Supporting Information

Coupling Efficient Biomass Upgrading with H_2 Production via Bifunctional Cu_xS@NiCo-LDHs Core-Shell Nanoarray Electrocatalysts

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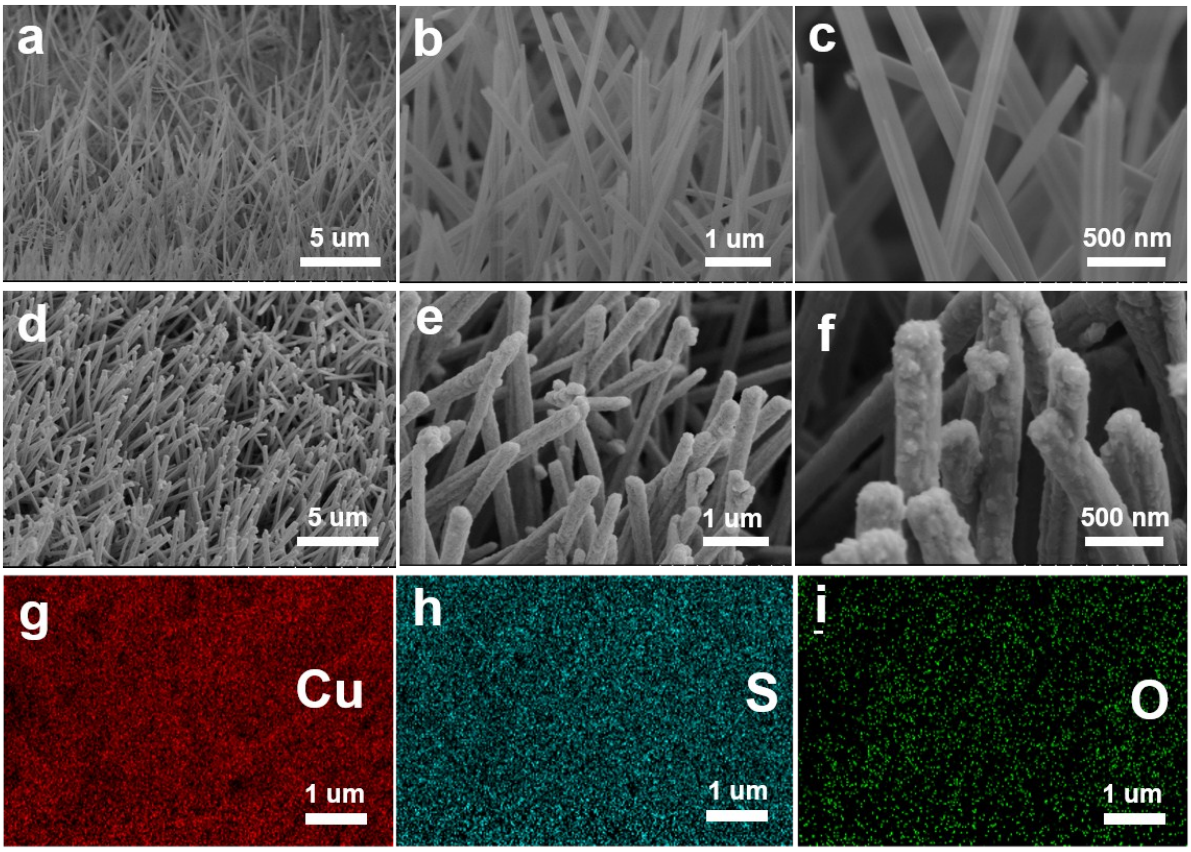


Figure S1. SEM images of $Cu(OH)_2$ NAs/CF (a, b, c), Cu_xS NAs/CF (d, e, f) and elemental mappings of Cu, S and O (g, h, i).

