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Supporting information

MoS_2-Catalyzed Selective Electrocatalytic Hydrogenation of Aromatic Aldehydes in an Aqueous Environment

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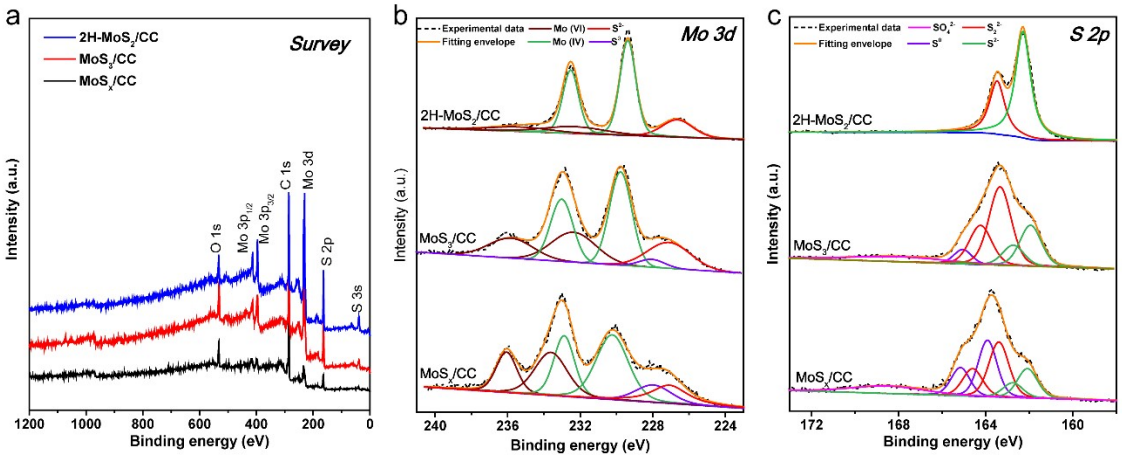


Figure S1 XPS data of the molybdenum sulfide seed layer obtained at different temperature.

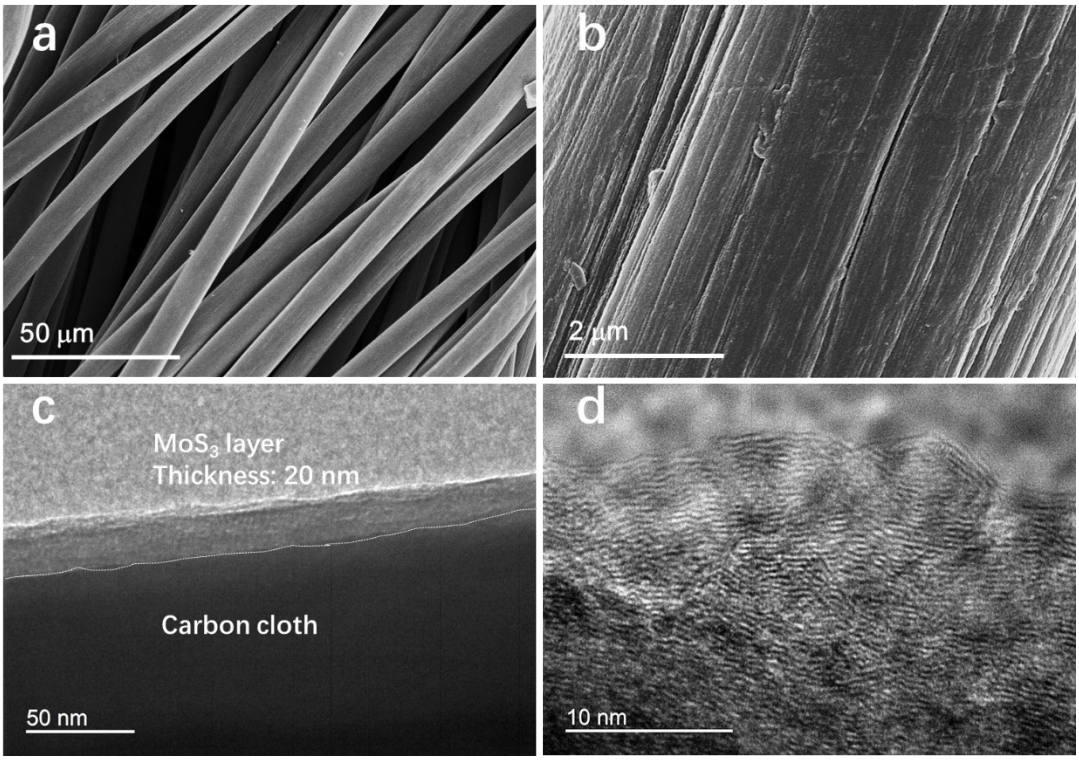


Figure S2 Surface characterization of the MoS_3/CC; (a) low magnification SEM image; (b) high magnification SEM image; (c) TEM and d) HRTEM.

