Supporting Information

Biomass Upgrading Coupled with H_2 Production via a Nonprecious and Versatile Cu-Doped Nickel Nanotube Electrocatalyst

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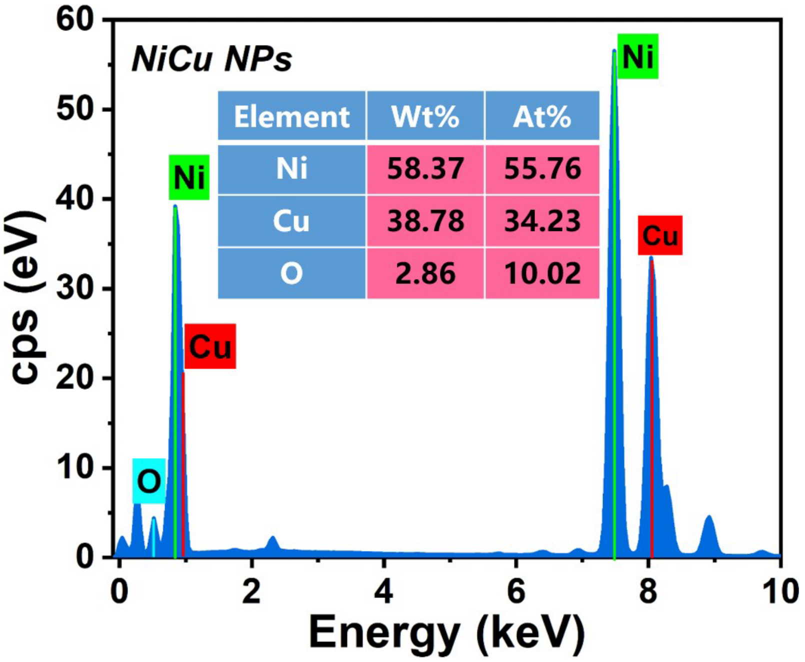


Figure S1. TEM-EDS of NiCu NPs catalyst.

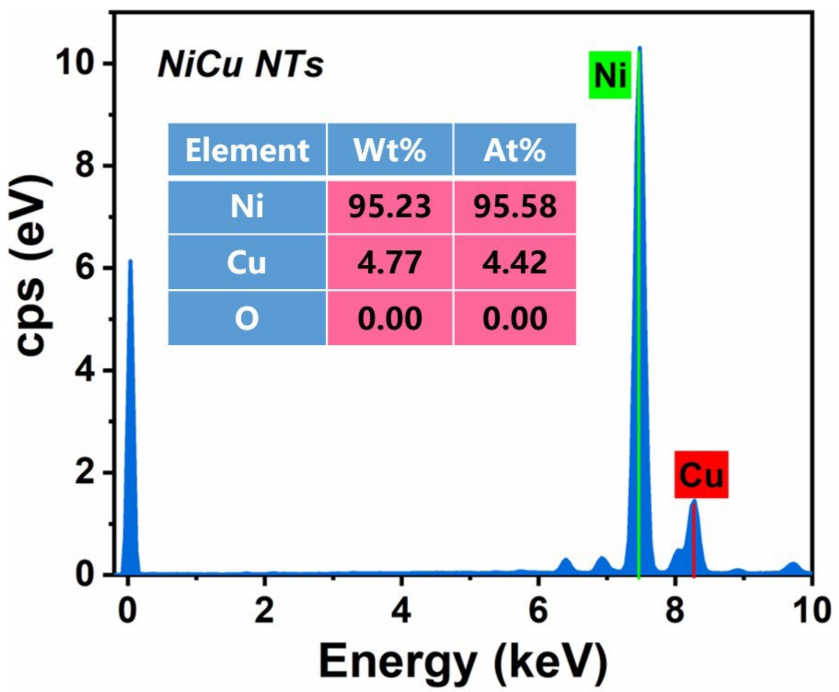


Figure S2. TEM-EDS of NiCu NTs catalyst.

