

## **Electrocatalytic hydrogenation of furfural using non-noble-metal electrocatalysts in alkaline medium**

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## Supplementary Information

### 1. Experimental:

#### 1.1 Materials:

Nickel sulphate hexahydrate ( $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ; 98%), copper sulphate pentahydrate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ; 98%), acetonitrile ( $\text{CH}_3\text{CN}$ ; 99.9%), furfural ( $\text{C}_5\text{H}_4\text{O}_2$ ; 99%), furfuryl alcohol ( $\text{C}_5\text{H}_6\text{O}_2$ ; 98%), furoic acid ( $\text{C}_5\text{H}_4\text{O}_3$ ; 98%), and diethyl ether ( $\text{C}_4\text{H}_{10}\text{O}$ ; 99%) were purchased from Sigma-Aldrich. Orthoboric acid ( $\text{H}_3\text{BO}_3$ ; 99%), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), platinum plate (Pt; 99.95%), and nickel foam were purchased from Fisher Scientific, Macron Fine Chemicals, Alfa Aesar, MTI KJ group, respectively. Hydrofuroin ( $\text{C}_{10}\text{H}_{10}\text{O}_4$ ; 95 %) was purchased from ChemSpace. Silver nitrate ( $\text{AgNO}_3$ ; 99%), Citric acid ( $\text{HOC}(\text{COOH})(\text{CH}_2\text{COOH})_2$ ; 99%), Nitric acid ( $\text{HNO}_3$ ; 70%) were purchased from Sigma-Aldrich. All the solutions were prepared in Millipore water (18.2 M $\Omega$  cm).

#### 1.2 Catalysts prepared and evaluated:

**Table S1.** Catalysts prepared for evaluation

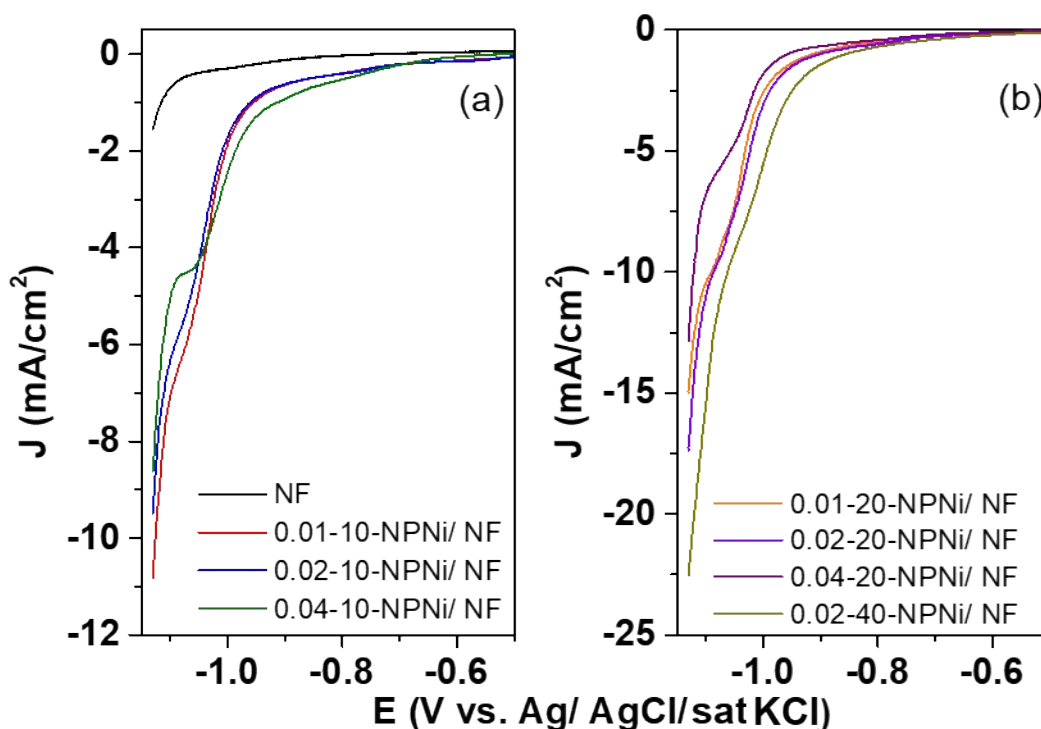
<b>Catalysts</b>	
Cu	
Pt	
Nickel Foam (NF)	
x y NPNi/NF	x=0.01 M, 0.02 M, 0.04 M y=10 min, 20 min, 40 min
0.02 z Cu – 0.02 40 NPNi/NF	z=5 min, 15 min, 30 min

