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Supporting information

Non-noble bimetallic alloy in the high selective electrochemical synthesis of biofuel 2, 5-dimethyl-furan from 5-hydroxymethyl-furfural

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1 Experimental Section

1.1 Materials

The foil of Cu of 0.2 mm in thickness (99.9% purity) and Ni of 0.1 mm in thickness (99.9% urity) were purchased in Beijing ZKKA Biotechnology Co., Ltd. (Beijing, China). $NiSO_4$, $CuSO_4$, H_2SO_4 and H_3BO_3 were obtained in Guangfu Tech Company (Tianjin, China). HMF (≥ 99%), BHMF (≥ 98%), DMF (≥ 99%) and MFA (97%) were purchased from Beijing HWRK Chem Co., LTD. (Beijing, China). All chemicals were used without further purification.

1.2 Preparation of Electrodes

Cu and Ni electrodes were prepared by cutting the foil into a dimension of 1.5 cm × 1.5 cm. Then the foils were cleaned with isopropanol and water before being immersed in 1 M HCl for 2 min. They were then rinsed with water, dried in vacuum box (DZF-6210). Then the foils were covered in the backside and top 0.5 cm with Teflon tape to make a 1.5 cm^2 working area (see Figure S 2).

For the construction of high surface area copper electrode (Cu_{hs}), the cupper atoms was deposited on the surface of clean Cu foil (1.5 cm^2) in the solution of $CuSO_4$ (0.15 M) and H_2SO_4 (0.3 M) with a current of 0.3 A/cm^2 applied to the foil using a galvanostat for 300 s. Then the foil was rinsed gently with water and dried in vacuum box (DZF-6210).

The CuNi bimetallic electrodes were prepared by electro-deposition on Cu_{hs} electrodes in a two-electrode cell for various times (30 s, 50 s, 70 s, 90 s, 110 s, 180 s) with Pt foil as the anode. The electrolyte consisted of a solution of 0.3 M H_3BO_3 with 0.1 M $NiSO_4$. After deposition, the electrode was rinsed gently with water and dried in vacuum drying box (DZF-6210).

1.3 Electrode Characterization

SEM images were acquired using a cold field emission scanning electron microscope (Hitachi SU-801, Japan) equipped with energy dispersive X-ray spectroscopy (EDS). The X-ray diffraction (XRD) patterns were collected on a Bruker D8 advance diffractometer equipped with a Lynx-Eye detector and parallel beam optics using a Ni-filtered Cu Kα radiation, λ=1.5418 Å. X-ray photoelectron spectroscopy (XPS) was performed using a 3400 KRATOS AMICUS/ESCA with an unmonochromatized Al-anode Kα X-ray source (1486.6 eV) operated at 15 mA and 10 kV (~1 ×

10^{-7}Pa). The specific surface area was calculated by the BET method with an ASAP 2000 (Micromeritics) analyser.

1.4 Electrochemistry

Linear sweep voltammetry (LSV) was employed in the comparison of catalytic HMF reduction on different electrodes, Cu, Ni, Cu_{hs}, and CuNi. The general experimental setup consisted of a system with three-electrode, the prepared electrodes as working electrode, Pt sheet as counter electrode, and Ag/AgCl (saturated KCl) as the reference electrode in an undivided cell controlled on a CHI 660E electrochemical workstation.

Constant potential electrolysis experiments were carried out using a two-compartment divided cell, linked by a KCl salt bridge (Figure S 1). The Cu, Ni or Cu-Ni working electrode were immersed in the cathodic compartment containing 2 g L^{-1} HMF in 40 mL of a 0.2 M sulfate buffer solution (pH 2.0), which stirred with magnetic stirrer in 1200 rpm during the electrochemical reaction. The counter electrode was immersed in the anodic compartment containing 40 mL of a 0.2 M sulfate buffer solution (pH 2.0).

1.5 Product Analysis

The electro-catalytic product were confirmed by pure components of GC spectra and were quantified by calibration curves (Figure S 4-7) using Shimadzu GC 2010 plus instrument equipped with a Shimadzu SHRIX-5MS and a flame induction detector (FID). Temperature of injector and detector were set at 250 ^{o}C and 285 ^{o}C, respectively. The program temperature starts from 50 ^{o}C (4 min) and then increased up to 250 ^{o}C with a heating rate of 10 ^{o}C /min.