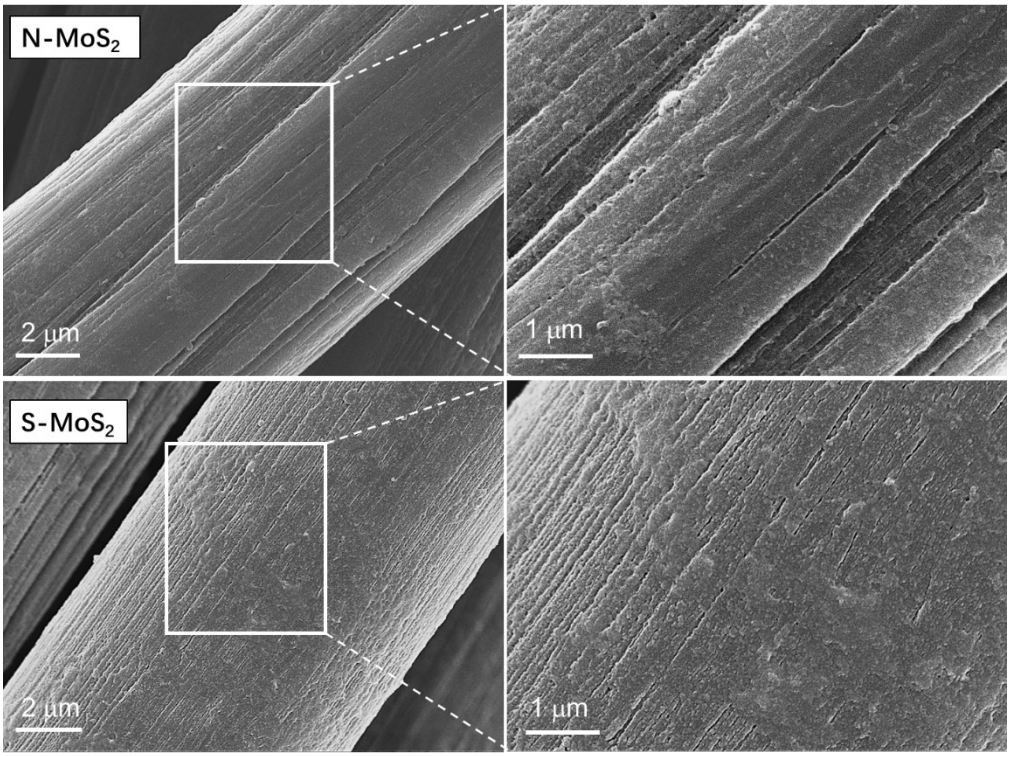


Figure S3 SEM images of the N-MoS_2 and S-MoS_2 electrode

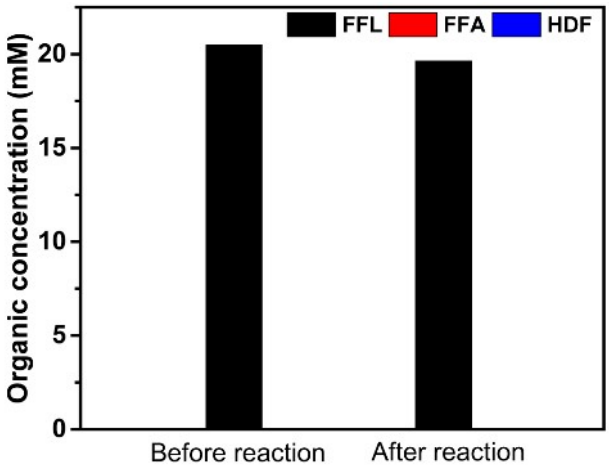


Figure S4 Open-circuit control experiment performed by bubbling H_2 into the electrolyte with FFL for 2h

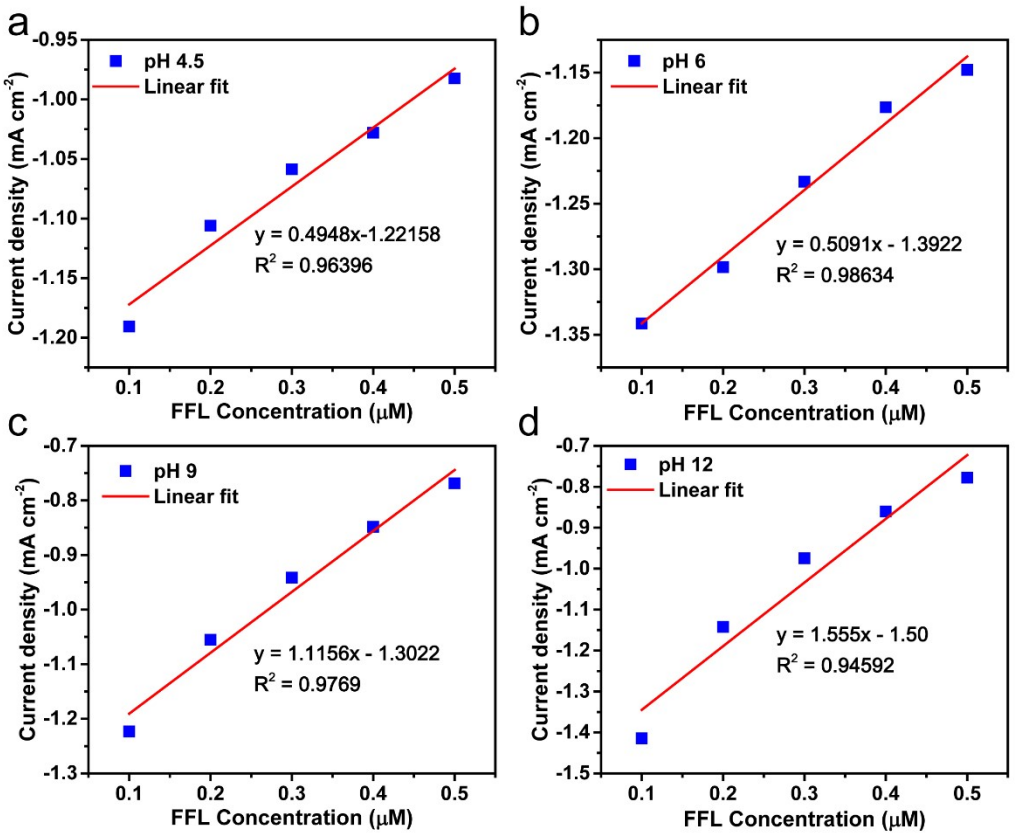


Figure S5 Fitting line shows the decrease in H_{UPD} current in the first five concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 μM) over the S-MoS_2 electrodes at (a) pH 4.5, (b) pH 6, (c) 9, and (d) 12 at room temperature.