NPNi/NF = 0.02 40 NPNi/NF and Cu-NPNi/NF = 0.02 15 Cu – 0.02 40 NPNi/NF

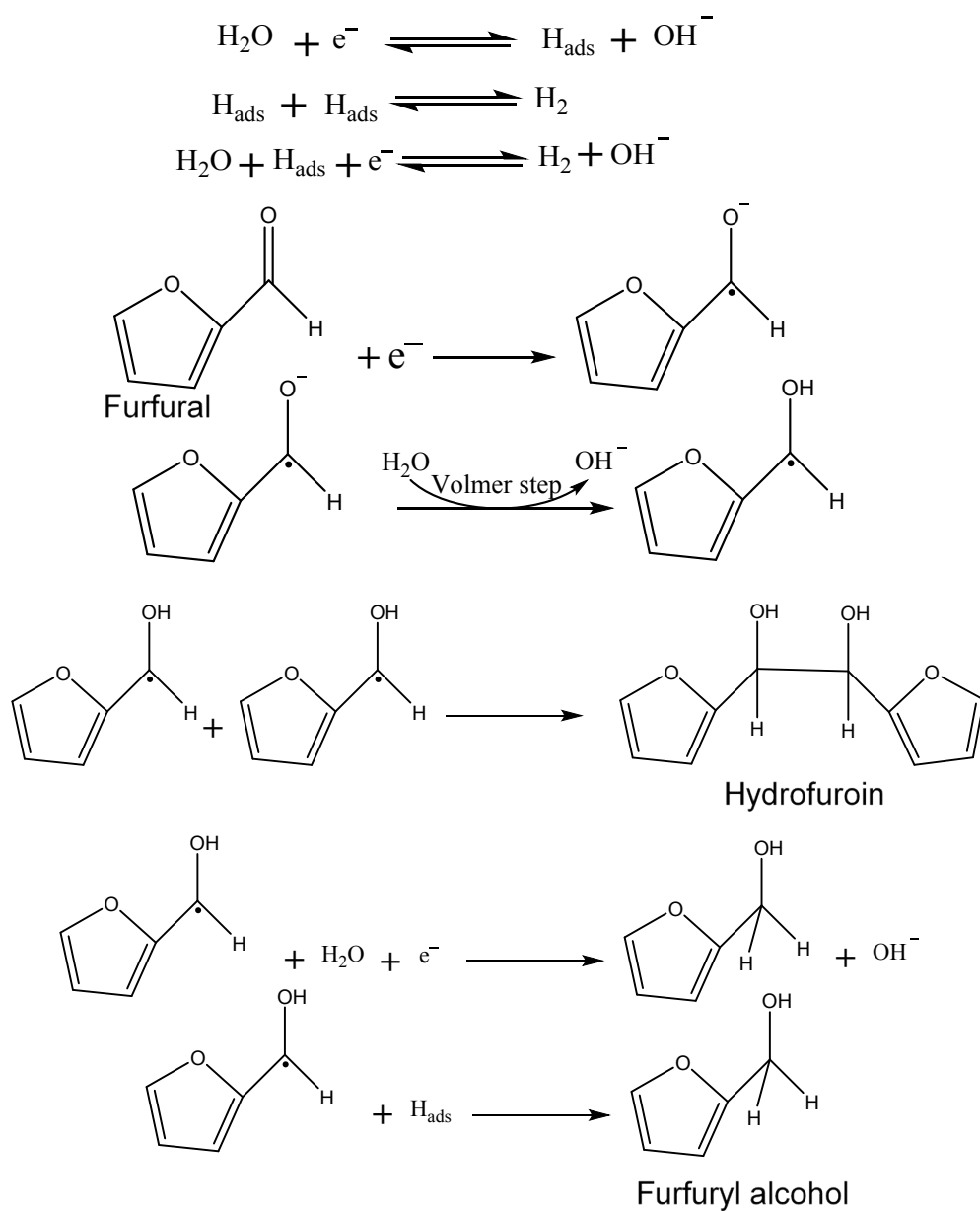
#### 1.3 Physical Characterization:

The morphology and elemental analysis of electrodeposited catalysts were performed by scanning electron microscope (SEM), JEOL JSM-7001 LVF Field Emission SEM, with Oxford Aztec Live X-Max Energy, energy dispersive x-ray spectroscopy (EDXS). XRD was performed