2 Device for the electro-catalysis

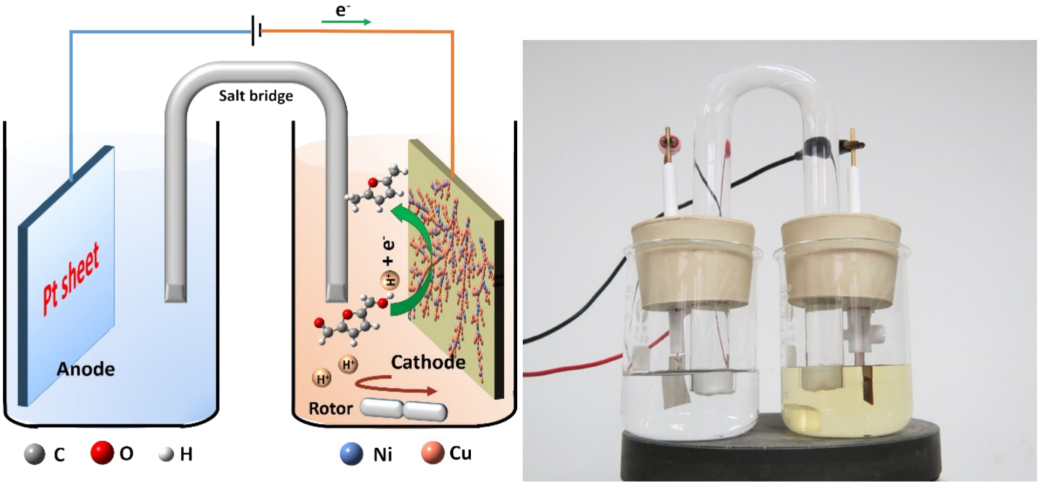


Figure S 1. Electrochemical set-up used for electro-catalysis of HMF into DMF.

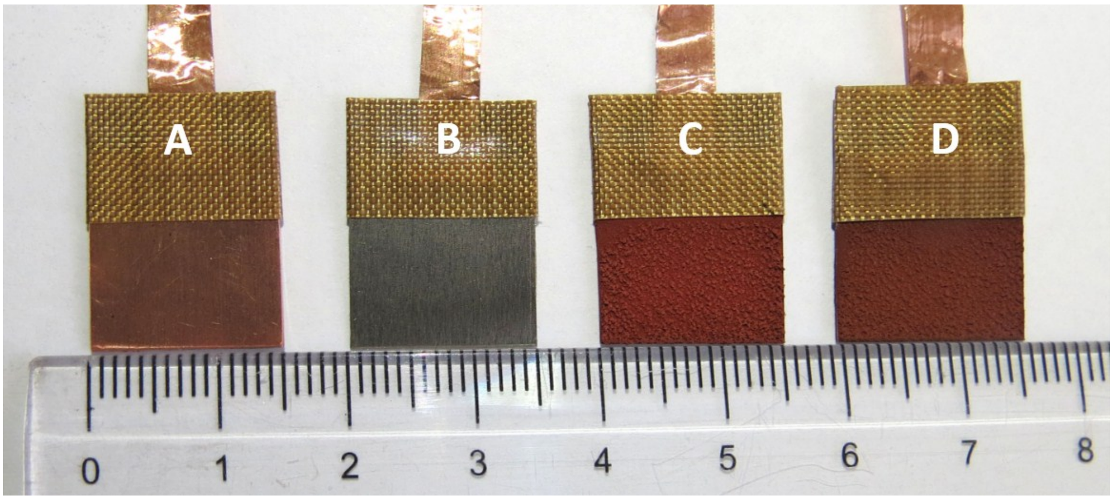


Figure S 2. Images of as-prepared electrodes: (A) Cu foil (B) Ni foil (C) Cu_{hs} and (D) CuNi.