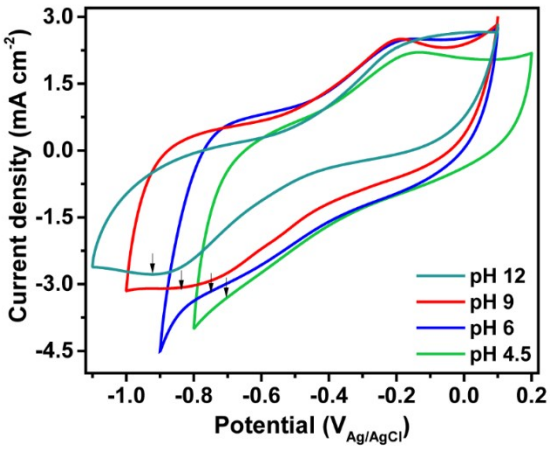


Figure S6 Cyclic voltammogram measurements on the S-MoS_2 electrode in the hydrogen underpotential deposition potential (H_{UPD}) range without adding FFL at 50 mV/s, pH 9 buffer at room temperature.

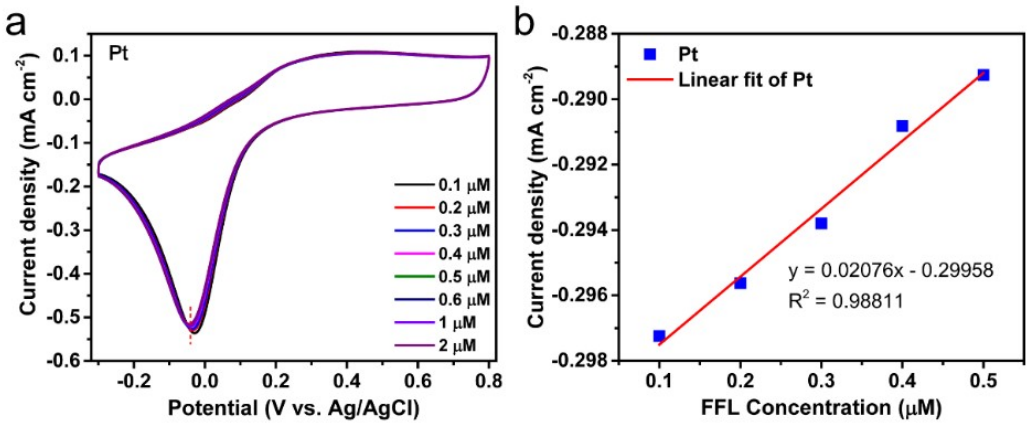


Figure S7 a) H_{UPD} experiment conducted on the Pt electrode at pH 9 electrolyte. The H_{UPD} potentials were marked with a red dotted line on the voltammograms; b) Fitting line shows the decrease in H_{UPD} current in the first five concentrations (0.1, 0.2, 0.3, 0.4 and 0.5 μM) over the Pt electrodes

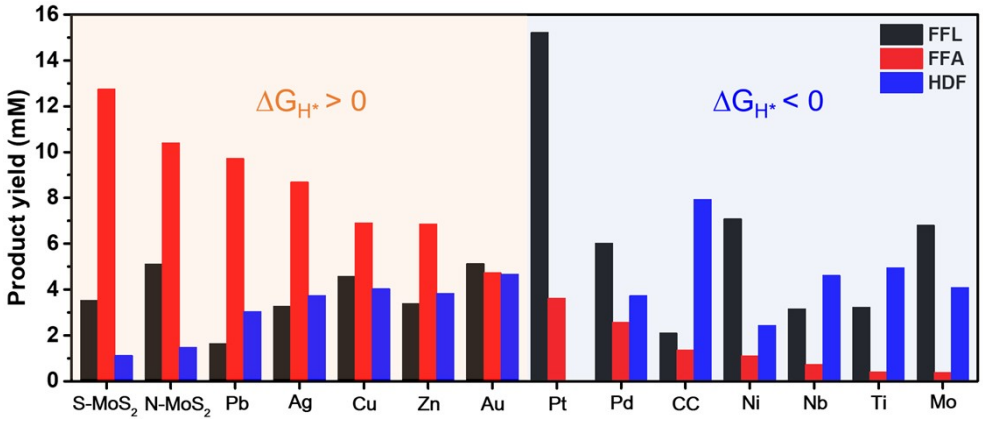


Figure S8 ECH study of furfural using different common ECH metals electrodes. All electrodes were evaluated from a bulk electrolysis of reaction of 20 mM furfural in 4:1 (v. /v.) pH 9 buffer: ACN at j = 10 mA cm^{-2} at room temperature. The plus or minus sign of ΔG_{H^*} of the electrodes are referring to the hydrogen volcano plot reported by Paola et al.[1]