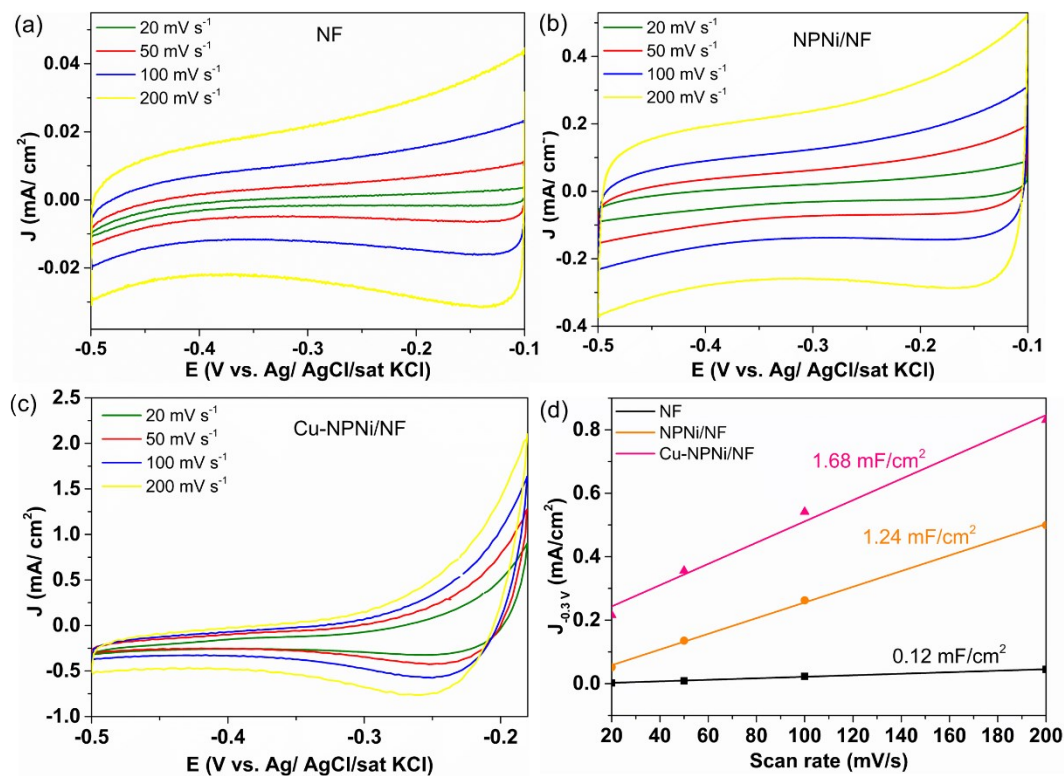
to determine the structural information of the electrocatalyst using Rigaku Miniflex 600 X-ray diffractometer (Cu  $K\alpha$ ,  $\lambda=1.5418 \text{ \AA}$ ). X-ray photoelectron spectrometer (XPS), PHI 5000 VersaProbe II, was used to analyze the quantitative and chemical state information of Ni, Cu, and O which were changing due to electrolysis. The samples were loaded into the introduction chamber of the instrument and the chamber was evacuated up to  $5 \times 10^{-6}$  Torr. Consequently, the sample was transferred into the main chamber for analysis and  $10^{-8}$  Torr was maintained. Monochromatic Al K-alpha x-ray source (1486.7 eV) was used at  $300 \times 700 \text{ \mu m}$  spot size to collect the survey spectrum (0 to 1200 eV) as well as spectrum for the elements in the specific binding energy range which is as follows: Ni (845 – 890 eV), Cu (928 – 958 eV), O (526 – 537 eV), and C (280 – 290 eV). The instrument was operated by Smartsoft-VP software, and the data was analyzed by Multipak software. The internal correction of C 1s was done by shifting the adventitious carbon to 284.5 eV. In the Multipak software, the baseline correction was done using Shirley type background correction. The plots were plotted with Gauss/Lorentzian function of (70:30).



**Figure S1.** Polarization curve using NF, and x y NPNi/ NF as working electrode and 0.5 M NaOH as electrolyte at the scan rate of  $50 \text{ mV s}^{-1}$ , where x is concentration of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in Ni-Cu electroplating solution, and y is Ni-Cu co-electrodeposition duration.



**Scheme S1.** The mechanism of Furfural electrocatalytic hydrogenation to generate furfuryl alcohol and hydrofuroin in alkaline electrolyte<sup>1</sup>



**Figure S2.** Cyclic voltammograms for (a) NF, (b) NPNi/NF, (c) Cu-NPNi/NF at the scan rates of 20 mV s<sup>-1</sup>, 50 mV s<sup>-1</sup>, 100 mV s<sup>-1</sup>, 200 mV s<sup>-1</sup> using 0.5 M NaOH as electrolyte. (d) Relation between current density and scan rate.