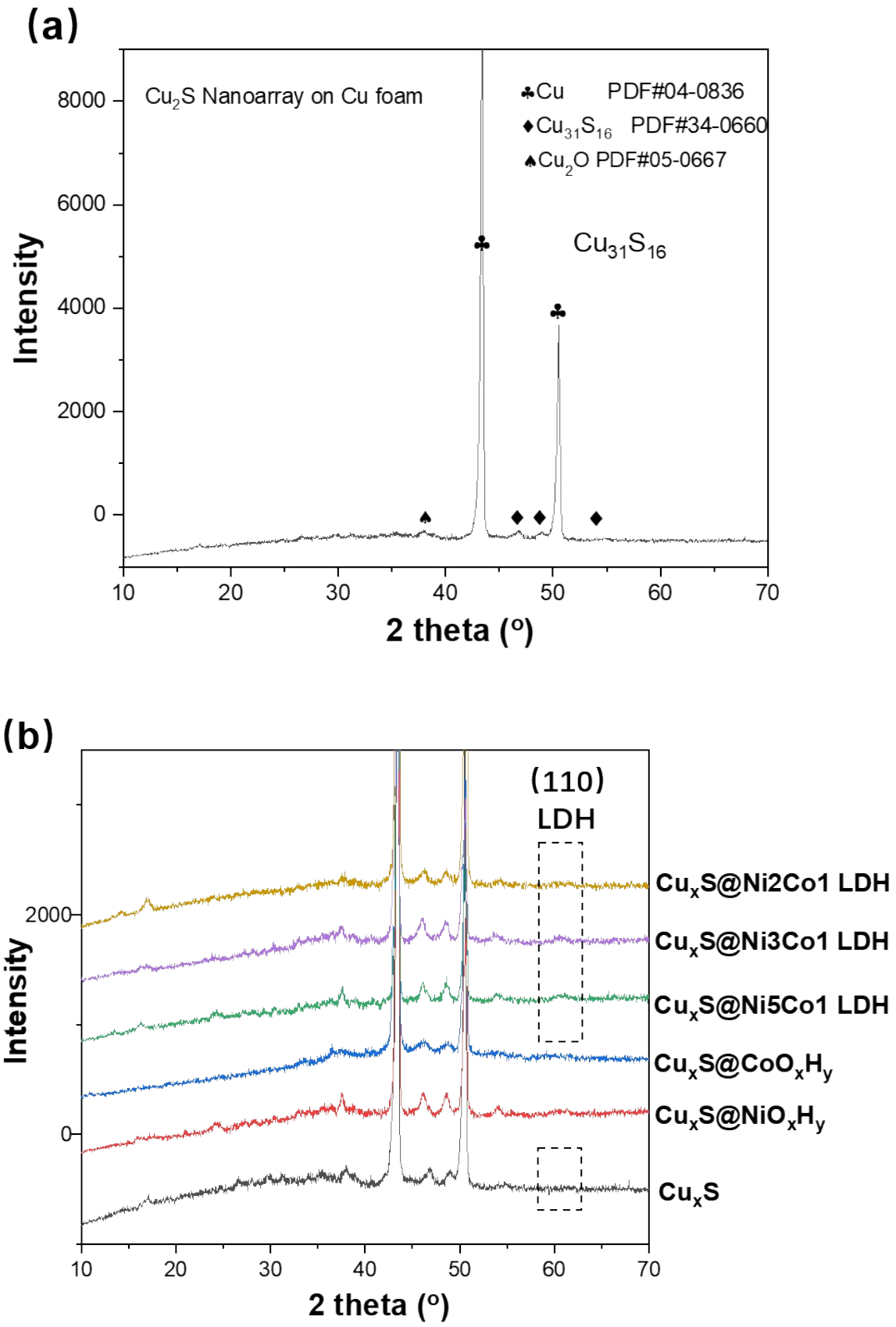


Figure S2. XRD patterns of (a) Cu_xS NAs/CF and (b) as-prepared $Cu_xS@NiO_xH_y$, $Cu_xS@CoO_xH_y$ and Cu_xS@NiCo LDHs.

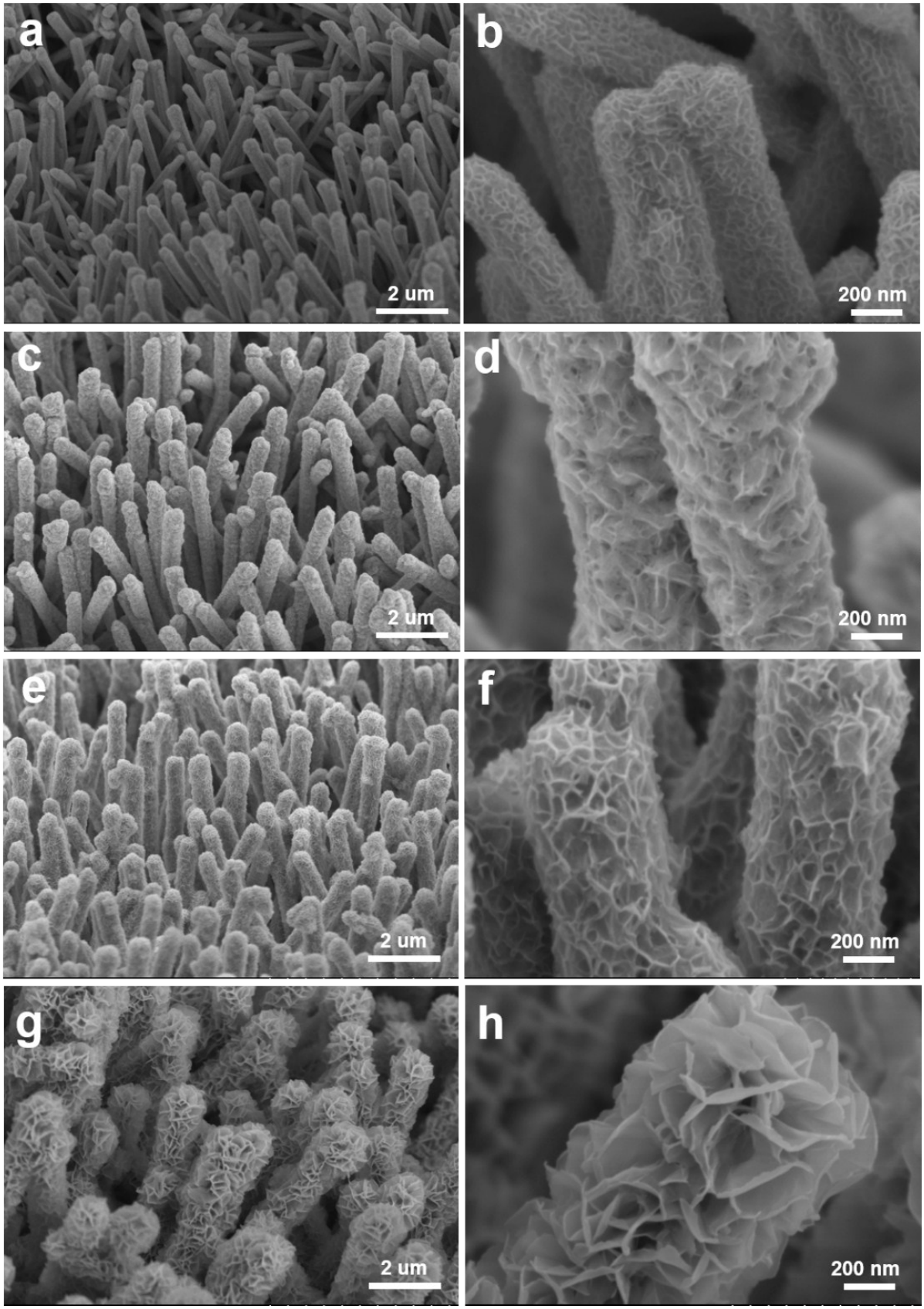


Figure S3. SEM images of (a, b) $Cu_xS@NiO_mH_n$, (c, d) $Cu_xS@Ni_{0.83}Co_{0.17}O_mH_n$, (e, f) $Cu_xS@Ni_{0.67}Co_{0.33}O_mH_n$ and (g, h) $Cu_xS@CoO_mH_n$.