3 Results of electro-catalytic reduction using electrodes with different Ni deposition time

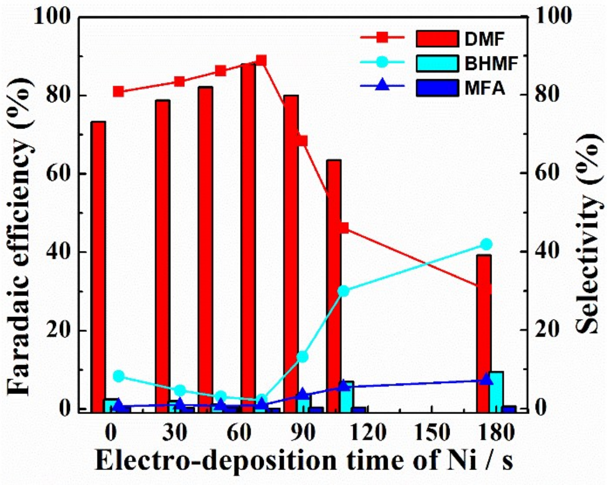


Figure S 3. Faradaic efficiency (column) and selectivity (line) of the electro-catalytic reduction of HMF on the electrode with different Ni deposition time (Other conditions: electrolyte, 0.2 M sulfate buffer solution (pH 2.0); HMF: 2 g L^{-1}; voltage: -0.8 V vs Ag/AgCl; Charge: 150 C).

4 Measurement of the products with GC

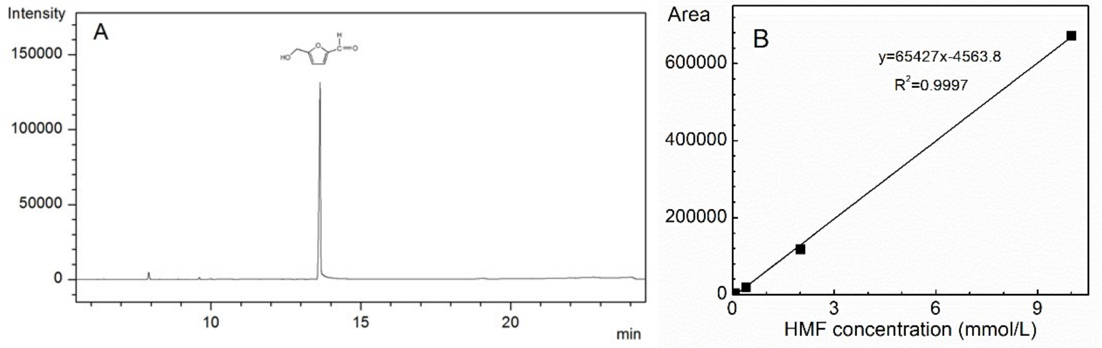


Figure S 4. GC spectra of standard sample (A) and calibration curve of HMF (B).

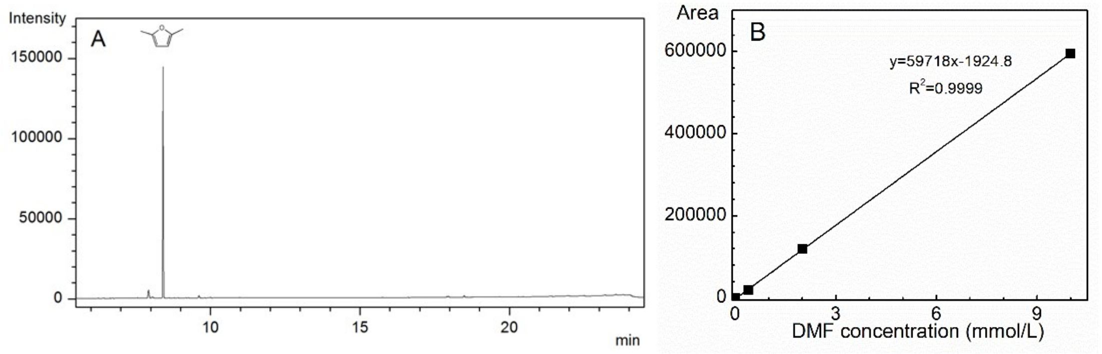


Figure S 5. GC spectra of standard sample (A) and calibration curve of DMF (B).