$C_{dl}$  for NF, NPNi/NF, and Cu-NPNi/NF were 0.12 mF cm<sup>-2</sup>, 1.24 mF cm<sup>-2</sup>, and 1.68 mF cm<sup>-2</sup>, respectively (Figure S2). The capacitance ( $C$ ) corresponding to the 10 cm<sup>2</sup> of geometric area for NF, NPNi/NF, and Cu-NPNi/NF were 1.2 mF, 12.4 mF and 16.8 mF, respectively. The specific capacitance ( $C_s$ ) was reported earlier as 0.045 mF cm<sup>-2</sup>.<sup>2</sup> Electrochemically active surface area (ECSA= $C/C_s$ ) of NF, NPNi/NF, and Cu-NPNi/NF were calculated as 26.7 cm<sup>2</sup>, 275.6 cm<sup>2</sup>, and 373.3 cm<sup>2</sup> respectively.

**Table S2.** Comparison of R ( $\mu\text{mole hr}^{-1} \text{cm}^{-2}$ ) based on geometric area and ECSA. Applied potential: -1.45 V, electrolysis duration: 1h, electrolyte: 0.5 M NaOH + 50 mM FF.

Catalysts	Geometric area		ECSA	
	$R_{\text{FA}}$	$R_{\text{HF}}$	$R_{\text{FA}}$	$R_{\text{HF}}$
<sup>a</sup> Cu	50.6	73.7	50.6	73.7
<sup>a</sup> Pt	11.7	23.4	11.7	23.4
NF	NA	49.1	NA	18.4
NPNi/NF	14.4	15.7	0.5	0.6

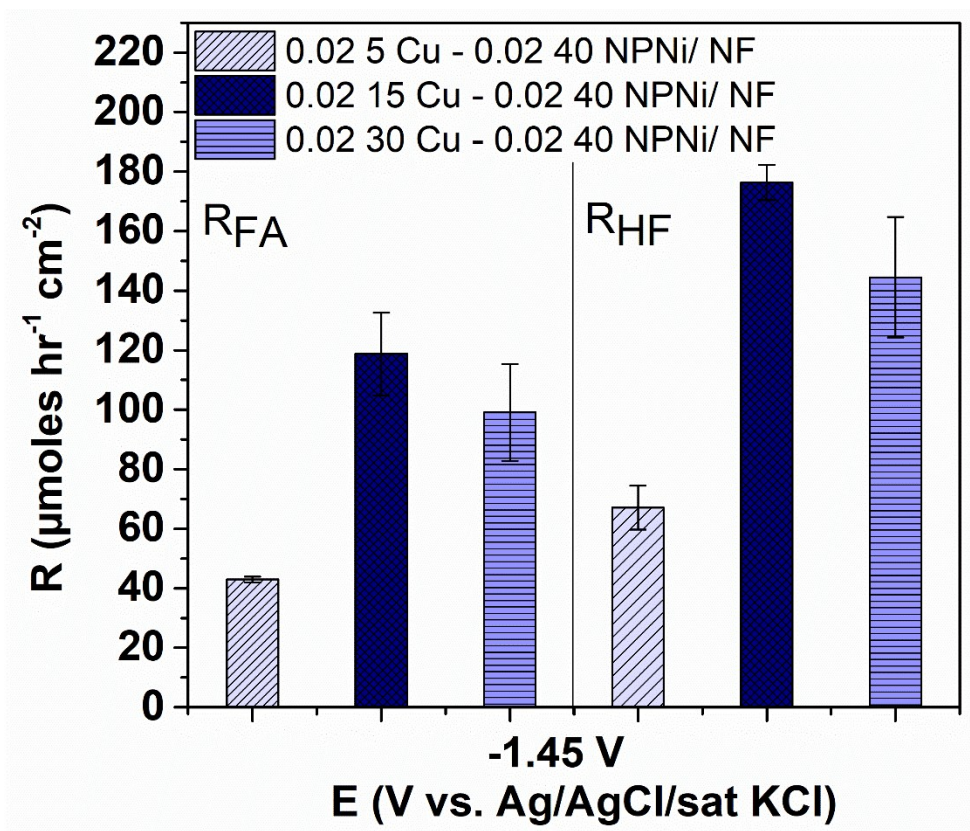
<sup>a</sup> Geometric area and ECSA were similar for plate electrodes.<sup>3</sup>

