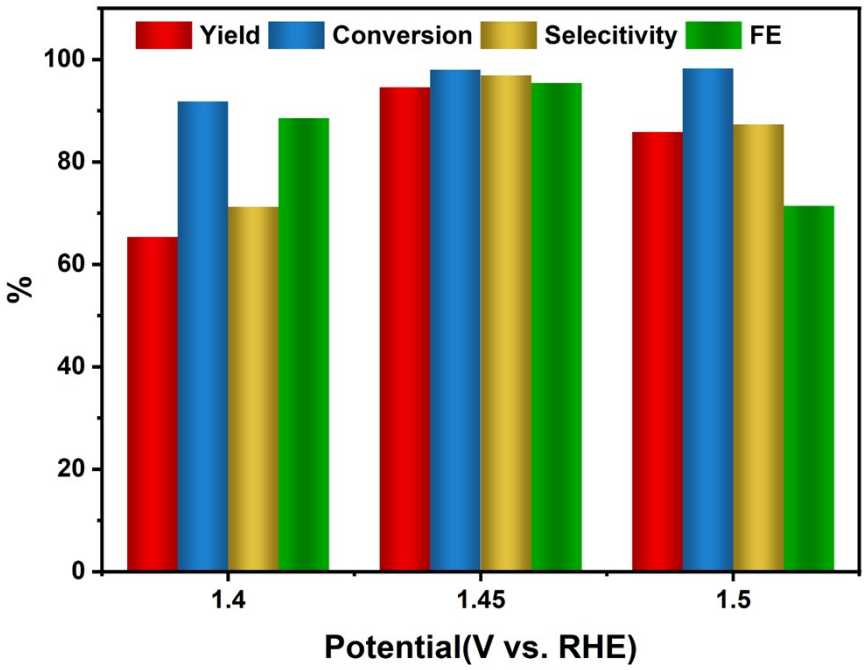

Fig. S6. Conversion of HMF and yield/FE/selectivity of FDCA obtained by NiCo-S electrode at different potential in 1 M KOH with 10 mM HMF.

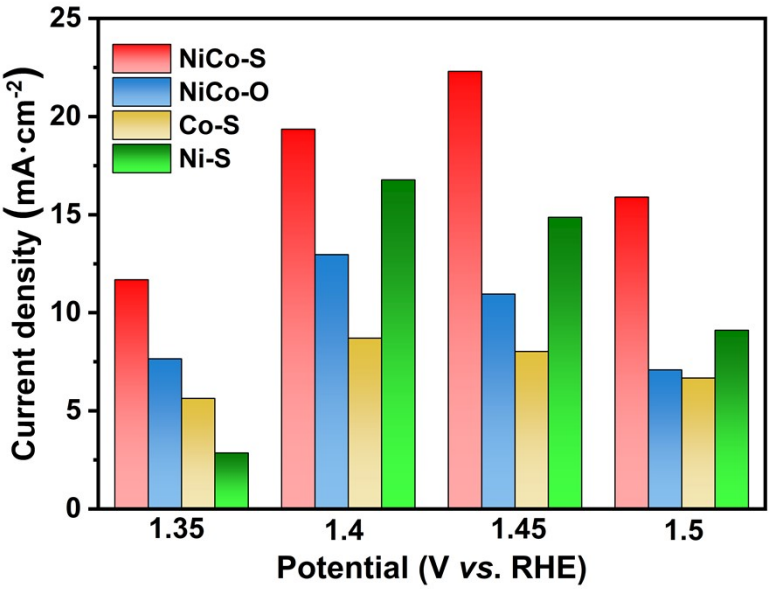

Fig. S7. Comparison of HMF oxidation current density at the potential between 1.35 to 1.5 V *vs* RHE.