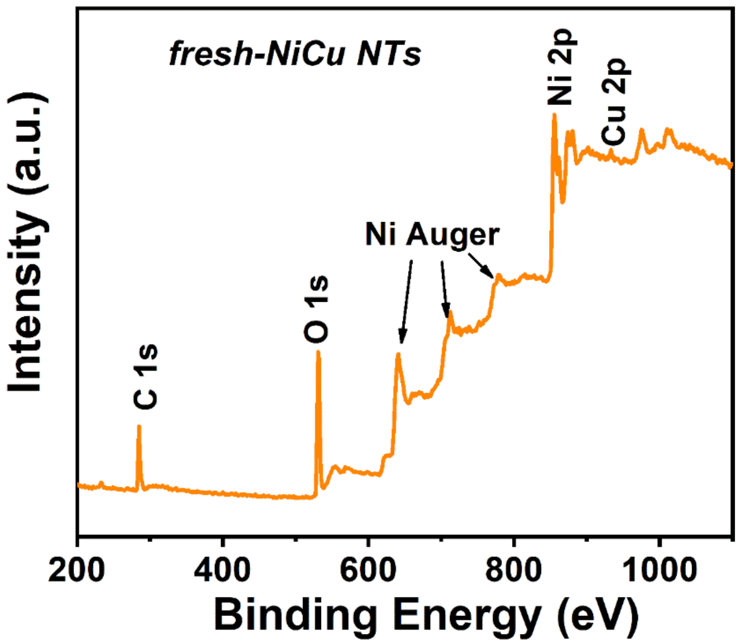


Figure S3. The survey spectrum of NiCu NTs catalyst and post-NiCu NTs.

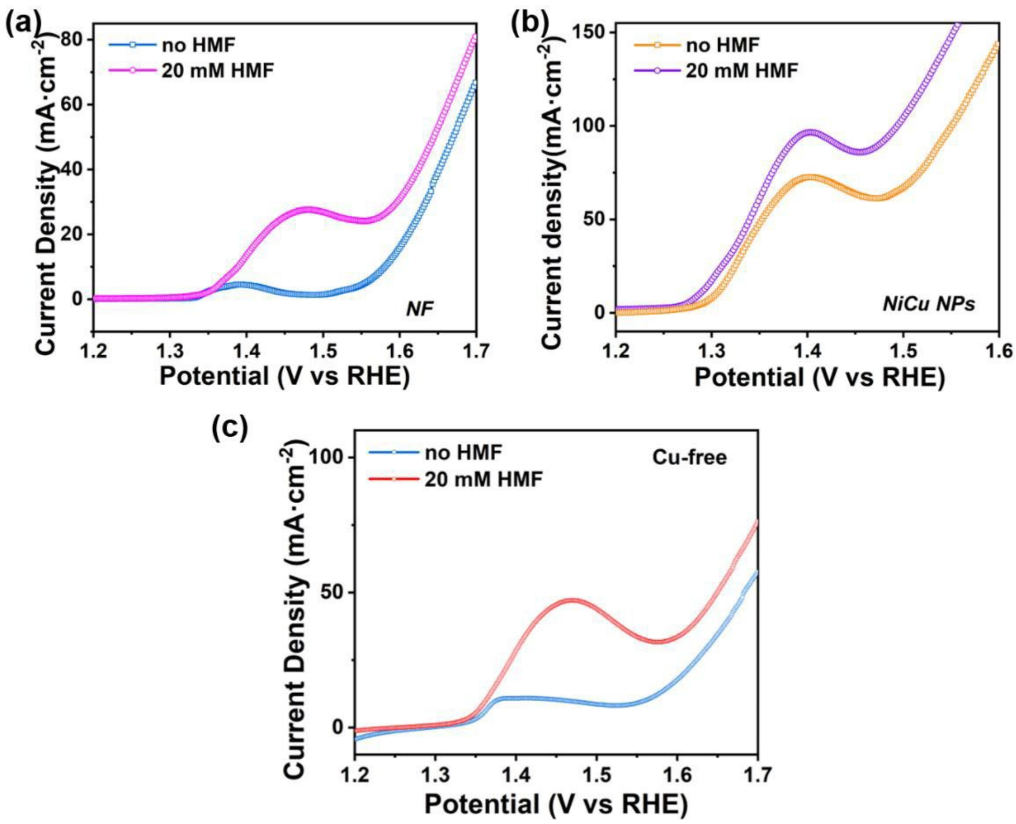


Figure S4. LSV curves at 5 mV s^{-1} in 1.0 M KOH with and without 20 mM HMF of (a) bare NF, (b) NiCu NPs and (c) Cu-free electrodes.

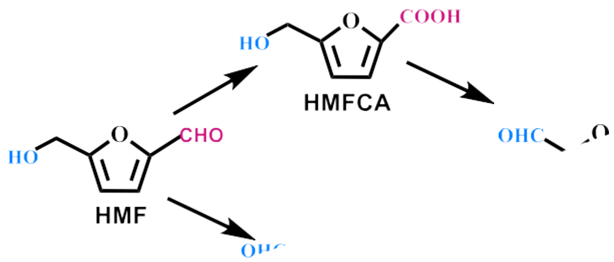


Figure S5. Possible pathways of HMF oxidation to FDCA.