## 2. Preparation of electrocatalysts:

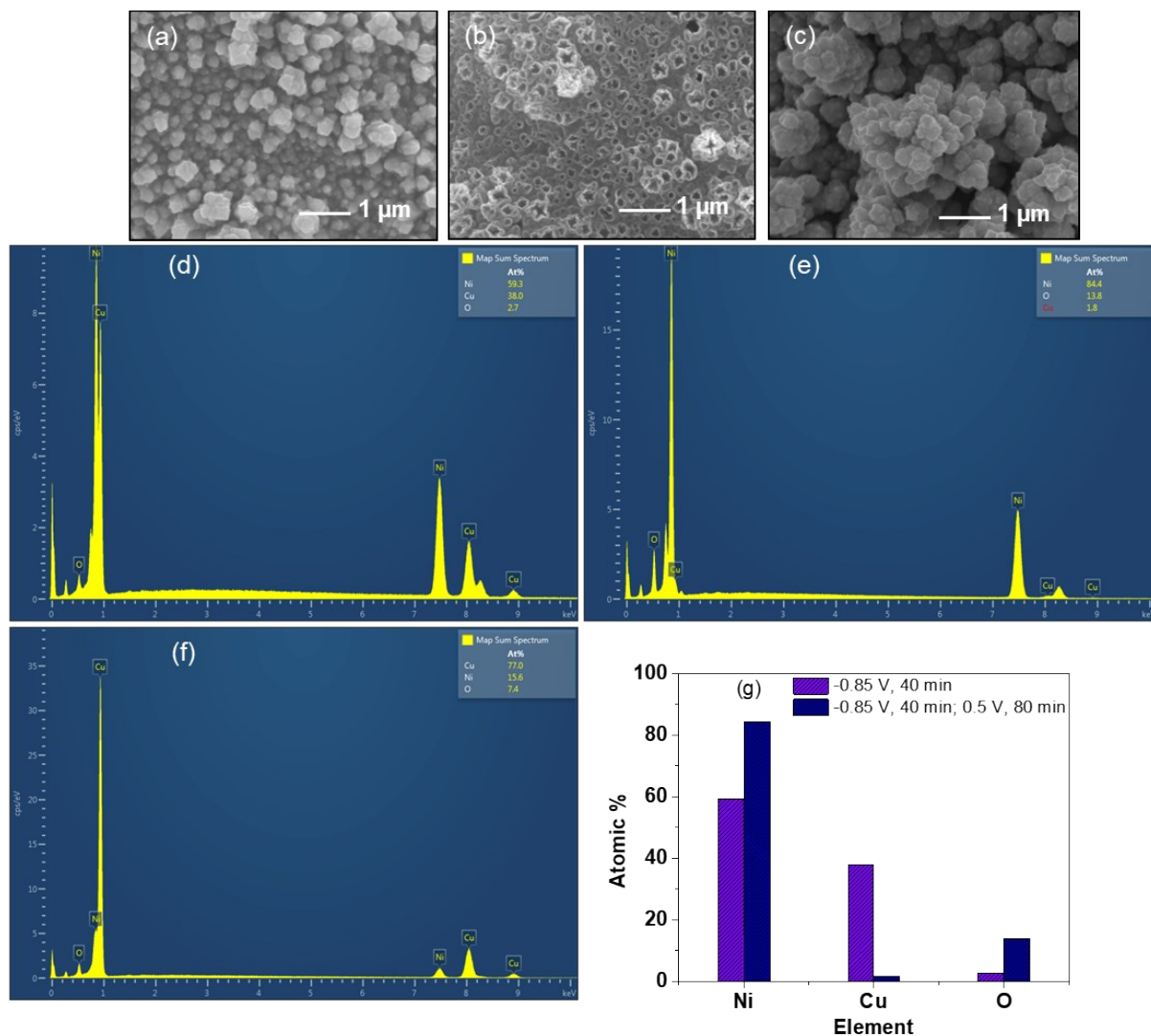
For Ni (II), no oxidation peak was observed when the potential was used to  $-0.3$  V, confirming the electrodeposition potential of Ni at  $-0.54$  V (Figure 1a inset). For Cu (II), a negligible oxidation current was observed during reduced potential window experiments (Figure 1b inset), confirming the absence of electrodeposition of Cu above a potential of  $0.08$  V. The reduction current was nearly constant, indicating the continuous deposition of  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  on the electrode surface; however, the oxidation current decreased, indicating that the metals on the electrode surface were continuously etching into the solution as free ions (Figure 1d). The atomic concentration of metals obtained by XPS and EDXS were compared (Table 1). XPS probes only a few surface layers whereas EDXS probes the bulk of the material. Therefore, a difference in the atomic concentration (at. %) was observed.