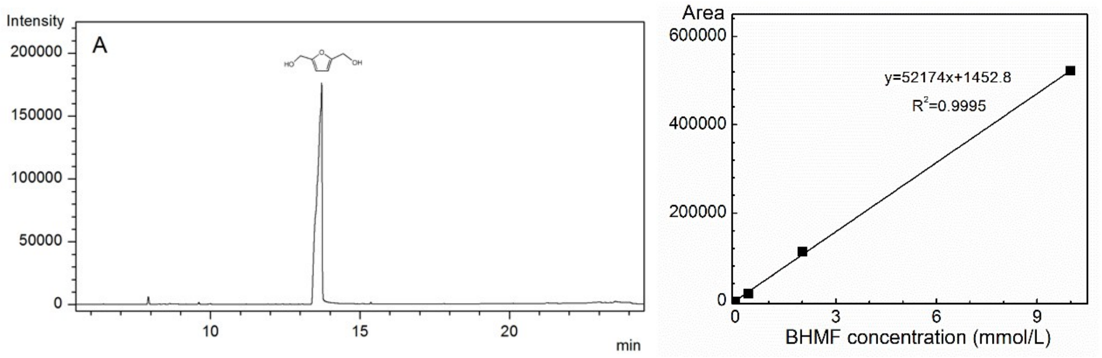


Figure S 6. GC spectra of standard sample (A) and calibration curve of BHMF (B).

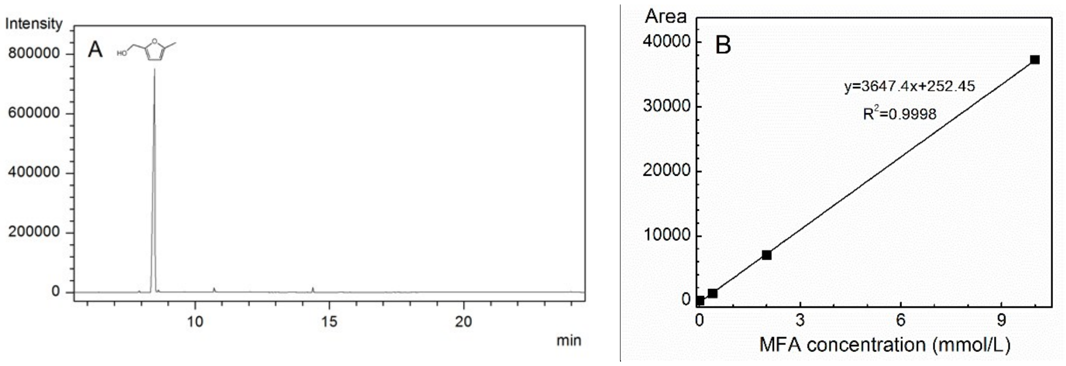
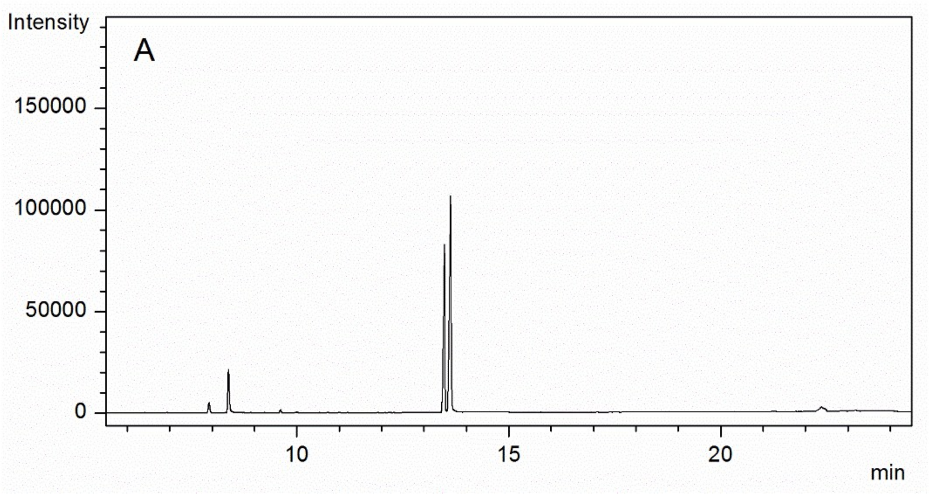