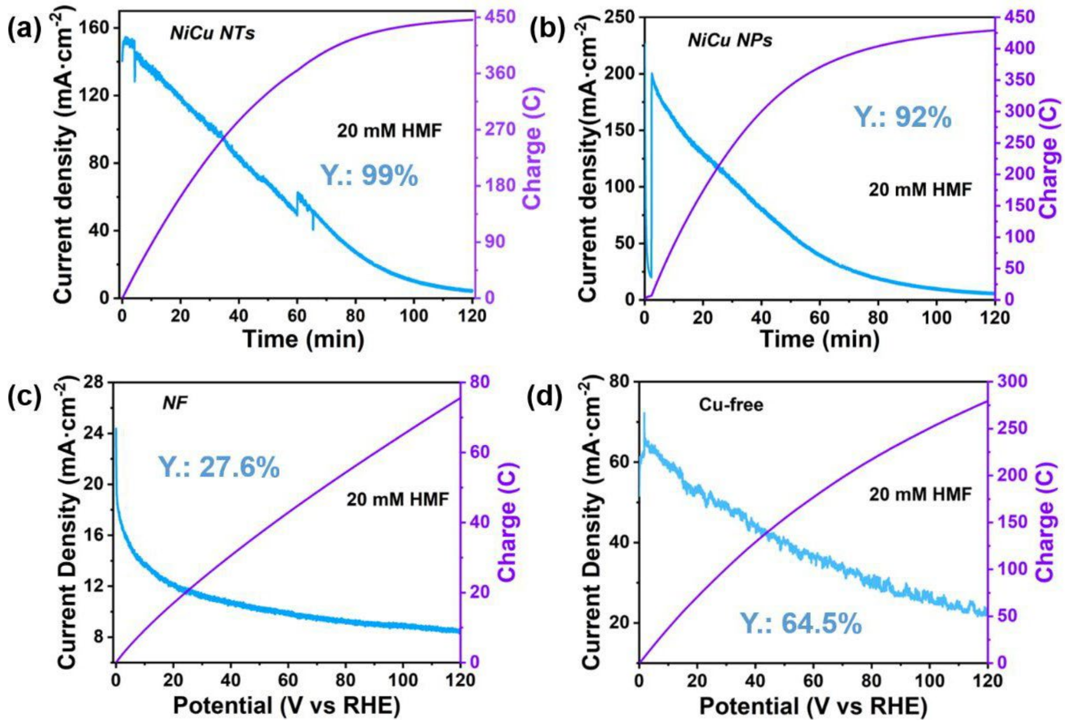


Figure S6. The *I-t* curves for the electrolysis of 20 mM HMF at a constant potential of 1.423 V vs. RHE for (a) NiCu NTs, (b) NiCu NPs, (c) NF electrode and (d) Cu-free catalysts.

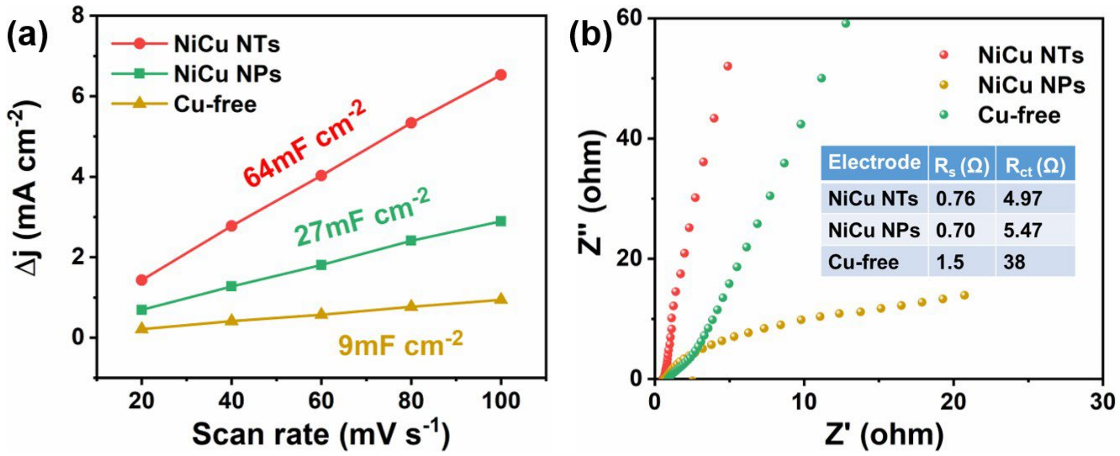


Figure S7. (a) Charging current density differences plotted against scan rates and (b) EIS spectra of NiCu NTs, NiCu NPs and Cu-free electrodes.