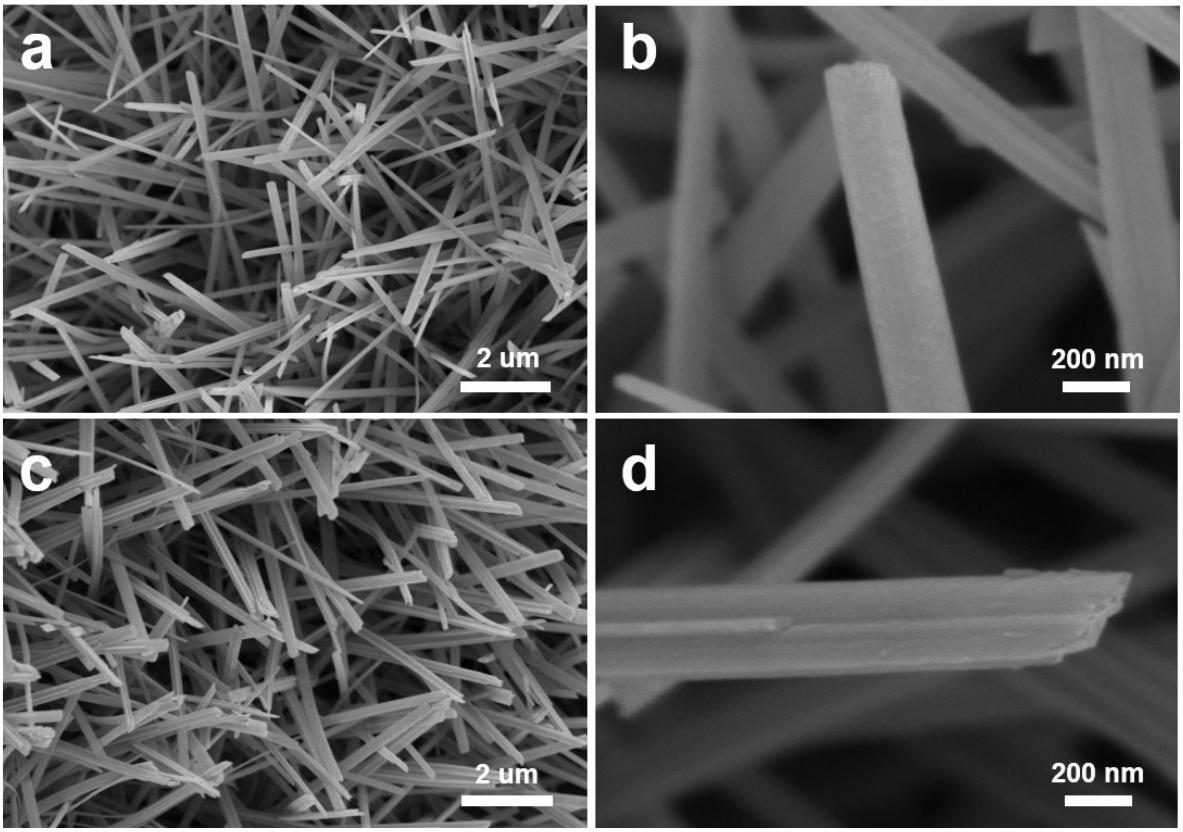


Figure S4. SEM images showing unsuccessful electrodeposition of $Ni_{0.75}Co_{0.25}$-LDH and $Co(OH)_2$ when $Cu(OH)_2$ NAs/CF were used as substrate. Without the sulfidation step the electrodeposition resulted in inhomogeneous electrode and large portion of the nanowires were not coated.

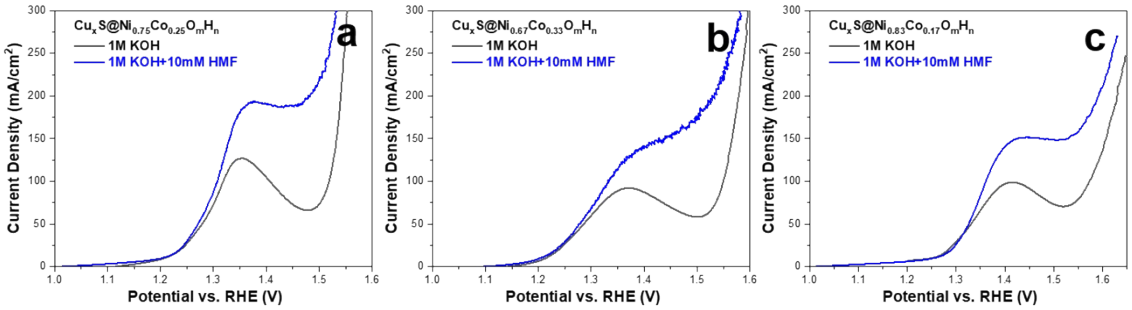


Figure S5. LSV curve comparisons of electrochemical HMF Oxidation (blue) and H_2O oxidation (black) catalyzed by $Cu_xS@Ni_{0.75}Co_{0.25}O_mH_n$, $Cu_xS@Ni_{0.67}Co_{0.33}O_mH_n$ and $Cu_xS@Ni_{0.83}Co_{0.17}O_mH_n$.