Figure S 7. GC spectra of standard sample (A) and calibration curve of MFA (B).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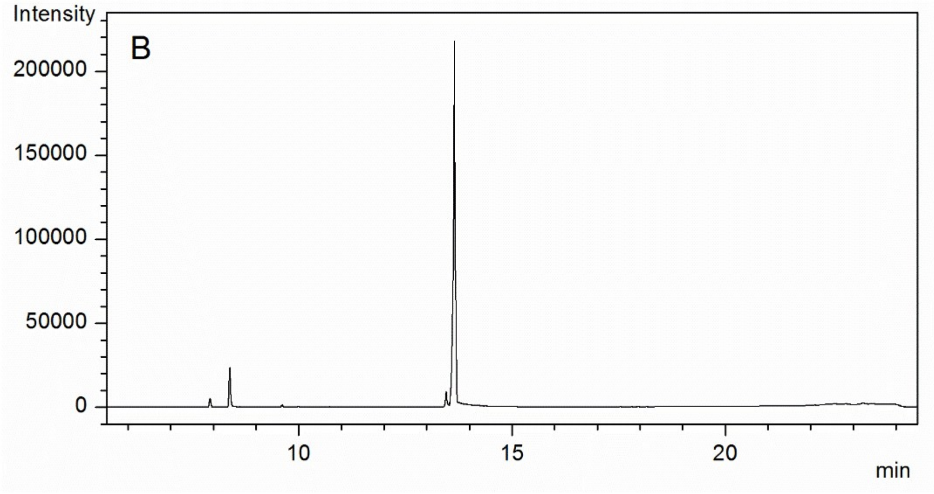
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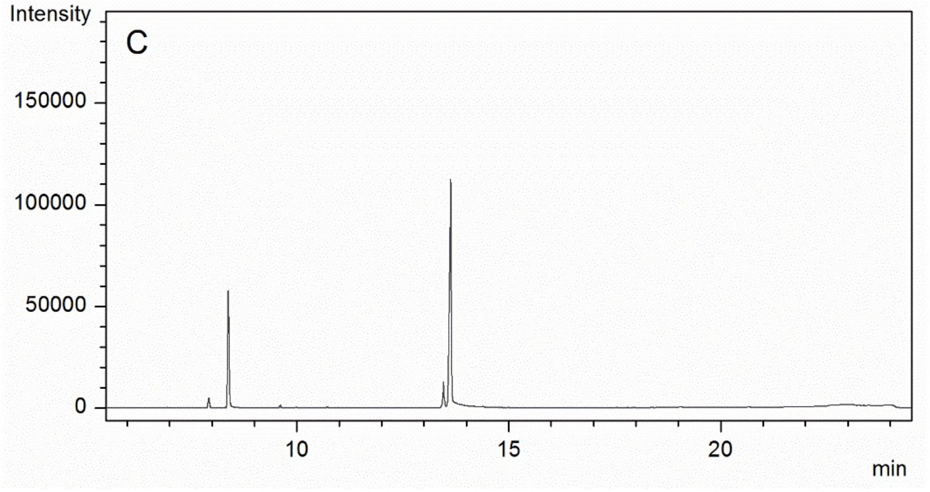
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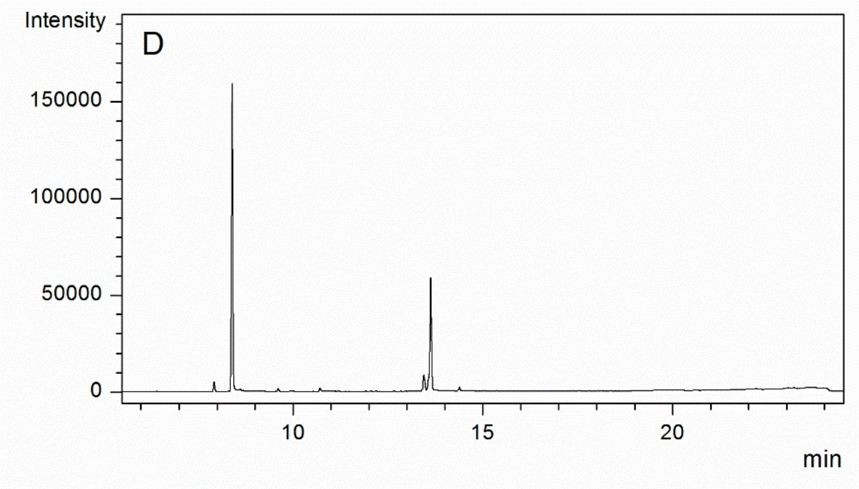

Figure S 8. GC spectra of the sample using Cu electrode at -0.8 V (A), the sample using Ni electrode at -0.6 V (B), the sample using Cu_{hs} electrode at -0.8 V (C) and the sample using CuNi electrode at -0.8 V (D).