Figure S1 represented the steady-state linear sweep voltammetry in  $\text{N}_2$ -saturated  $0.5$  M NaOH at the scan rate of  $50$  mV/sec. NF and nano-porous Ni deposited on NF using various Cu concentrations and deposition times (Table S1). It was analyzed that developed porous Ni exhibited higher currents as compared to NF. When Cu concentration was increased, Cu reduced before Ni reduction because of its less reduction potential and provided fewer sites for Ni reduction. During the oxidation, most of the deposited Cu was etched and leaving the substrate (Ni foam) with lesser roughness which caused the decrease in HER current. Therefore, very high and very low concentration of Cu in the electrolyte didn't provide optimized electrodes and NPNi/NF was observed as optimized catalysts in which copper concentration was moderate. The high HER current represented the highly accessible pores as well as immense roughness. Roughness can be

analyzed by ECSA which is related to double layer capacitance ( $C_{dl}$ ) of the electrode.  $C_{dl}$  was plotted in Figure S2 and it was observed that NPNi/NF exhibited higher charging and discharging currents as compared to NF at all the analyzed scan rates. The  $C_{dl}$  value for NF and 0.02 40 NPNi/NF (NPNi/NF) was 0.12 mF/cm<sup>2</sup> and 1.24 mF/cm<sup>2</sup> respectively which illustrated that NPNi/NF possessed higher ECSA as compared to NF. So far, this investigation explained that the optimized porous structure NPNi/NF developed by Ni-Cu co-deposition and selective Cu etching comprised of high active site density and good mass transport which reported as the characteristics of a good electrocatalyst. NPNi/NF was then used for electro-catalytic reduction of furfural in this work.