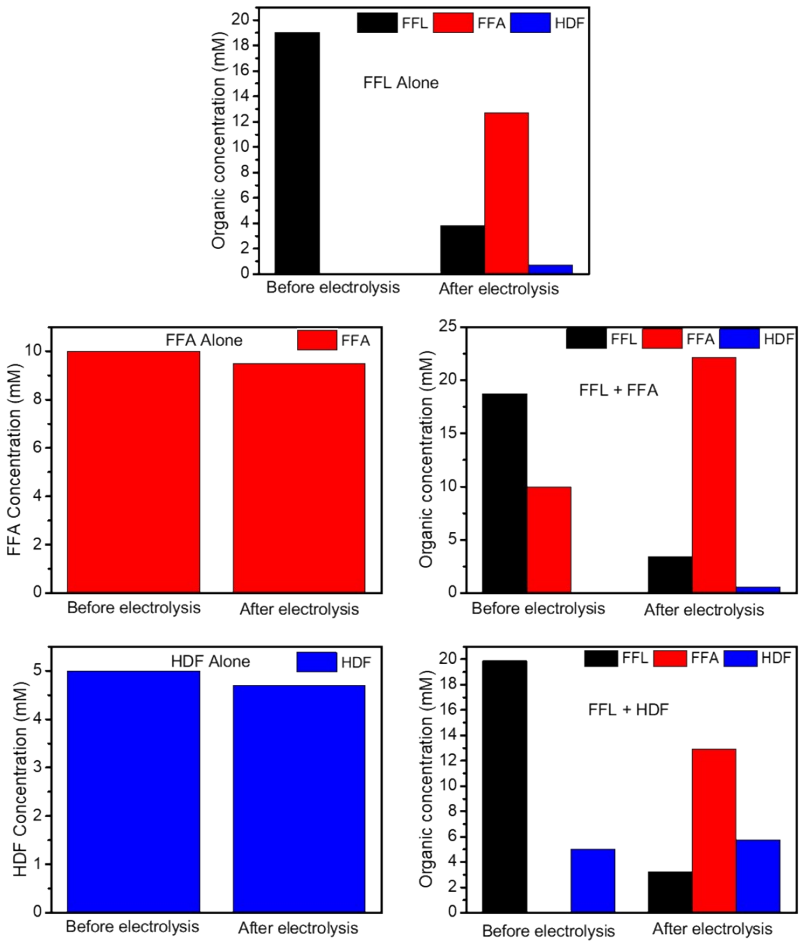


Figure S9 Control experiments on the electrolysis of reactant and products.

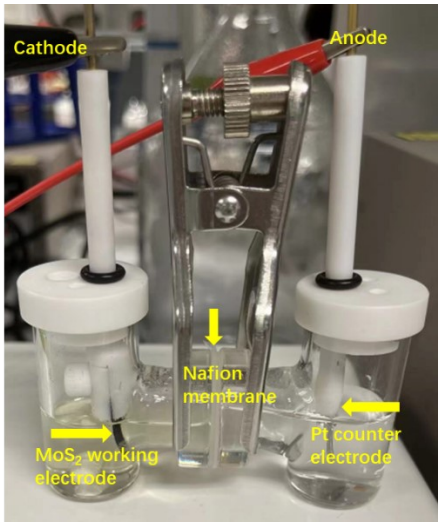


Figure S10 Electrochemical reaction setup

Appendix: GC-MS and HPLC results for organic substrates electrolysis

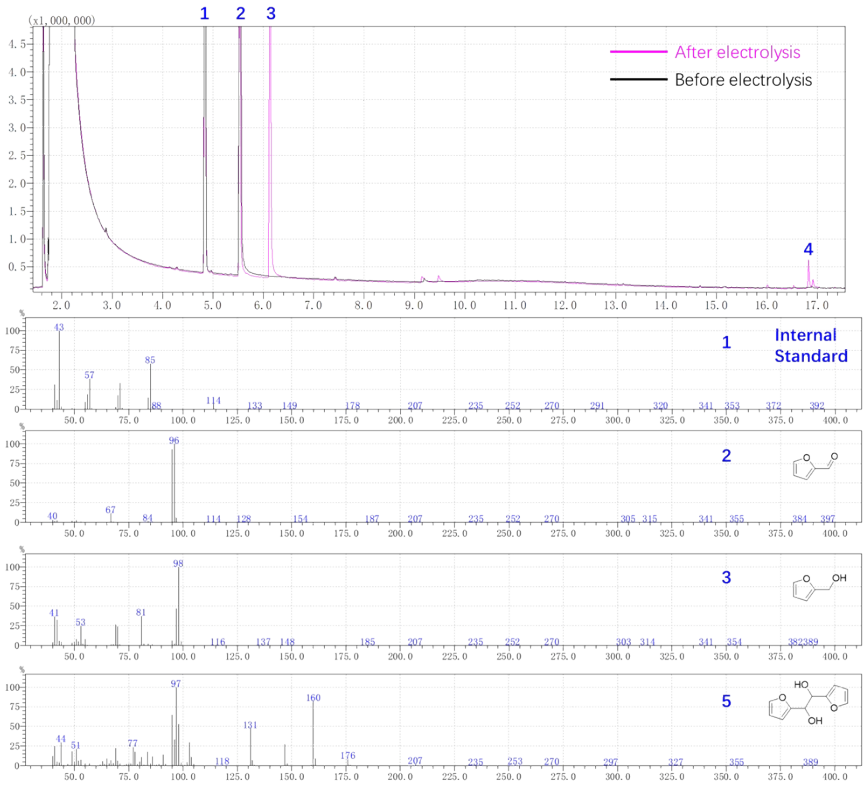


Figure S11 Represents GC-MS spectra for ECH of furfural at pH 9.

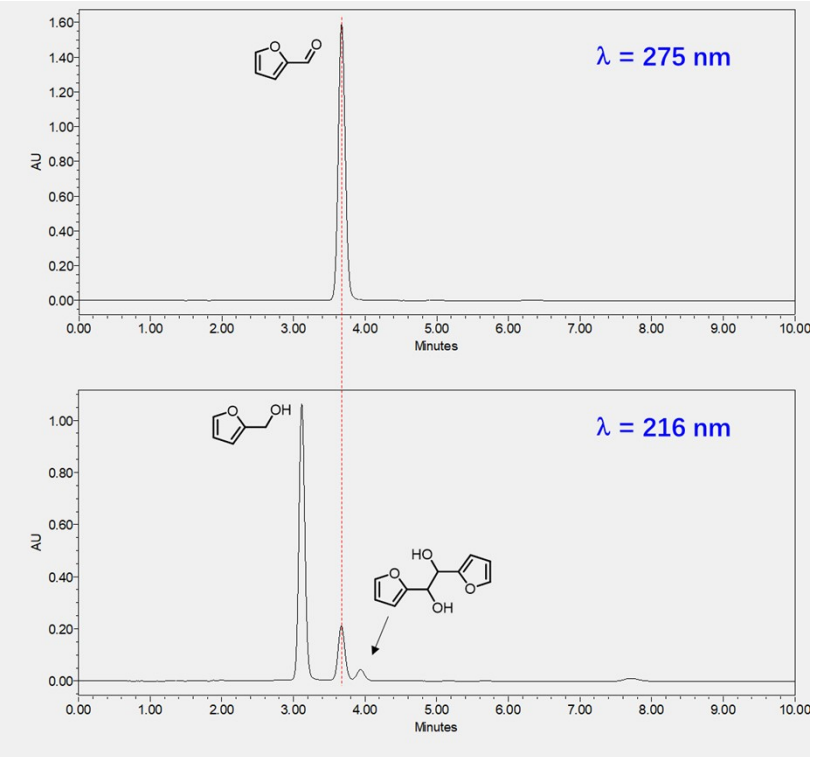


Figure S12 Representative HPLC spectra of ECH of furfural at pH 9. Detect wavelength: λ = 216 nm.