5 LSVs of prepared electrodes

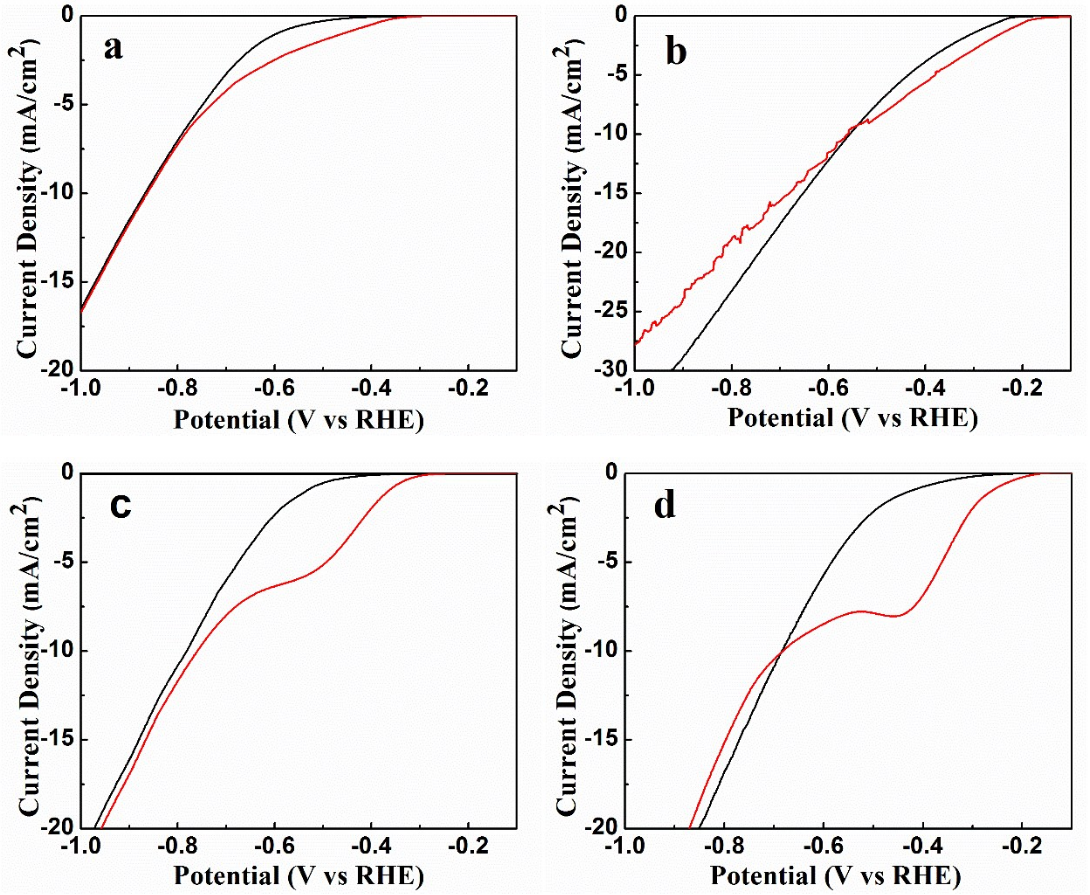

Figure S 9. LSVs of (a) Cu, (b) Ni, (c) Cu_{hs}, and (d) CuNi electrodes in 0.2 M sulfate buffer solution (pH 2.0) without (black) and with (red) 2 g $L^{-1}$of HMF at the scan rate of 2 mV/s.

6 The scheme of electro-catalytic reduction mechanism proposed

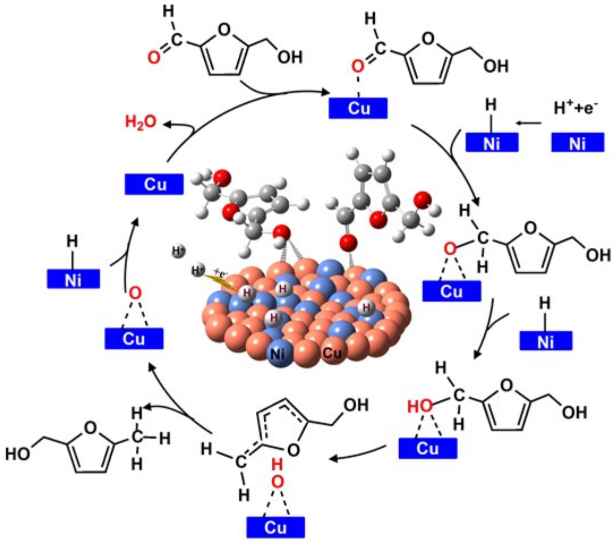

Figure S 10. The mechanism speculated for the reduction of HMF to DMA over CuNi electrode.