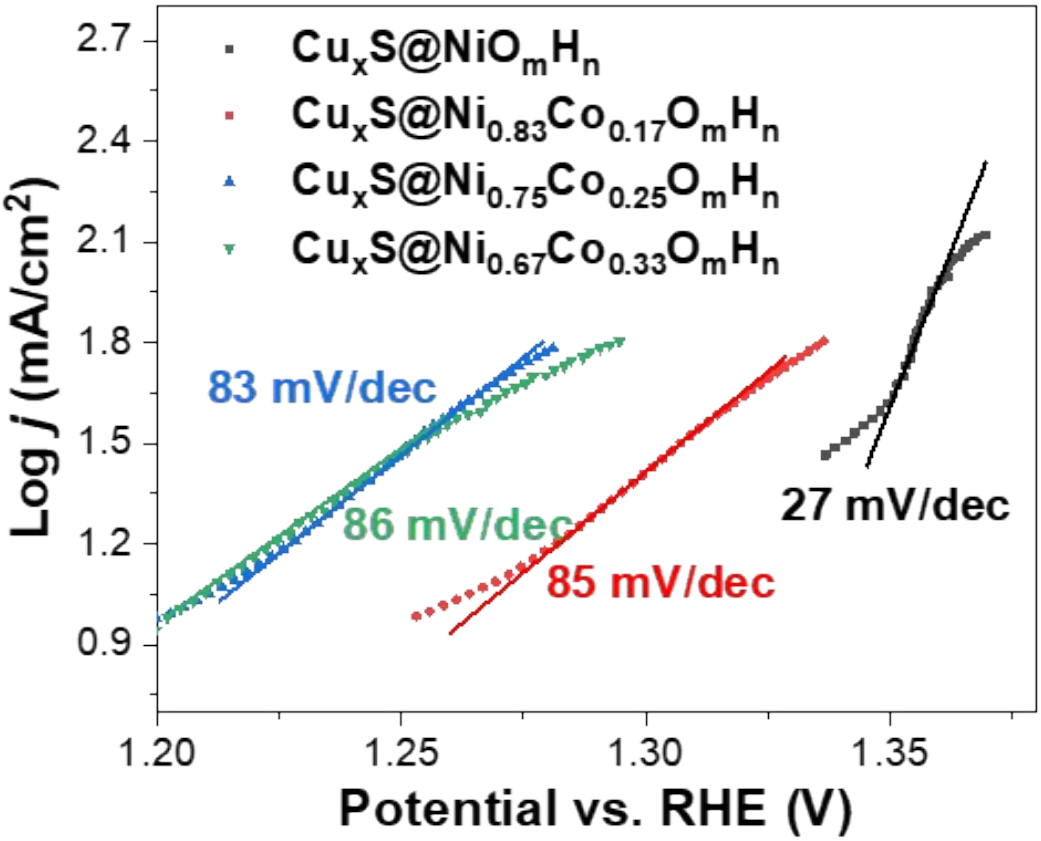


Figure S6. Tafel plots of as-prepared core-shell composites with various Ni to Co ratio towards HMF oxidation.

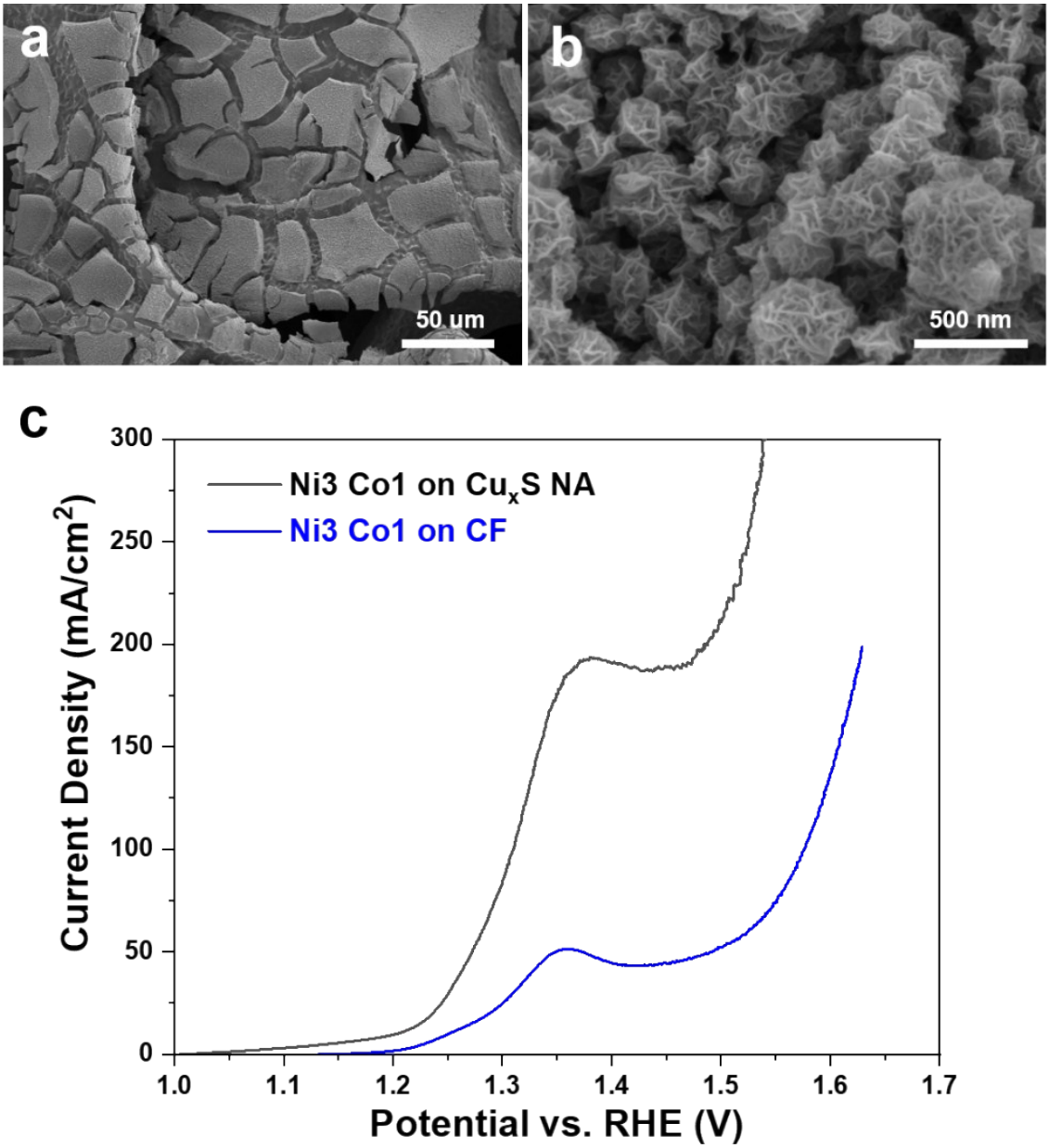


Figure S7. a, b) SEM images of electrodeposited $Ni_{0.75}Co_{0.25}O_mH_n$ on copper foam. c) Comparison of electrochemical HMF oxidation activity of $Ni_{0.75}Co_{0.25}O_mH_n$/CF and Cu_xS@$Ni_{0.75}Co_{0.25}O_mH_n$.