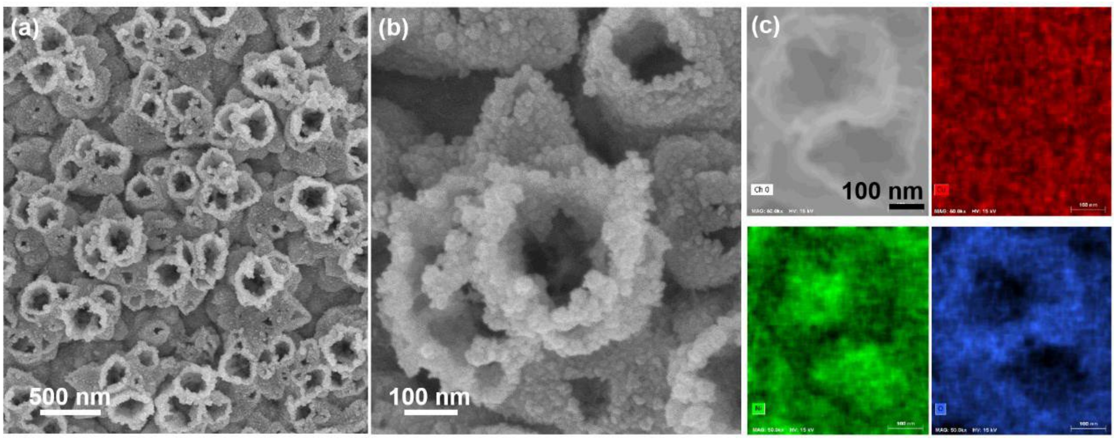


Figure S8. (a) SEM image and (b) mapping results of NiCu NTs electrode after ECO.

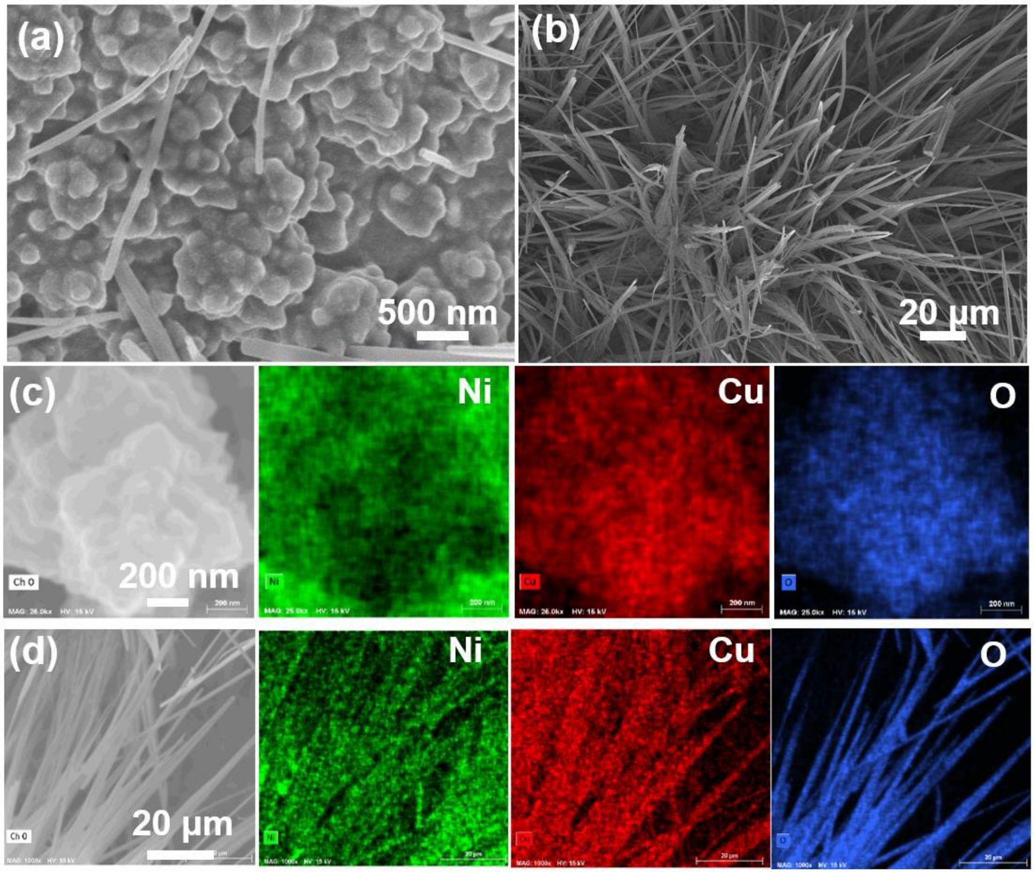


Figure S9. (a,b) SEM images and (c,d) mapping results of NiCu NPs electrode after ECO.