7 Results of electro-catalysis reaction

Table S1. Results of electrochemical reduction of HMF, faradic efficiency and selectivity on the-prepared electrode

Potential (V vs Ag/AgCl)	Electrode	HMF consumed (mmol)	Products formed (mmol)			Faradic Efficiency (%)			Selectivity (%)		
			DMF	BHMF	MFA	DMF	BHMF	MFA	DMF	BHMF	MFA
-0.5	Cu foil	0.039	0.007	0.008	0.001	2.581	1.022	0.226	17.300	20.990	4.326
-0.6	Cu foil	0.055	0.016	0.024	0.005	6.320	3.055	1.242	29.700	23.152	5.542
-0.7	Cu foil	0.108	0.056	0.035	0.007	21.711	4.546	1.845	52.100	10.258	3.745
-0.8	Cu foil	0.113	0.085	0.016	0.002	32.683	2.054	0.456	75.200	4.508	1.161
-0.9	Cu foil	0.111	0.090	0.000	0.000	34.639	0.000	0.000	80.900	0.000	0.000
-1.0	Cu foil	0.069	0.055	0.000	0.000	21.177	0.000	0.000	79.300	0.000	0.000
-0.5	Ni foil	0.148	0.008	0.103	0.002	3.236	13.257	0.526	5.677	22.458	0.726
-0.6	Ni foil	0.255	0.010	0.218	0.015	3.687	26.017	3.842	3.745	32.557	4.059
-0.7	Ni foil	0.208	0.009	0.149	0.028	3.433	19.189	7.145	4.273	31.936	10.368
-0.8	Ni foil	0.146	0.014	0.089	0.021	5.240	11.413	5.356	9.290	34.228	12.560
-0.9	Ni foil	0.074	0.016	0.044	0.006	6.020	5.699	1.659	21.189	26.627	10.194
-1.0	Ni foil	0.056	0.011	0.023	0.001	4.347	2.950	0.245	20.189	15.686	3.345
-0.5	Cu_{hs}	0.085	0.030	0.021	0.002	11.695	2.654	0.626	35.800	3.897	1.826
-0.6	Cu_{hs}	0.151	0.067	0.049	0.007	25.779	6.275	1.842	44.100	9.140	2.542
-0.7	Cu_{hs}	0.238	0.156	0.045	0.014	60.386	5.747	3.545	65.700	6.527	4.769
-0.8	Cu_{hs}	0.235	0.190	0.019	0.001	73.311	2.485	0.356	80.800	2.978	0.567
-0.9	Cu_{hs}	0.217	0.187	0.009	0.000	72.231	1.118	0.000	86.300	2.007	0.000
-1.0	Cu_{hs}	0.182	0.157	0.000	0.000	60.443	0.000	0.000	85.900	0.000	0.000
-0.5	CuNi	0.178	0.066	0.038	0.003	25.356	4.897	0.826	36.985	7.042	1.126
-0.6	CuNi	0.255	0.111	0.074	0.009	42.815	9.574	2.242	43.449	11.265	1.742
-0.7	CuNi	0.256	0.200	0.028	0.014	77.258	3.631	3.645	78.345	4.305	3.954
-0.8	CuNi	0.257	0.228	0.006	0.002	87.980	0.720	0.556	88.840	1.462	0.796
-0.9	CuNi	0.240	0.219	0.000	0.000	84.619	0.000	0.000	91.169	0.000	0.000
-1.0	CuNi	0.206	0.183	0.000	0.000	70.686	0.000	0.000	89.010	0.000	0.000

Note: Conditions: electrolyte, 0.2 M sulfate buffer solution (pH 2.0) and HMF 2 g L^{-1}; voltage, -0.5 V ≥ E ≥ -1.0 V vs Ag/AgCl; Charge, 150 C (the initial amount of HMF (0.635 mmol) was not totally consumed with the charge used).