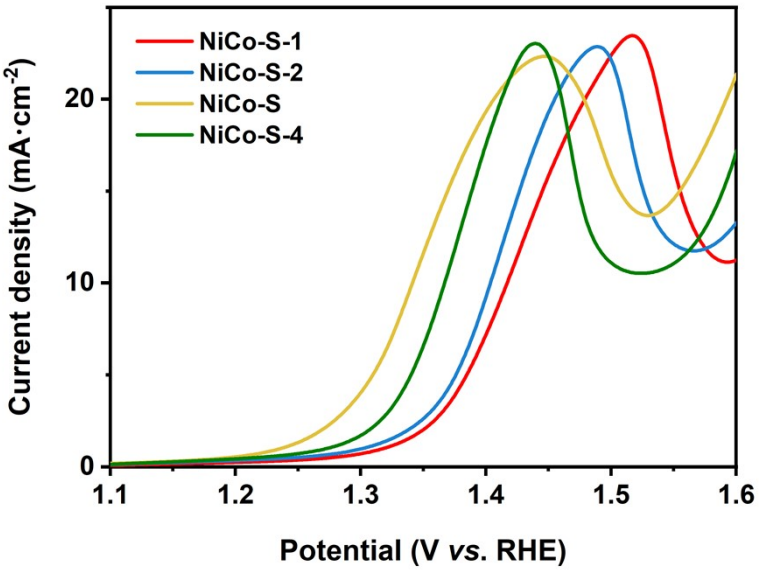

Fig. S8. The LSV for bimetallic sulfide catalysts with various Ni to Co ratio measured from 1.1 V to 1.6 V *vs*. RHE at a scan rate of 10 mV s^{-1} in 1 M KOH with 10 mM HMF.

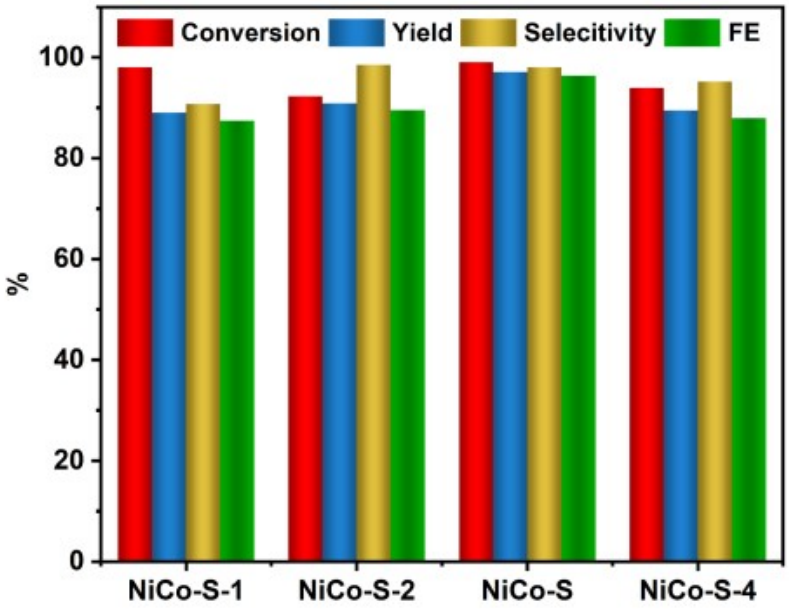

Fig. S9. Conversion of HMF and yield/FE/selectivity of FDCA of sulfides with varied Ni/Co ratios. The above tests were examined in 1 M KOH with 10 mM HMF at 1.45 V vs. RHE.

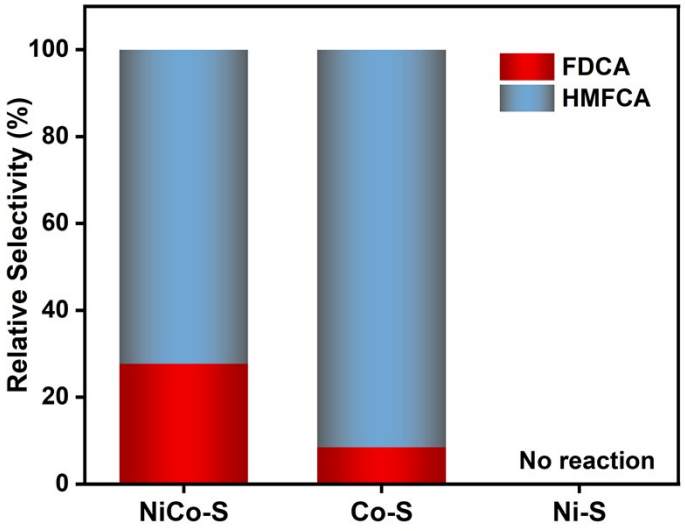

Fig. S10. The relative selectivity of different products obtained by NiCo-S, Ni-S, and Co-S electrodes. The above tests were carried out in 1 M KOH with 10 mM HMF at 1.3 V *vs* RHE.