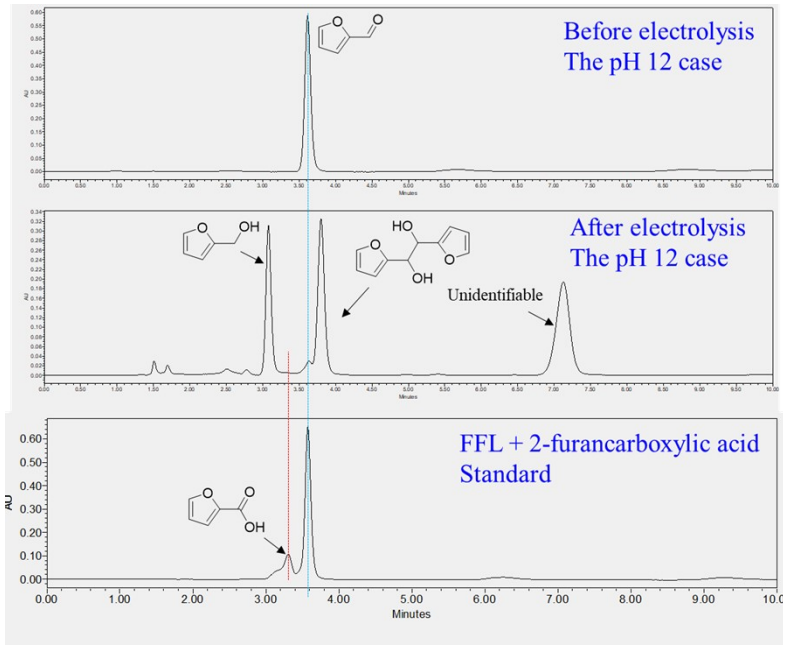
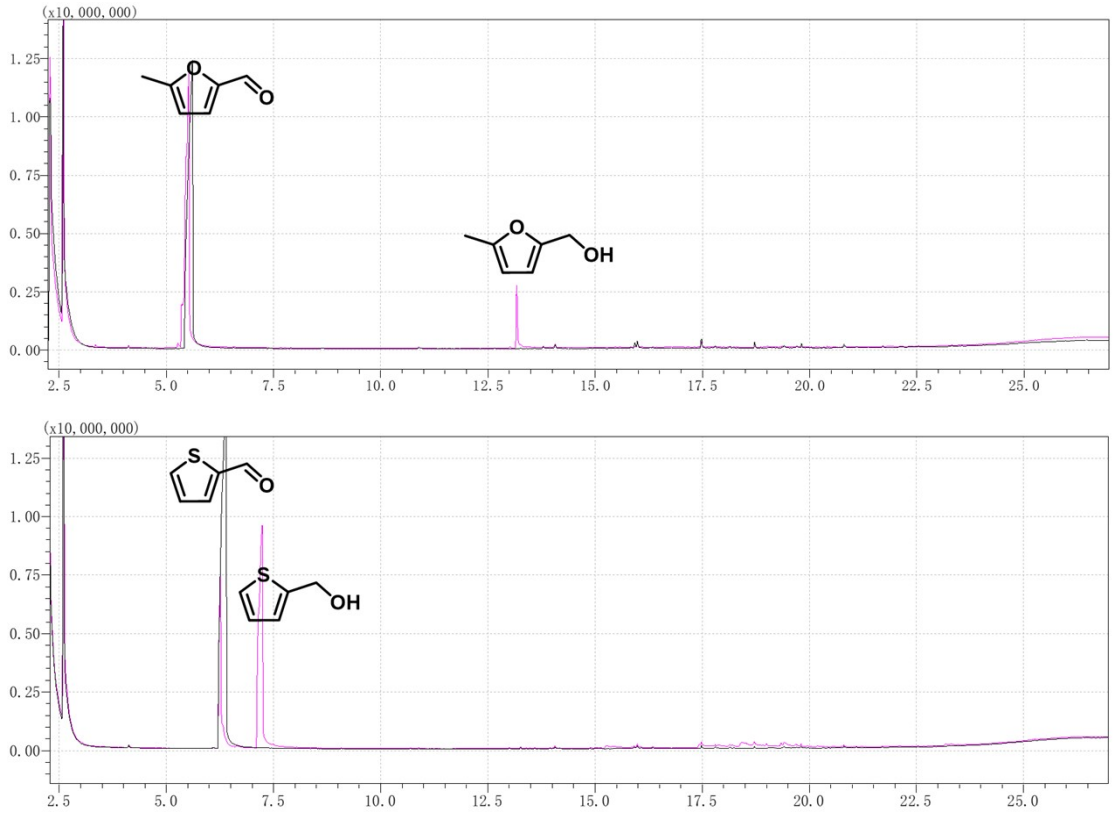
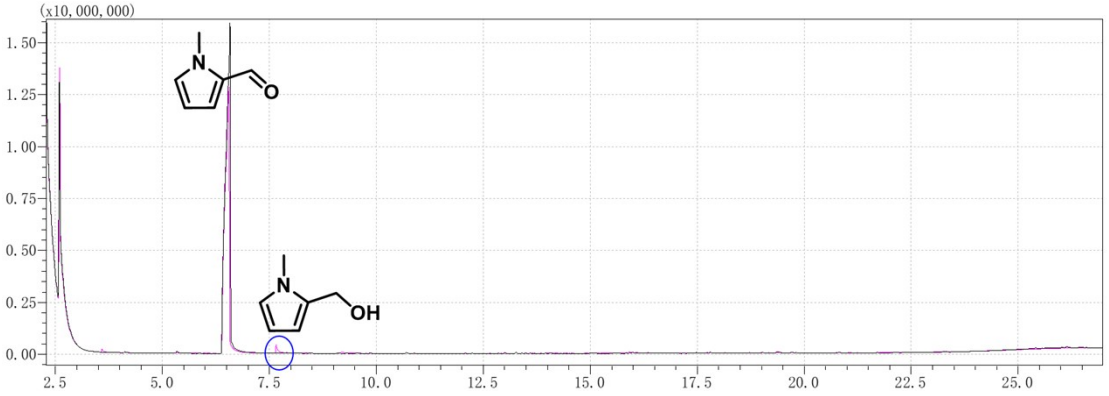