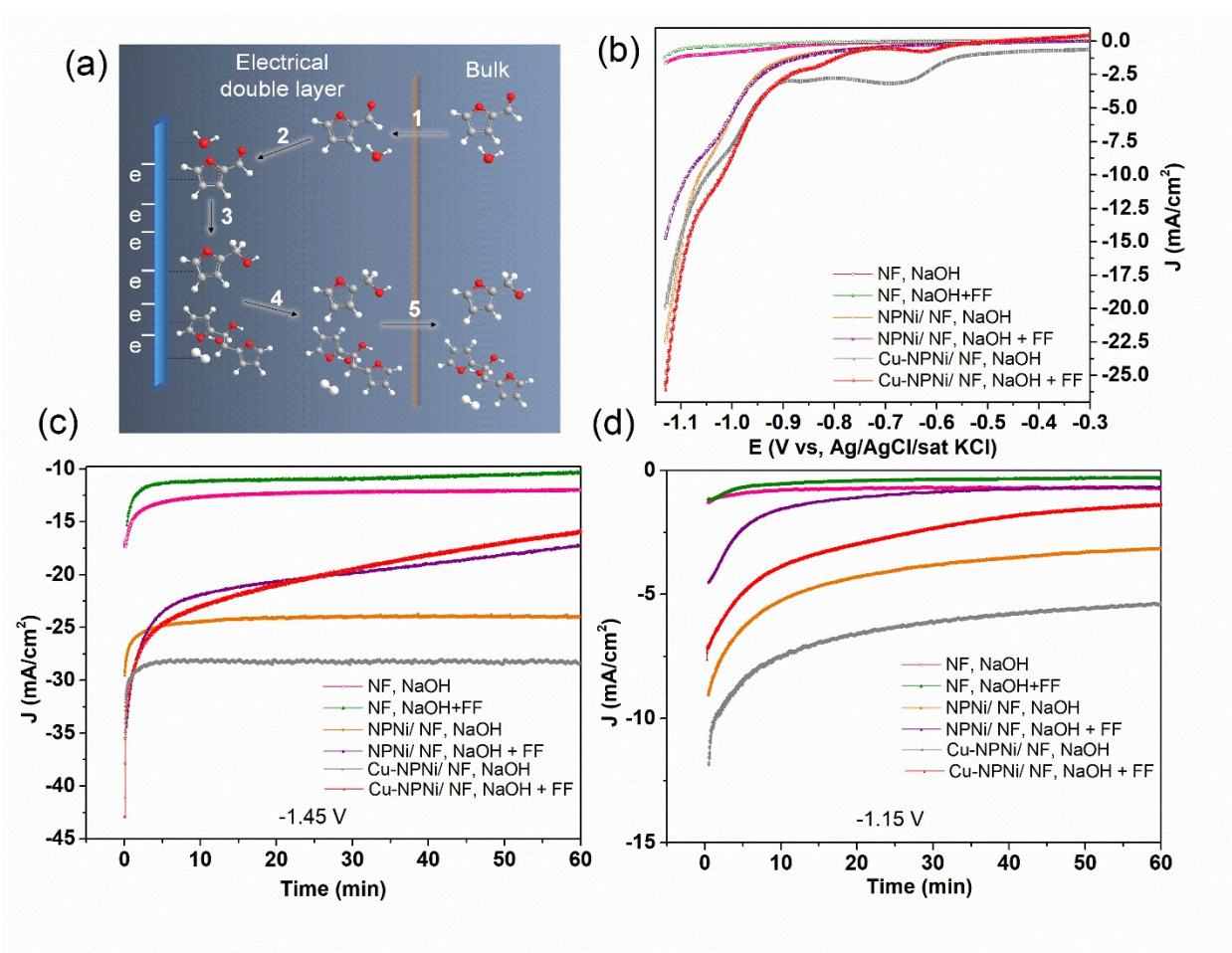


**Figure S3.** Rate of formation of furfuryl alcohol ( $R_{FA}$ ) and hydrofuroin ( $R_{HF}$ ) at  $-1.45$  V after 1 h of electrolysis using 0.5 M NaOH + 50 mM Furfural as electrolyte and 0.02 z Cu – 0.02 40 NPNi/NF as working electrode, where z is the Cu electrodeposition duration on 0.02 40 NPNi/NF.



**Figure S4.** SEM analysis of (a) 0.01 10 Ni-Cu/ NF, (b) 0.01 10 NPNi/ NF, (c) 0.02 40 Ni-Cu/ NF. EDXS analysis of (d) 0.02 40 Ni-Cu/ NF, (e) 0.02 40 NPNi/ NF (NPNi/ NF), (f) 0.02 15 Cu – 0.02 40 NPNi/ NF (Cu–NPNi/ NF). (g) Atomic % vs. Elements for the samples prepared by 40 minutes of Ni–Cu deposition at  $-0.85$  V ( $-0.85$  V, 40 min) and  $-0.85$  V, 40 min samples followed by 80 minutes of oxidation at  $0.5$  V using  $1$  M  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $0.02$  M  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  with  $0.5$  M  $\text{H}_3\text{BO}_3$  as electrolyte.





**Figure S5.** (a) Mechanism for the transport of reactants (Furfural and  $\text{H}_2\text{O}$ ) from bulk towards electrodes followed by electrochemical reaction and transport of products (Furfuryl alcohol, hydrofuroin, and  $\text{H}_2$ ) to bulk, (b) Polarization curves at  $50 \text{ mV s}^{-1}$ , Chronoamperometry analysis for 60 min duration at (c)  $-1.45 \text{ V}$ , (d)  $-1.15 \text{ V}$ . Electrolytes:  $0.5 \text{ M NaOH}$  (NaOH) and  $0.5 \text{ M NaOH} + 50 \text{ mM Furfural}$  (NaOH + FF), working electrodes: NF, NPNi/ NF, and Cu-NPNi/ NF

### 3. Effect of catalyst on electrocatalytic hydrogenation of furfural:

The ECH of FF occurred on the electrode surface by 5 distinct consecutive steps as follows: (i) transport of FF and water molecules from bulk towards electrode to electrical double layer, (ii) formation of  $\text{FF}_{\text{ads}}$  and  $\text{H}_2\text{O}_{\text{ads}}$ , (iii) products FA, HF, and  $\text{H}_2$  generation and their adsorption on the electrode surface, (iv) desorption of adsorbed product from the electrode surface and (v) transportation of the products towards the bulk (Figure S5a). The difference in current density in the presence and absence of FF confirmed the competition between HER and FF ECH (Figure S5b). The diffusion limitation was eliminated via continuous stirring. In the absence of FF, a constant current was observed confirming no catalyst degradation over time at -1.45 V. However, a decrease in current density in the presence of FF for all electrocatalyst was observed which may be attributed to the combined effect of active reactant (FF) depletion and catalytic sites deactivation via products and reactant adsorption (Figure S5c). The decrease in current density was found to be in the following order:  $\text{NF} < \text{NPNi/NF} < \text{Cu-NPNi/NF}$  which confirmed the higher extent of organics adsorption and FF ECH for Cu-NPNi/NF as compared to the other samples (Figure S5c). At lower cathodic potentials (-1.15 V) in the presence as well as absence of FF, a similar decreasing trend in current density was observed which may be due to adsorption of active components ( $\text{FF}_{\text{ads}}$  and  $\text{H}_{\text{ads}}$ ) on surface and less extent of FF ECH at low potentials (Figure S5d and 3c).