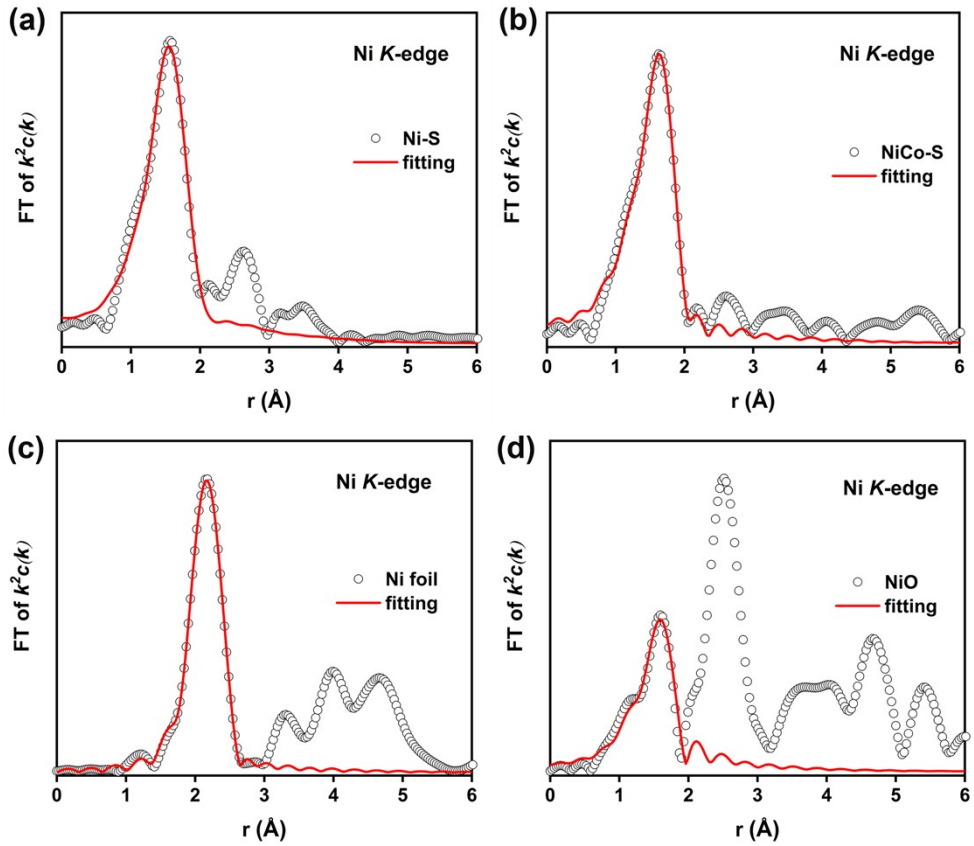

Fig. S11. Experimental and best fitted EXAFS spectra in the R space of Ni-S (a), and NiCo-S (b) with Ni foil (c) and NiO (d) as the references at the Ni K-edge.