Figure S13 Representative HPLC spectra of ECH of furfural at pH 12. Detect wavelength: λ = 216 nm

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0.75
0.50
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7.5
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12.5
15.0
17.5
20.0
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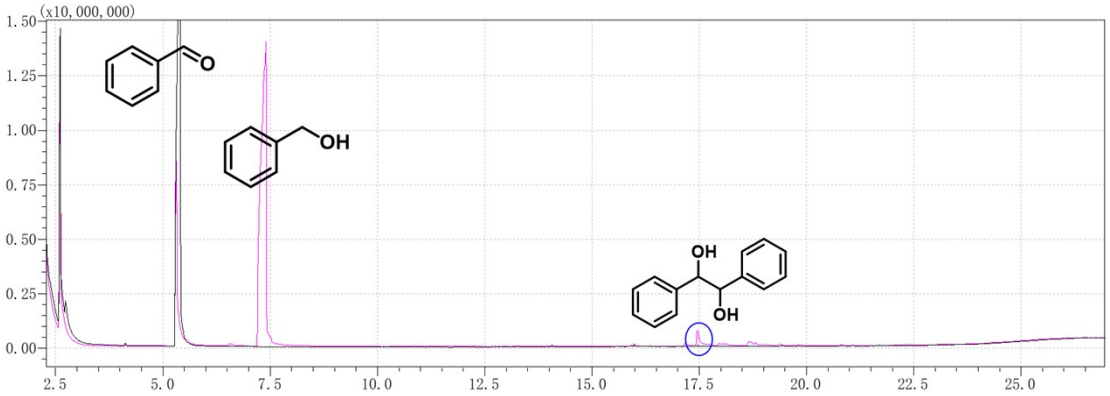