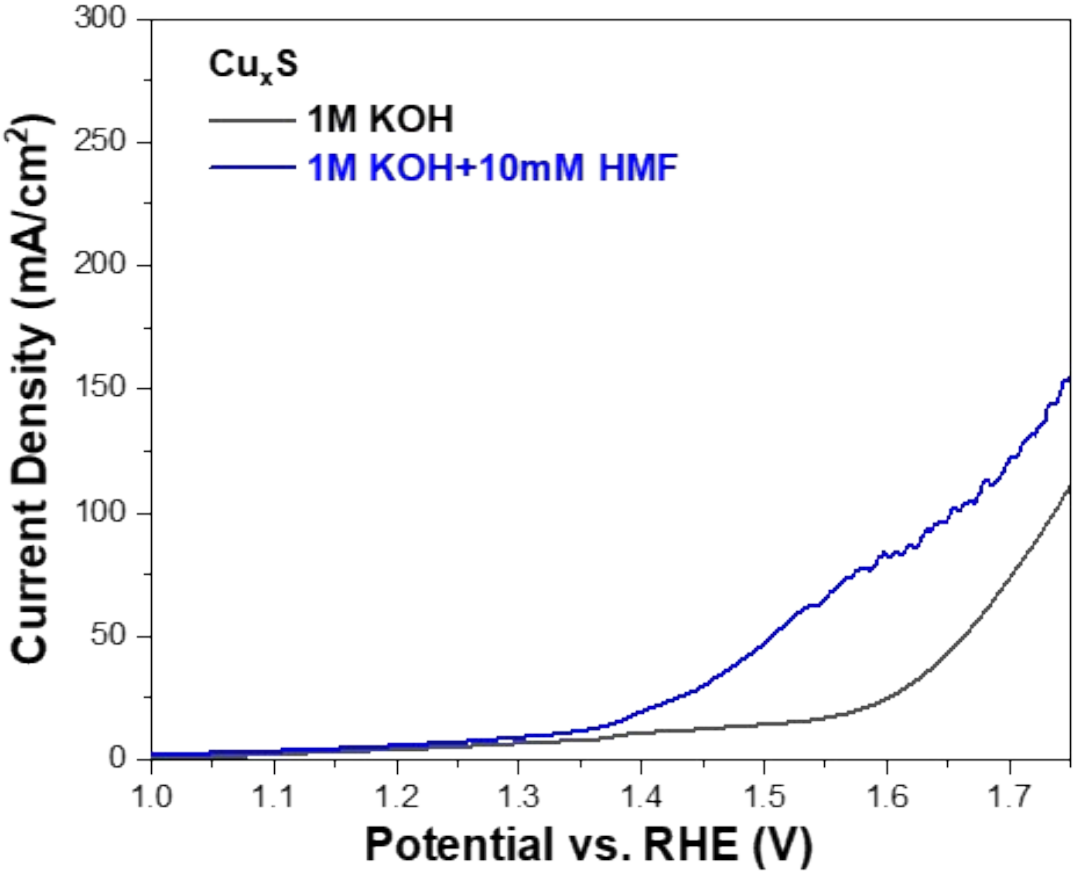


Figure S8. LSV curve comparisons of electrochemical HMF Oxidation (blue) and H_2O oxidation (black) catalyzed by Cu_xS NAs/CF.

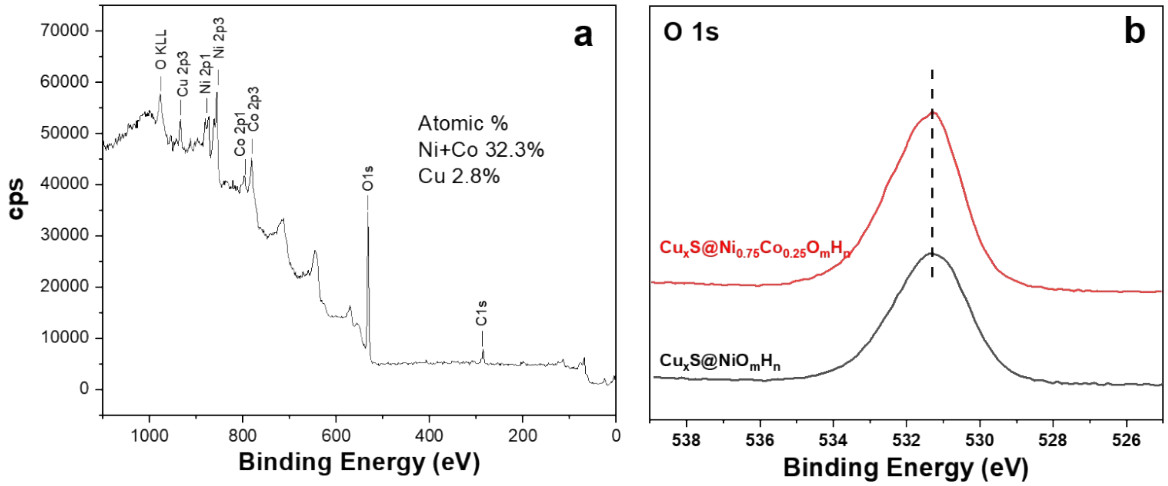


Figure S9. a) Full-range XPS spectra of $Cu_xS@Ni_{0.75}Co_{0.25}O_mH_n$. b) O1s spectra of $Cu_xS@NiO_mH_n$ and $Cu_xS@Ni_{0.75}Co_{0.25}O_mH_n$.