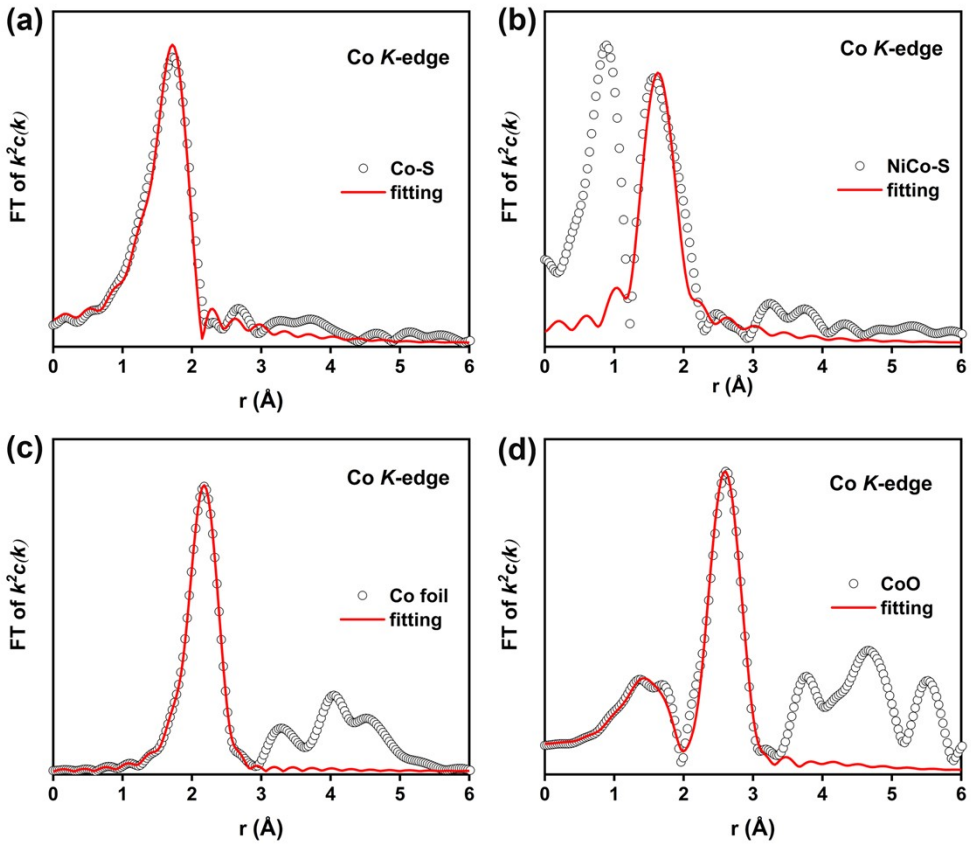

Fig. S12. Experimental and best fitted EXAFS spectra in the R space of Co-S (a), and NiCo-S (b) with Co foil (c) and CoO (d) as the references at the Co K-edge.

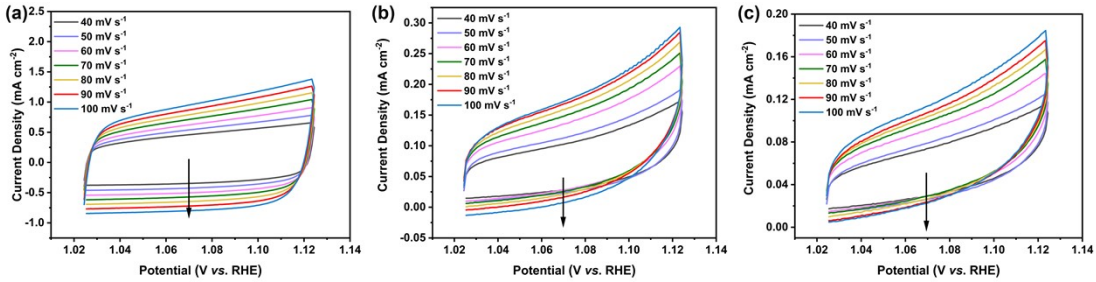

Fig. S13. Cyclic voltammetry curves of the (a) NiCo-O, (b) Ni-S and (c) Co-S electrodes from 40 to 100 mV s^{-1}.