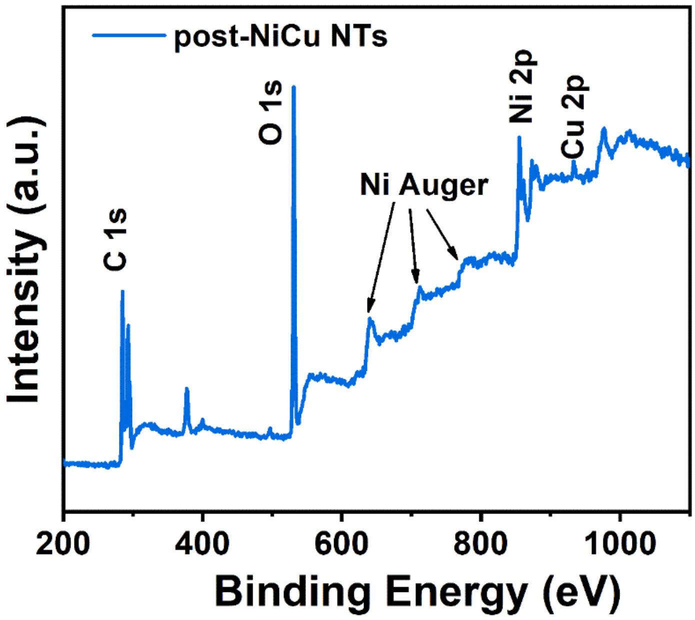


Figure S10. The survey XPS spectrum of post NiCu NTs.

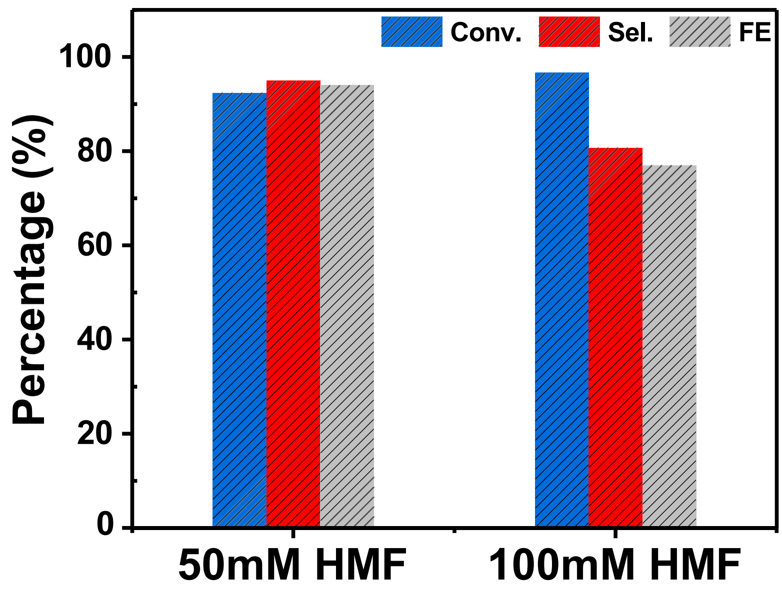


Figure S11. The electrolysis results over NiCu NTs in (a) 50 mM and (b) 100 mM HMF.