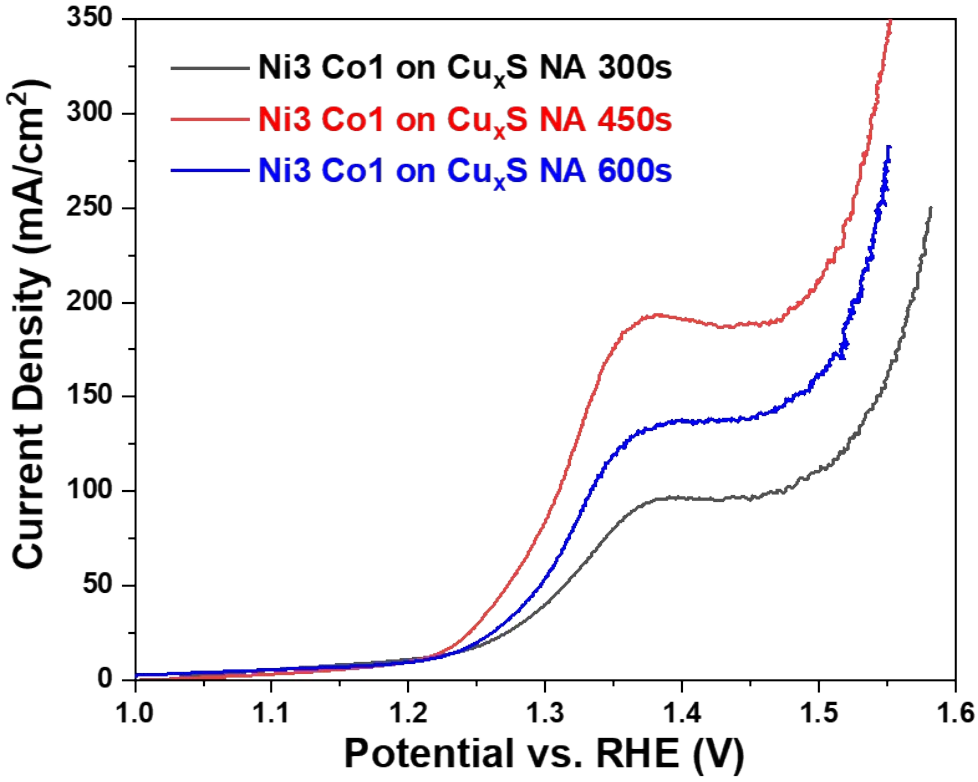


Figure S10. LSV curves of electrochemical HMF oxidation catalyzed by $Cu_xS@Ni_{0.75}Co_{0.25}O_mH_n$ with various electrodeposition time.

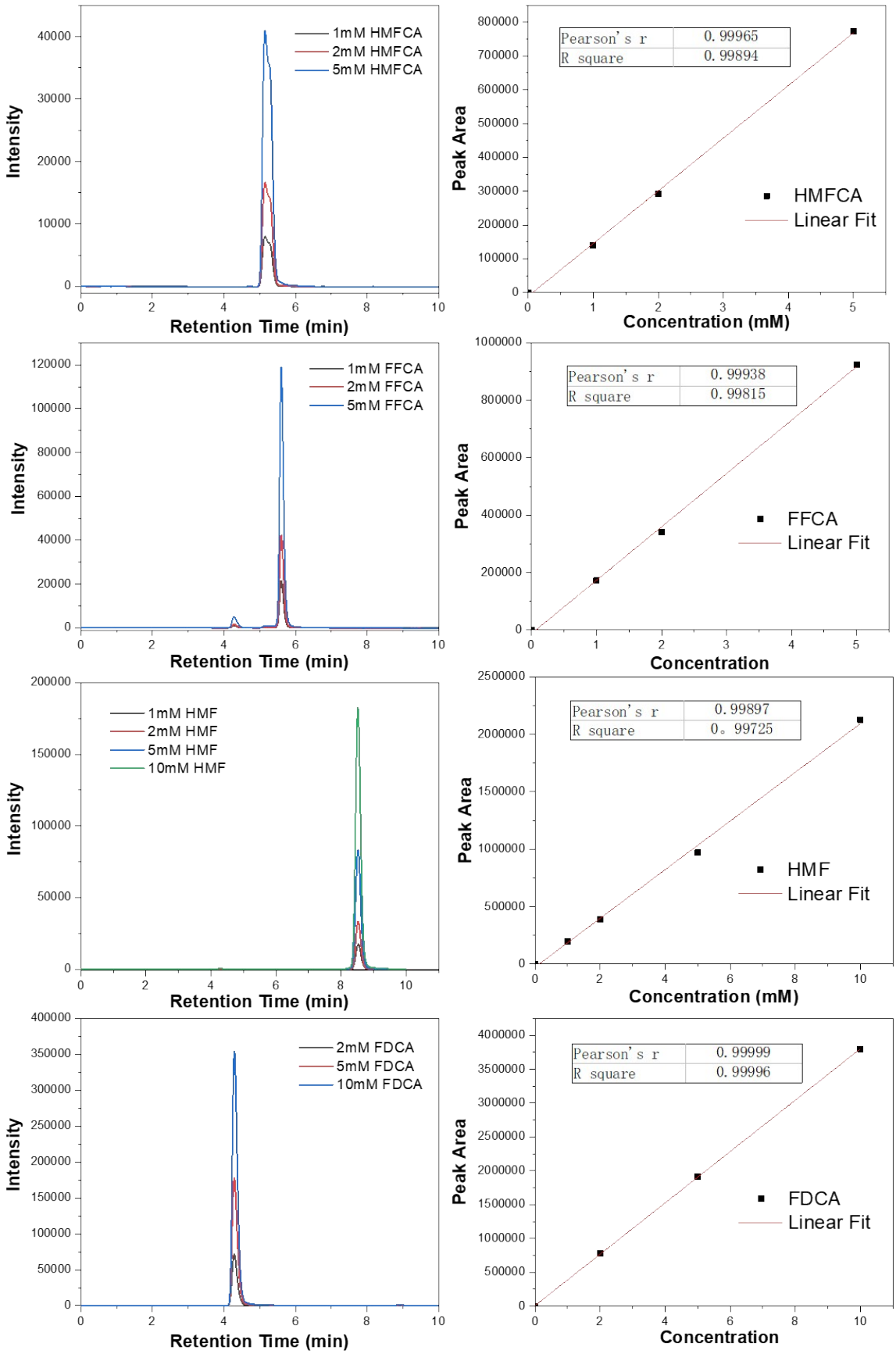


Figure S11. Reference HPLC spectra and calibration curves for HMFCA, FFCA, HMF and FDCA.