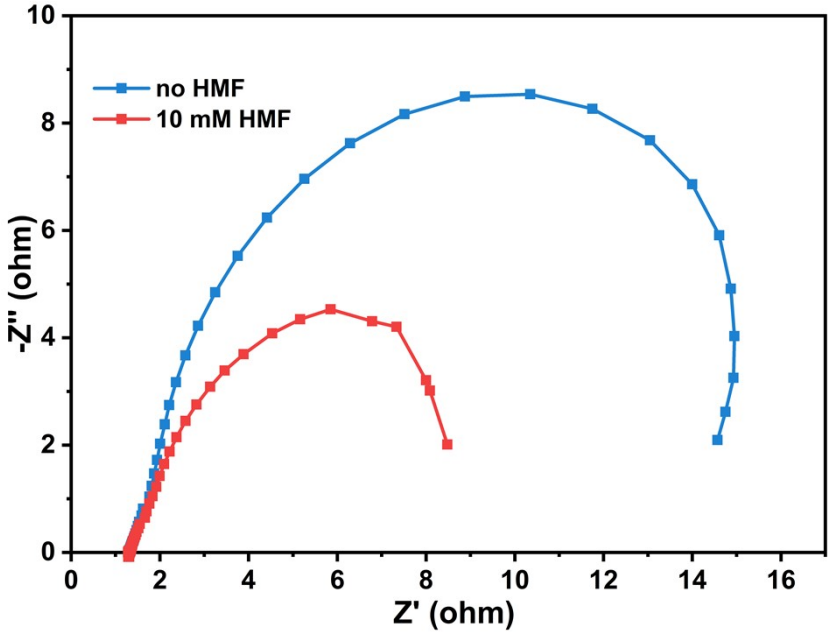

Fig. S14. EIS of NiCo-S electrode with or without 10 mM HMF.

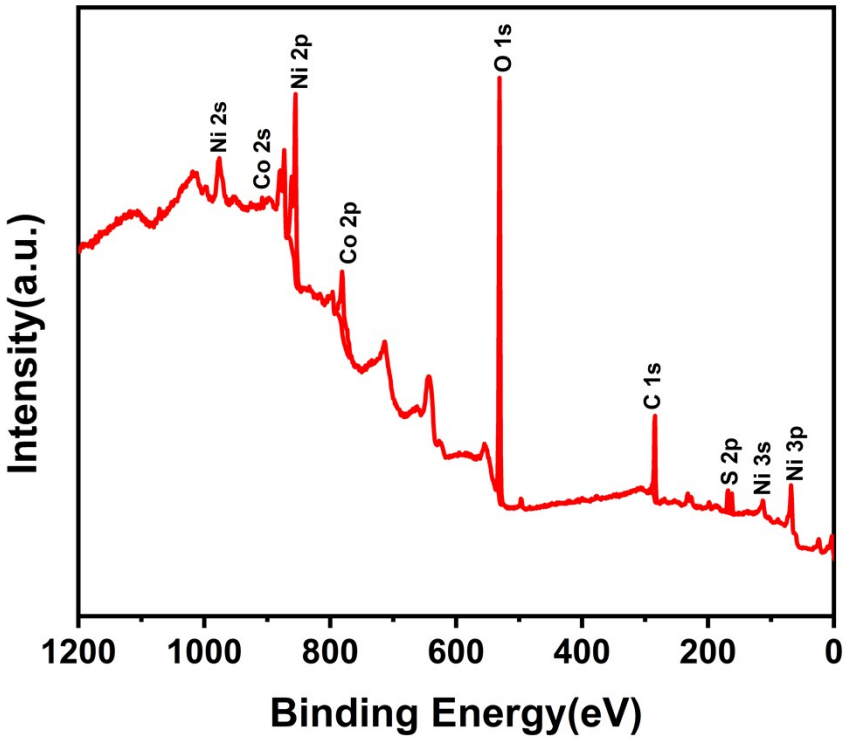

Fig. S15. XPS survey of the NiCo-S catalyst.