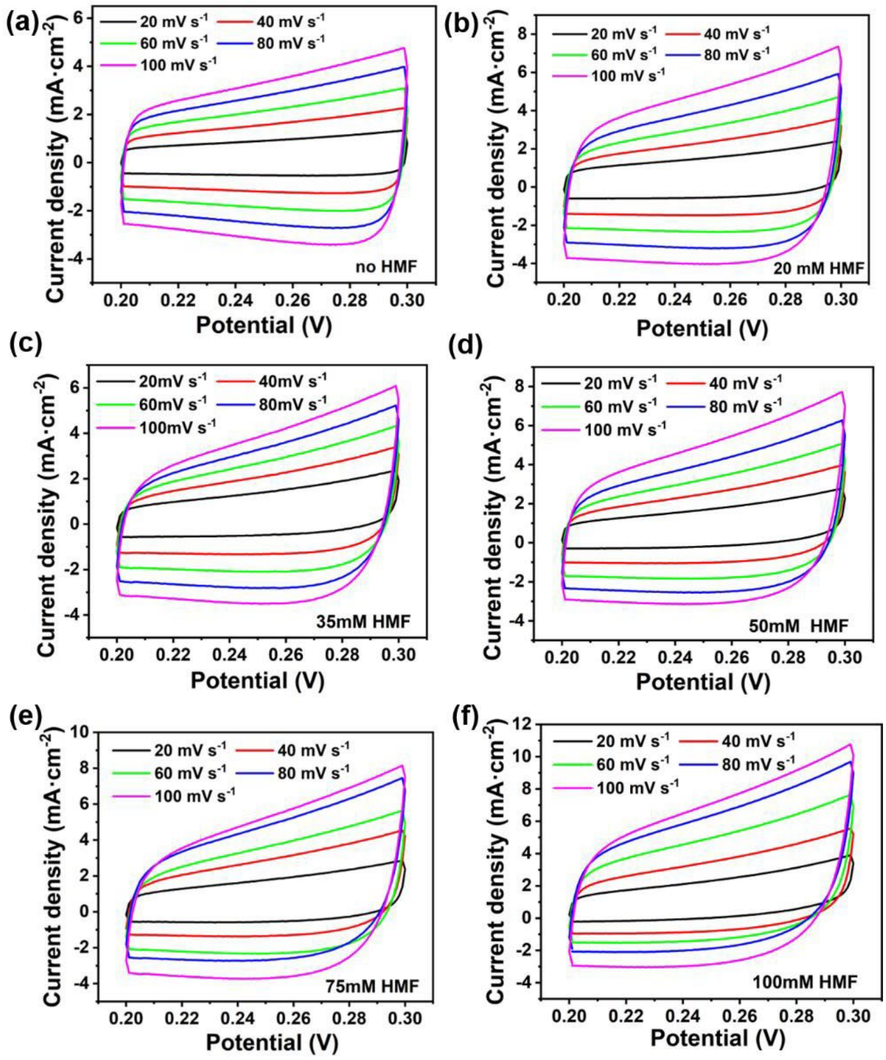


Figure S12. Cyclic voltammogram (CV) curves of NiCu NTs electro-oxidation HMF with different concentrations (a) no HMF, (b) 20 mM HMF, (c) 35 mM HMF, (d) 50 mM HMF, (e) 75 mM HMF and (f) 100 mM HMF in non-Faradic region at 20, 40, 60, 80 and 100 mV s^{-1}.

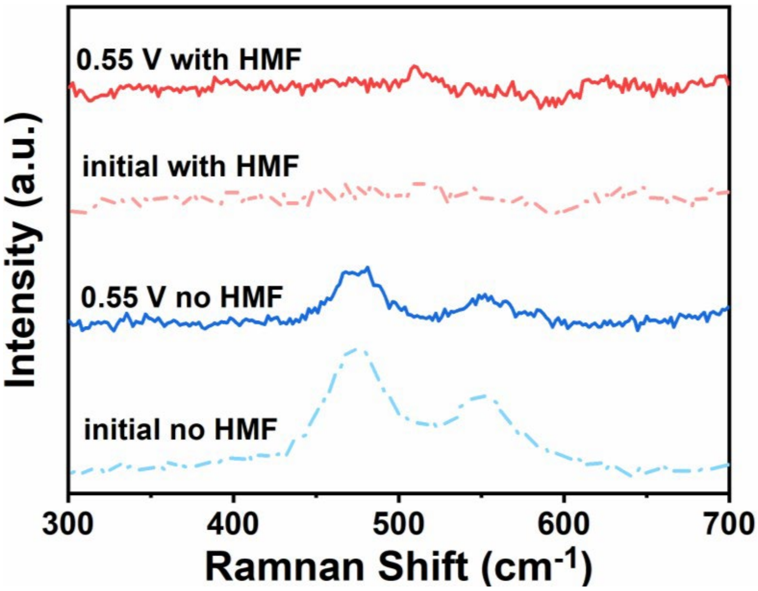


Figure S13. Raman spectra of NiCu NTs in KOH with and without HMF at a potential of 0.55 V.