25.0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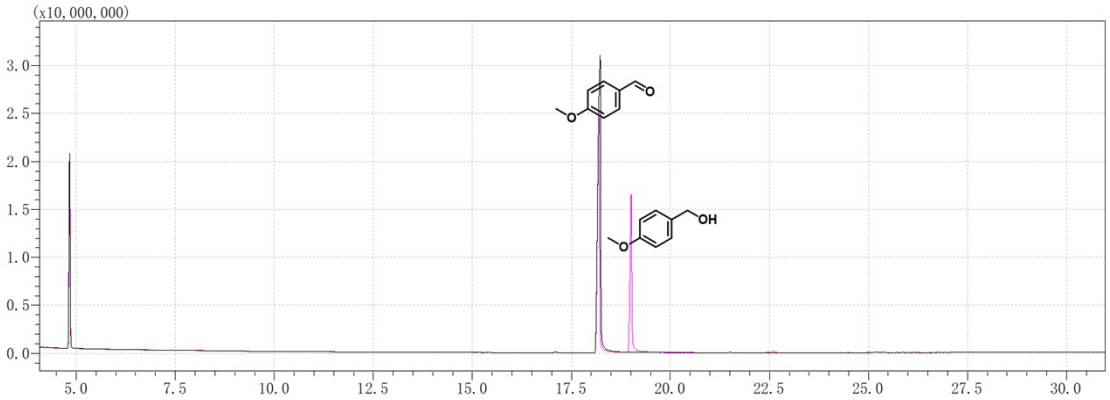
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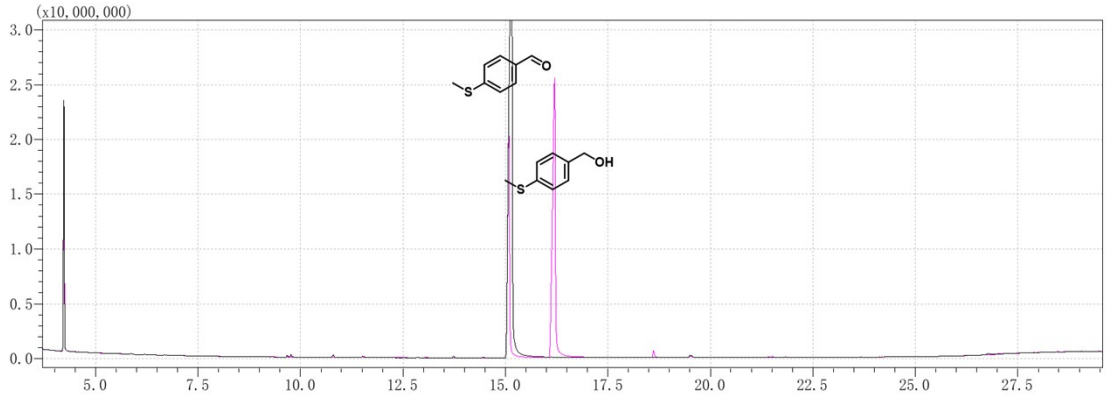
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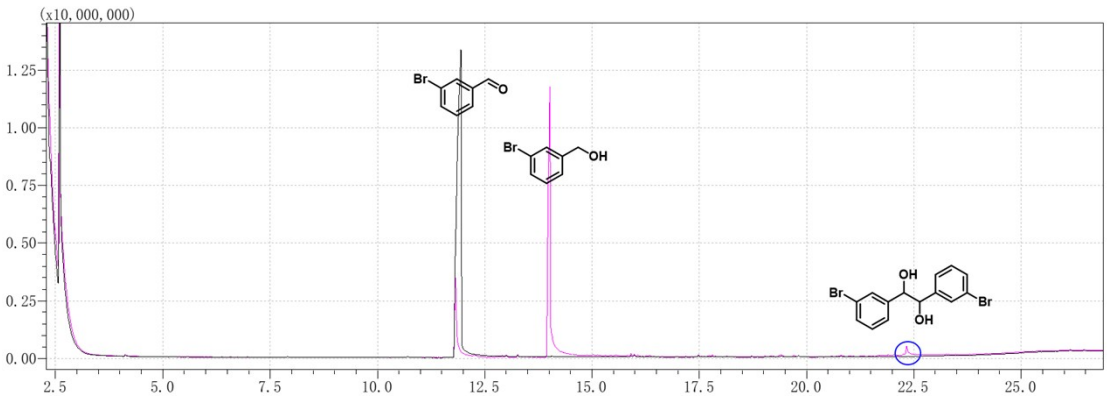
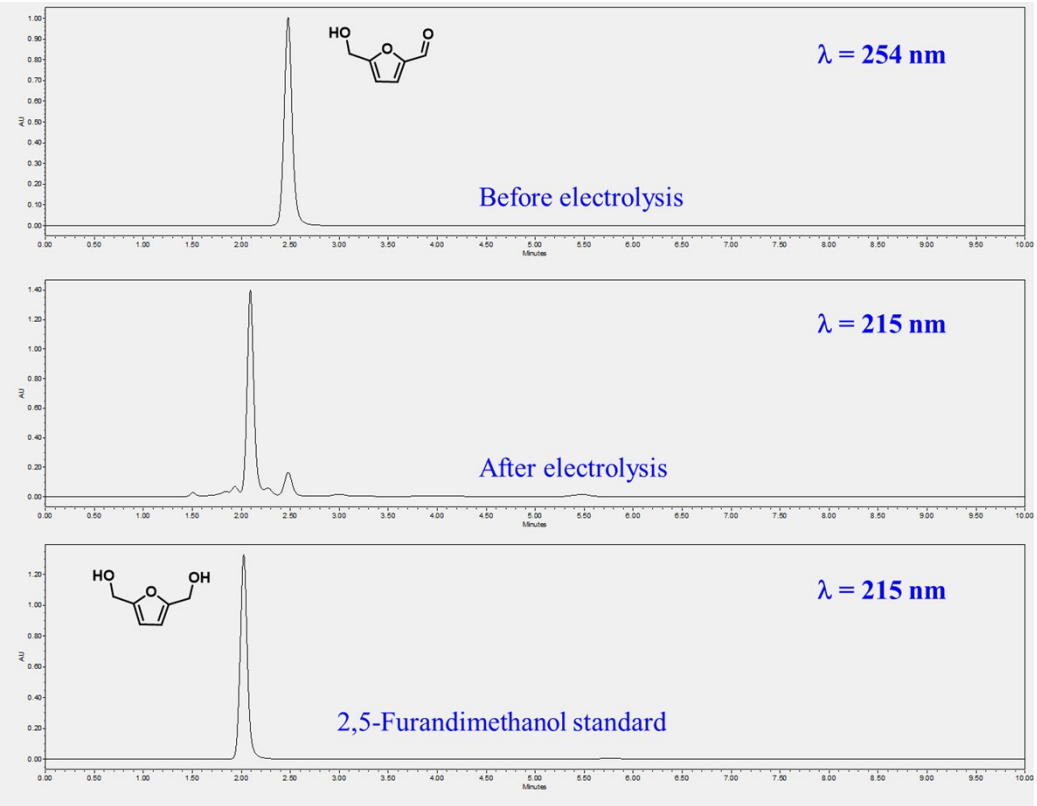