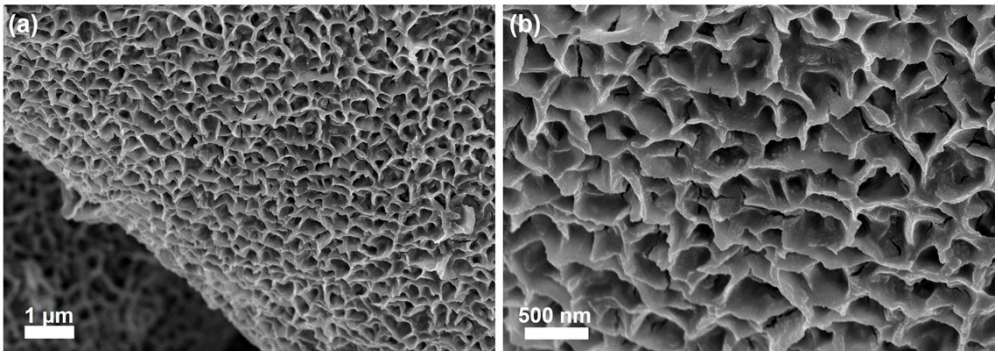

Fig. S16. SEM images of NiCo-S electrode after electrolysis.

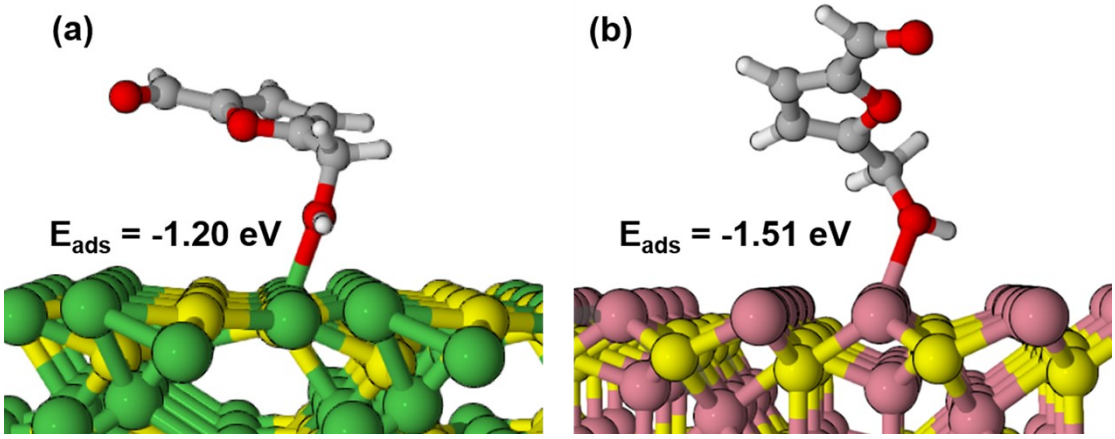

Fig. S17. The most sable C-OH single group adsorption model on NiS and Co_3S_4.

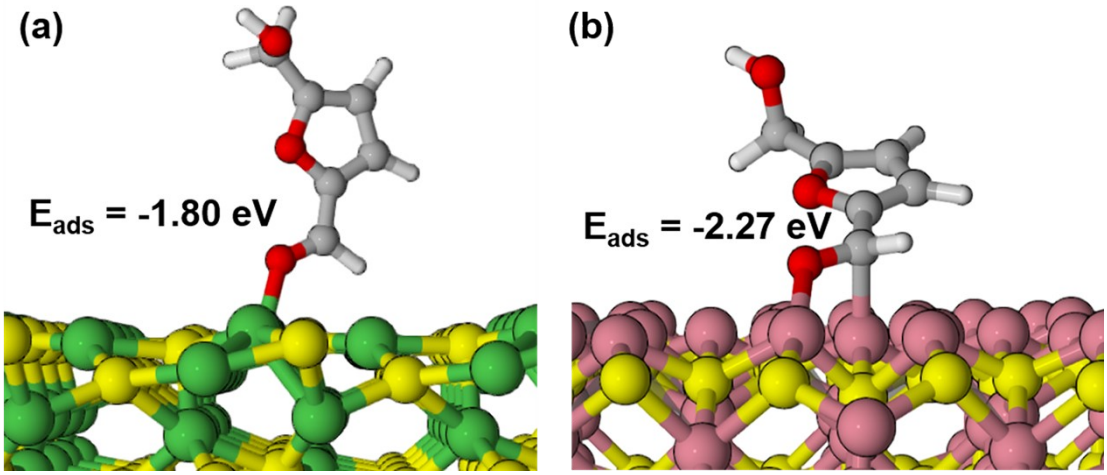

Fig. S18. The most sable CH=O single group adsorption model on NiS and Co_3S_4.