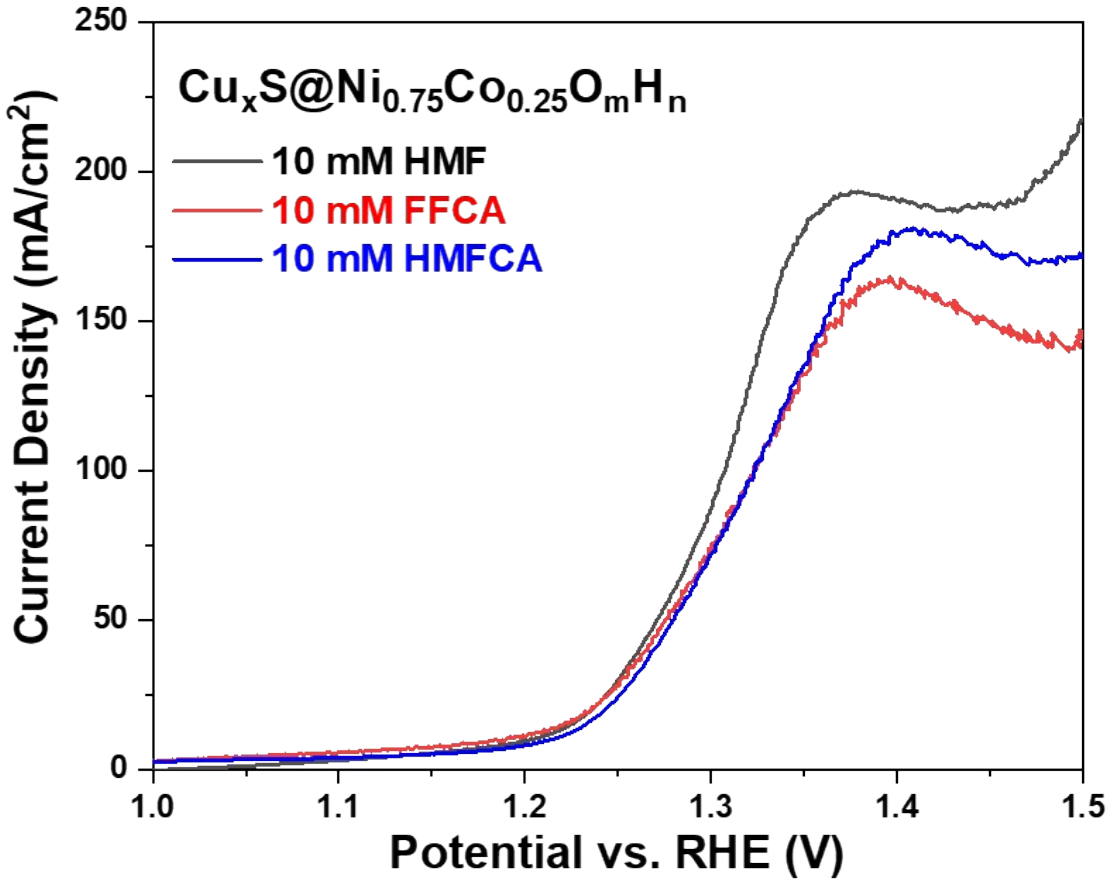


Figure S12. LSV curve comparison of HMF, FFCA and HMFCA oxidation catalyzed by $Cu_xS@Ni_{0.75}Co_{0.25}O_mH_n$.

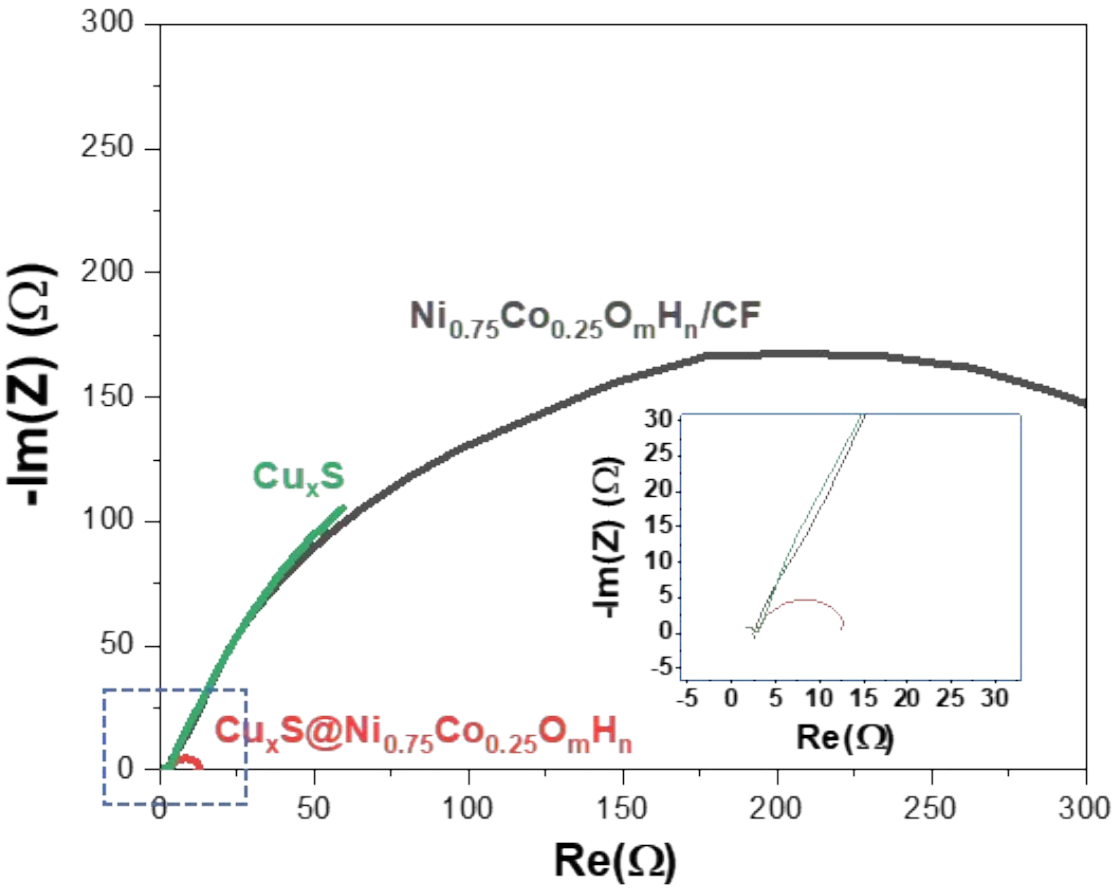
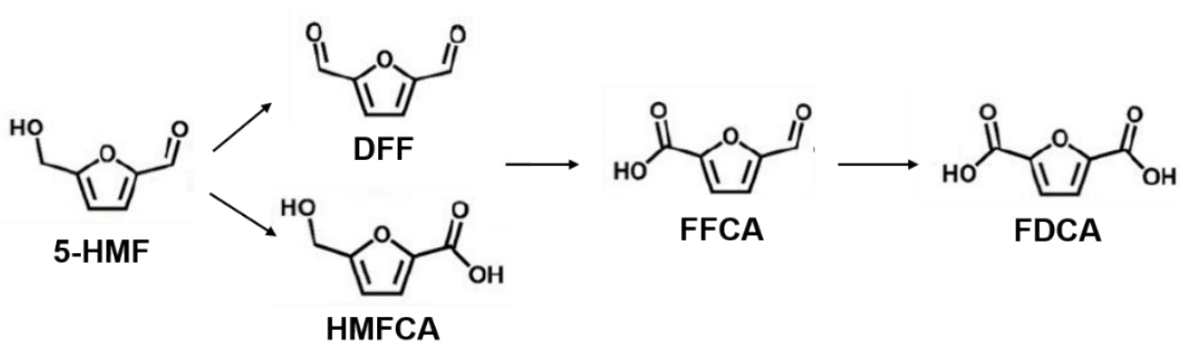