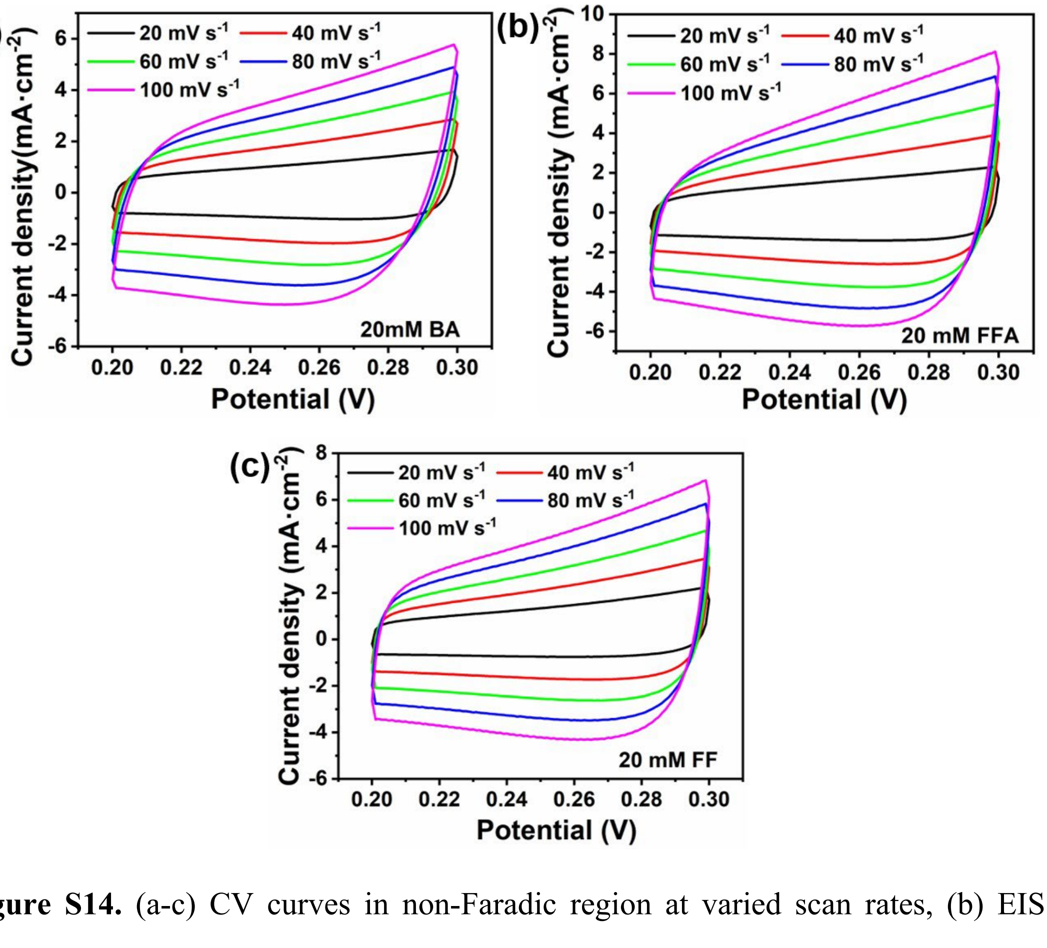


Figure S14. (a-c) CV curves in non-Faradic region at varied scan rates, (b) EIS spectrum of NiCu NTs with 20 mM BA, FFA and FF, respectively.

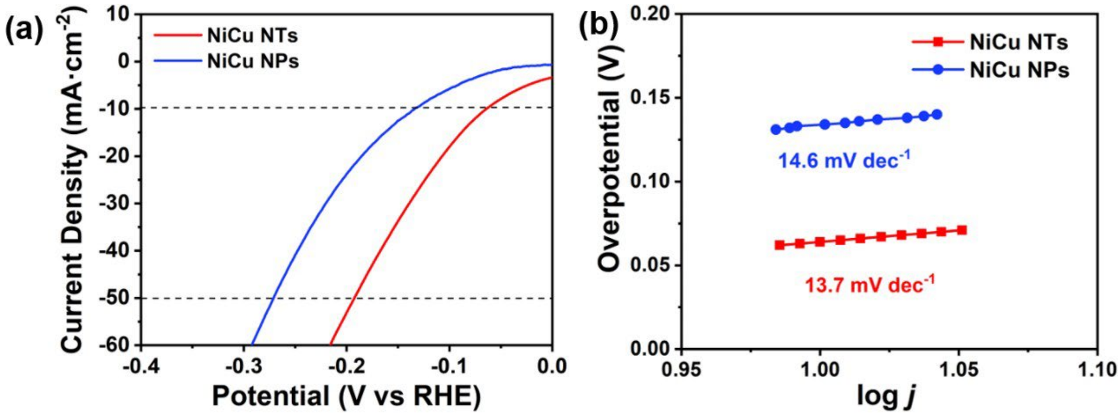
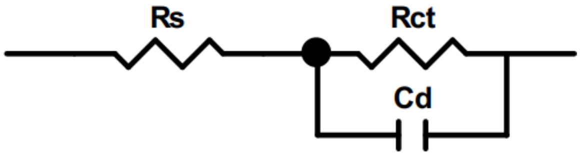