Table S1. Percentage composition of NiCo-S from ICP-OES results.

Sample	Elements	Sample element content Cx(mg kg^{-1})	Sample element content W(%)
NiCo-S	Ni	100992.65	10.10
	Co	228036.42	22.80
	S	186272.20	18.63

Table S2. The BET surface area and pore diameter of the different catalysts.

Samples	**S_{BET} (m^2 g^{-1})**	**Pore diameter (nm)**
NiCo-S	59.90	10.12
NiCo-O	57.80	16.10
Ni-S	8.29	6.81
Co-S	31.50	6.848

Table S3. Comparison of the performance for bimetallic catalysts.

Catalysts	Eletrolyte	Onset potential/V (*vs.* RHE)	Oxidation potential/V (*vs.* RHE)	Yield (%)	Conversion (%)	Selectivity (%)	FE (%)	Ref.
Pd_1Au_2/C	0.1M KOH+20mM HMF	0.3	0.9	83	100			1
CuxS@NiCo-LDH	1M KOH+10mM HMF	1.25	1.32	99	100		99	2
$NiCo_2O_4$	1M KOH+5mM HMF	1.2	1.5	90.4	99.6	90.8	87.5	3
$NixCo_3$-xO_4	0.1M KOH+10mM HMF	1.35	1.55	90	100		100	4
NiFe-LDH	1M KOH+10mM HMF	1.25	1.33	98	98		98.6	5
$CuNi(OH)_2$/C	1M KOH+5Mm HMF	1.38	1.45	93.3	98.8		94.4	6
$NiCo_2S_4$	1M KOH+10mM HMF	1.2	1.45	97.1	99.1	98	96.4	This work

Table S4. Summary of coordination number of Co-Co, Co-S, Ni-Ni and Ni-S in catalysts corresponding to Fig. 4.

Sample	Shell	Bond length (Å)	Coordination Number	σ^2 ($Å^2$)	E_0 shift (eV)	R-factor ($*10^{-3}$)
Co foil	Co-Co	2.49	12	0.006	7.9	4.2
Co-S	Co-S	2.31	6	0.006	-5.8	12.2
NiCo-S	Co-S	2.33	5.2	0.006	0.0	18.2
Ni foil	Ni-Ni	2.48	12	0.006	5.9	1.4
Ni-S	Ni-S	2.28	6	0.0011	-5.3	11.9
NiCo-S	Ni-S	2.29	5.4	0.007	-8.5	4.7

Table S5. Summary of the ECSA results for NiCo-S, NiCo-O, Ni-S and Co-S catalysts.

	NiCo-S	NiCo-O	Ni-S	Co-S
C_{dl} (mF)	15.89	15.72	1.52	0.78
C_s (mF cm^{-2})	0.04	0.04	0.04	0.04
ECSA (cm^2)	397.25	393	38	19.50

Table S6. Corresponding fitted parameters of proposed equivalent circuit for NiCo-S, NiCo-O, Ni-S and Co-S catalysts.

Catalysts	R_s (mΩ)	R_{ct} (mΩ)	Q_{dl} (μF)	ZW (DW)
NiCo-S	129	668	28.8	1.98
NiCo-O	0.0739	824	66.2	5.37
Co-S	0.726	1060	28.2	6.91
Ni-S	126	777	55.3	2.65

Table S7. Percentage composition of Ni and Co for the fresh and post NiCo-S samples from XPS results.

Percentage (%)	Ni^{3+}	Ni^{2+}	Co^{3+}	Co^{2+}
Fresh NiCo-S	11.2	35.2	24.1	44.25
Post NiCo-S	15.5	30.4	15.48	39.15

Table S8. Percentage composition of post-electrolytic solution from ICP-OES results.

Elements	Sample element content Cx (mg L^{-1}) in solution
Ni	<0.02
Co	<0.02
S	0.17

References

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7. Deng, M. Li, Y. Fan, L. Wang, X.-Z. Fu and J.-L. Luo, Applied Catalysis B: Environmental, 2020, **278**, 119339-119351.s