Figure S13. Nyquist plots of Cu_xS, $Cu_xS@Ni_{0.75}Co_{0.25}O_mH_n$ and $Ni_{0.75}Co_{0.25}O_mH_n$ electrodeposited on copper foam (@-1.1 V *vs* Hg/HgO). The inset is the enlarged EIS plots of the square region.



Scheme S1. Proposed reaction pathways of 5-HMF oxidation.

Table S1. Atomic percentage of O, S and Cu as obtained from the EDX measurements.

Element	wt%	wt% Sigma	Atom%
O	2.04	0.12	6.52
S	18.60	0.14	29.65
Cu	79.36	0.17	63.83
Total	100.00		100.00

Table S2. Ni/Co ratio in prepared Cu_xS@NiCo LDHs as determined by ICP-OES.

Samples	Theoretical Ni/Co	Measured Ni/Co by ICP-OES
$Cu_xS@Ni_{0.83}Co_{0.17}O_mH_n$	83.3%/16.7%	85.7%/14.3%
$Cu_xS@Ni_{0.75}Co_{0.25}O_mH_n$	75%/25%	74.3%/25.7%
$Cu_xS@Ni_{0.67}Co_{0.33}O_mH_n$	66.7%/33.3%	68.4%/31.6%

Table S3. Comparison of electrocatalytic activity towards HMF/organic substrate oxidation for recently reported electrocatalysts.

Electrode materials	Electrolyte/ Oxidized substrate	[a] Current density at 1.3 V vs RHE (mA/cm^2)	[b] Current density at 1.4 V vs RHE (mA/cm^2)	Tafel Slope (mV/dec)	Reference
Ni_xB/Nickel Foam (NF)	1 M KOH/ 10 mM HMF	0 (onset at ~ 1.38 V)	~ 10	-	1
CoxB/NF	1 M KOH/ 10 mM HMF	~ 3	~ 22	-	2
Ni_2P/NF	1 M KOH/ 10 mM HMF	0 (onset at ~ 1.36 V)	> 200	-	3
Ni_3S_2/NF	1 M KOH/ 10 mM HMF	0	~ 200	-	4
NiFe LDH/Carbon Fiber Paper	1 M KOH/ 10 mM HMF	~ 10	~ 90	75	5
$NiCo_2O_4$ nanoarrays/NF	1 M KOH/ 10 mM HMF	~ 1.5	~ 3.5	135.7	6
Co-P/CF	1 M KOH/ 50 mM HMF	~ 2	~ 50	-	7
NiSe/NF	1 M KOH/ 10 mM amines	0	~ 170	-	8
$Cu_xS@NiO_mH_n$	**1 M KOH/ 10 mM HMF**	**15.6**	**189.7**	**24**	**This work**
$Cu_xS@CoO_mH_n$	**1 M KOH/ 10 mM HMF**	**11.4**	**80.0**	**188**	**This work**
$Cu_xS@Ni_{0.75}Co_{0.25}O_mH_n$	**1 M KOH/ 10 mM HMF**	**87.6**	**[c]187 @ 1.36 V**	**83**	**This work**

[a,b] It should be mentioned that these values are not provided in most cases, therefore they are read from the figures in the corresponding publication.
[c] As can be observed from the linear scan, the oxidation current is likely limited by the mass transport and does not increase after this potential.

Table S4. Comparison of electrocatalytic activity towards hydrogen evolution reaction for recently reported transition metal-based electrocatalysts.

Electrode materials	Electrolyte	Overpotential @ 10 mA/cm^2 (mV)	Tafel Slope (mV/dec)	Reference
Au doped-Ni Co hydroxide	1 M KOH	200	92	9
Cu@NiFe LDH/CF	1 M KOH	116	58.9	10
$NiCoP_x$	1 M KOH	63	34.3	11
NiFe LDH/CeO_x/NF	1 M KOH	154	101	12
CoP/CC	1 M KOH	209	129	13
$Ni_{4.3}Co_{4.7}S_8$	1 M KOH	148	90	14
CoS_x ultrathin nanosheets	1 M KOH	127	117	15
$Co_{5.47}N$ NP@N-doped porous carbon	1 M KOH	149	86	16
TiO_2@Co_9S_8	1 M KOH	139	65	17
$NiFeO_x$@NiCu alloy	1 M KOH	66	67.8	18
$(NiCo)_{0.85}Se$	1 M KOH	169	115.6	19
Cu_xS@$Ni_{0.75}Co_{0.25}O_mH_n$	**1 M KOH**	**107**	**35**	**This work**

Table S5. Performance comparison of reported two-electrode electrolyzer coupling novel anodic reactions and hydrogen production.

Electrode materials	Anodic Reaction	Cell Voltage @ 10 mA/cm^2 (V)	Cell Voltage @ 50 mA/cm^2 (V)	Cell Voltage @ 100 mA/cm^2 (V)	Reference
Ni_2P/Nickel Foam (NF) || Ni_2P/Nickel Foam (NF)	HMF Oxidation	1.44	1.58	-	3
Ni_3S_2/NF || Ni_3S_2/NF	HMF Oxidation	1.46	1.58	1.64	4
NiSe/NF || CoP	Primary Amines Oxidation	~1.44	-	-	8
NiMoO-Ar/NF || NiMoO-H_2/NF	Urea Oxidation	1.38	1.48	1.55	20
$Cu_xS@Ni_{0.75}Co_{0.25}O_mH_n$ || $Cu_xS@Ni_{0.75}Co_{0.25}O_mH_n$	**HMF Oxidation**	**1.34**	**1.49**	**1.58**	**This work**

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