Figure S15. (a) Polarization curves at a scan rate of 5 mV s^{-1} and (b) Tafel slopes of NiCu NTs and NiCu NPs electrodes for HER in 1.0 m KOH.

Table S1. Performance comparison of NiCu NTs catalyst with recent reported catalysts in literatures for electrocatalytic oxidation of HMF

Catalyst	HMF concentration	Electrolytic potential (V)	FDCA yield	FE. %	Ref
NiCu NTs	20 mM	1.424V vs RHE	99%	96.4%	This work
$Ni_{0.9}Cu_{0.1}(OH)_2$	5 mM	1.45 V vs RHE	91.2%	91.20%	[1]
CoB	10 mM	1.45 V vs RHE	94%	100%	[2]
t-NiCo-MOF	10 mM	1.4 V vs RHE	~100%	98 %	[3]
nanocrystalline Cu	5 mM	1.69V vs RHE	96.40%	>95%	[4]
CuxS@NiCo-LDH	10 mM	1.34 V vs. RHE	100%	99%	[5]
$NiCo_2O_4$	5 mM	1.5 V vs. RHE	90.40%	87.50%	[6]
Ni_3N@C	10 mM	1.38 V vs.RHE	98%	99%	[7]
Ni_xB	10 mM	1.45 Vvs. RHE	98.50%	100%	[8]
MnO_x	20 mM	2.0 Vvs. RHE	53.8%	69.50%	[9]
NiFe LDH	10 mM	1.23 V vs RHE	98.0%	99.4%	[10]
$NiCo_2O_4$	10 mM	1.55 V vs. RHE	90%	~100%	[11]
NiSe@NiO_x	10 mM	1.423V vs RHE	99.00%	99.00%	[12]
CoFe@NiFe	10 mM	1.40 V vs RHE	100%	100%	[13]
Ag/C	10 mM	0.7 V VS Ag/AgCl	97%	98%	[14]
Ni2P NPA/NF	10 mM	1.423 V vs RHE	100%	98%	[15]
CoAl-LDH-NSA	10 mM	1.52 V vs. RHE	99.5%	99.4%	[16]

Table S2. Calculated results of EIS measured by different concentrations of HMF



HMF concentration	R_s (Ω)	R_{ct} (Ω)
0 mM	0.58	5.59
20 mM	0.76	4.97
35 mM	0.76	4.76
50 mM	0.75	3.22
75 mM	0.73	2.44
100 mM	0.74	2.20

Table S3. Comparison of overall organic oxidation performance with other reported works in different organic concentration

Catalyst	organic concentration	Current density (mA cm^{-2})	Potential (V)	Ref.
NiCu NTs	1M KOH + 20mM HMF	10	1.26	This work
CoAl-LDH	1M KOH + 10mM HMF	50	1.74	[16]
Ni2 NPA/NF	1M KOH + 10mM HMF	10	1.44	[15]
t-NiCo-MOF	1M KOH + 10mM HMF	100	1.392	[3]
CuxS@NiCo-LDHs	1M KOH + 10mM HMF	10	1.34	[5]
Ni_3S_2/Ni/NF	1M KOH + 0.5M urea	10	1.36	[17]
NiS@Ni_3S_2/$NiMoO_4$	1M KOH + 0.5M urea	10	1.40	[18]
MOF-Ni@MOF-Fe-S	1M KOH + 0.5M urea	10	1.54	[19]
e-Ni_3S_2@FeNi3-8	1M KOH + 0.33M urea	10	1.50	[20]
Ni@NCNT-3	1 MKOH+0.5M urea	10	1.56	[21]
Ni_4N/Cu_3N	1 MKOH+0.5M urea	10	1.48	[22]
Mo-Co-S-Se/CC	1M KOH + 0.5M urea	10	1.40	[23]
NF@Acid-H_2	1M KOH + 0.33M urea	10	1.49	[24]
$NiMoO_4$	1M KOH + 1mM urea	10	1.61	[25]
a-Ni_2P/G	1M KOH + 0.5M urea	10	1.39	[26]

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