Figure S14 Representative GC-MS results for selected substrates. Before electrolysis (black line); and after electrolysis (magenta line)



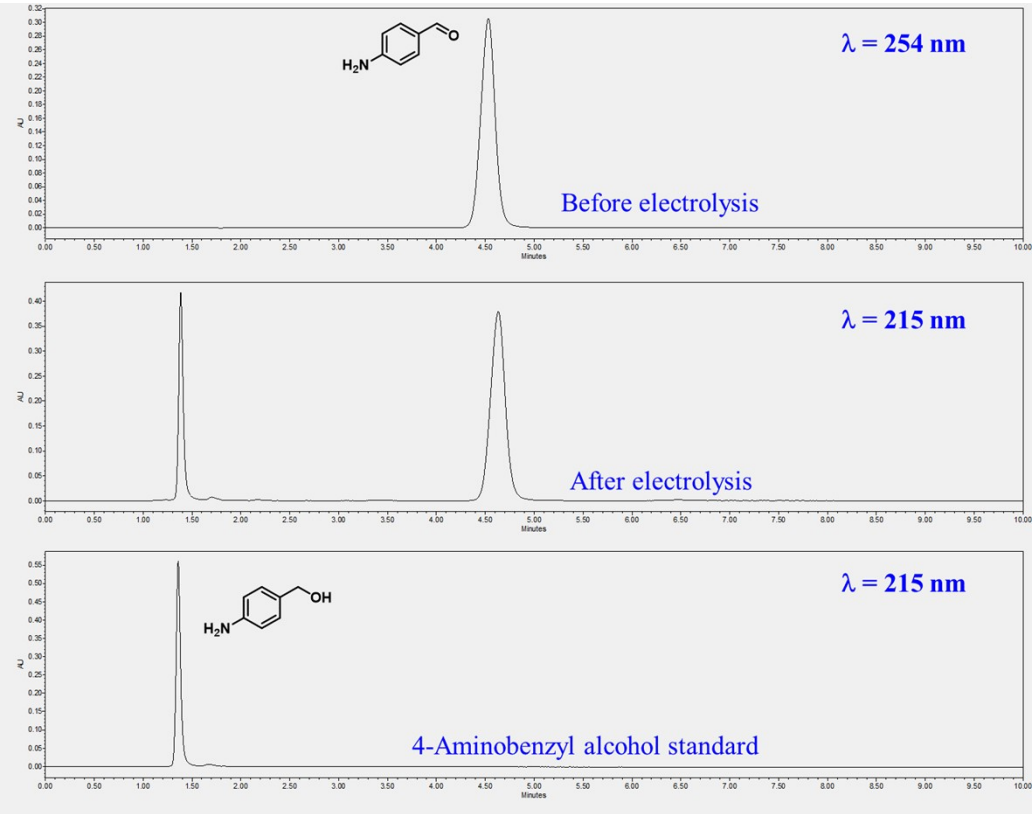


Figure S15 Representative HPLC spectra for selected substrates

Table S1 Surface elemental composition analysis of the molybdenum sulfide seed layer by XPS

Sample ID	Mo (at%)	S (at%)	O (at%)	C (at%)	Mo:S
MoS_x/CC	3.58	15.17	16.63	47.8	1:4.2
MoS_3/CC	5.82	15.82	13.59	47.53	1:2.7
2H-MoS_2/CC	9.79	19.81	9.73	47.7	1:2.0

Table S2 Relative atomic percentage (at.%) of different Mo 3d species calculated from the high-resolution XPS spectra of Mo 3d of the N-MoS_2 and S-MoS_2 electrode.

Sample ID	$Mo^{4+}3d_{5/2}$				$Mo^{4+}3d_{3/2}$				$Mo^{6+}3d_{5/2}$		$Mo^{6+}3d_{5/2}$		1T : 2H : MoOx
	1T		2H		1T		2H						
	B.E. (eV)	at%	B.E. (eV)	at%	B.E. (eV)	at%	B.E. (eV)	at%	B.E. (eV)	at%	B.E. (eV)	at%	
N-MoS_2	229.1	0.2584	229.9	0.2796	232.2	0.1722	233.5	0.1864	233.0	0.0619	236.2	0.0412	**43 : 46 : 11**
S-MoS_2	228.9	0.2691	229.7	0.2845	232.1	0.1794	233.3	0.1896	232.9	0.046	236.1	0.0308	**44 : 47 : 7**

Table S3 Relative atomic percentage (at.%) of different S 2p species calculated from the high-resolution XPS spectra of S 2p of the N-MoS_2 and S-MoS_2 electrode.

Sample ID	$S\ 2p_{3/2}$				$S\ 2p_{1/2}$				1T : 2H
	1T		2H		1T		2H		
	B.E. (eV)	at%	B.E. (eV)	at%	B.E. (eV)	at%	B.E. (eV)	at%	
N-MoS_2	162.0	0.2753	162.6	0.3074	163.4	0.2302	164.5	0.1869	**50.5 : 49.4**
S-MoS_2	161.9	0.4003	162.9	0.2663	163.3	0.2001	164.5	0.1331	**60.0 : 39.9**

Table S4 Working voltage records during the electrolysis at various current densities.

Electrode	Current density (mA cm^{-2})	Working potential ($V_{Ag/AgCl}$)	
		Start	End
S-MoS_2	5	1.12	1.30
	10	1.31	1.37
	15	1.40	1.48
	20	1.47	1.53

Table S5 *FFL convert, Selectivity, Product yield, and Faradaic efficiency for the as-prepared S-MoS_2 electrode in different pH conditions.*

pH	FFL Conv. (%)	F.E. (%)	Yield (%)		Sel. (%)	
			FFA	HDF	FFA	HDF
4.5	37.7	10.2	29.9	0.7	97.5	2.4
6	45.2	12.5	37.3	1.0	97.3	2.6
9	82.3	23.5	64.5	6.1	91.3	8.6
12	92.3	18.6	29.9	25.9	53.5	46.4

Table S6 *FFL convert, Selectivity, Product yield, and Faradaic efficiency for the as-prepared S-MoS_2 electrode under different current densities.*

Current density (mA cm^{-2})	FFL Conv. (%)	F.E. (%)	Yield (%)		Sel. (%)	
			FFA	HDF	FFA	HDF
5	47.7	29.6	37.2	2.1	94.7	5.2
10	82.3	26.4	64.5	6.1	91.3	8.7
15	73.6	13.2	41.0	12.8	76.2	23.8
20	65.6	8.9	29.7	14.1	67.8	32.2

Table S7 *FFL convert and Product yield for these base metal electrodes.*

Electrode	FFL Conv. (%)	Yield (%)	
		FFA	HDF
S-MoS_2	81.1	67.1	5.9
N-MoS_2	72.5	54.7	7.8
Pb	91.1	51.2	15.9
Ag	82.4	45.7	19.7
Cu	75.4	36.3	21.2
Zn	81.8	36.1	20.2
Au	72.4	24.9	24.5
Pt	18.2	19.1	--
Pd	67.7	13.5	19.6
CC	88.7	7.2	41.7
Ni	61.9	5.7	12.8
Nb	83.1	3.8	24.3
Ti	82.7	2.1	26.1
Mo	63.4	2.0	21.4

Reference

1. Quaino, P.; Juarez, F.; Santos, E.; Schmickler, W., Volcano plots in hydrogen electrocatalysis - uses and abuses. *Beilstein J Nanotechnol* **2014,** *5*, 846-854.