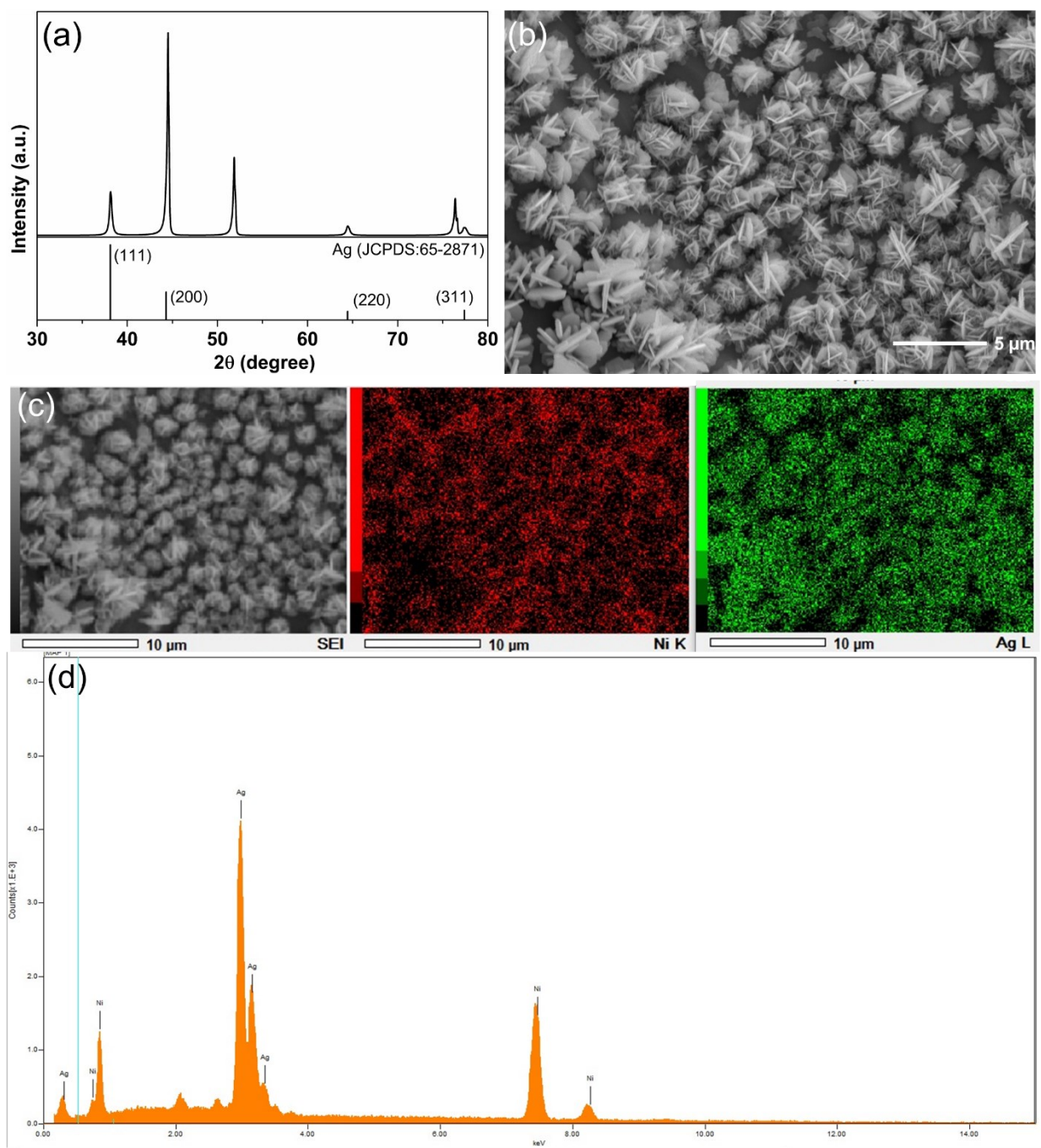
**Table S3.** % Selectivity for FA (% S<sub>FA</sub>) and HF (% S<sub>HF</sub>) analyzed using 50 mM FF with 0.5 M NaOH electrolyte along with ECH duration of 1 hour.

E (V)	Cu		Pt		NF		NPNI/ NF		Cu-NPNI/ NF	
	% S <sub>FA</sub>	% S <sub>HF</sub>	% S <sub>FA</sub>	% S <sub>HF</sub>	% S <sub>FA</sub>	% S <sub>HF</sub>	% S <sub>FA</sub>	% S <sub>HF</sub>	% S <sub>FA</sub>	% S <sub>HF</sub>
<b>-1.15</b>	5.2	26.8	22.0	NA	13.2	NA	4.2	NA	13.3	56.6
	± 0.26	± 1.54	± 1.1		± 0.7		± 0.2		± 0.67	± 2.9
<b>-1.25</b>	6.0	49.4	24.9	6.6	1.9	4.1	7.3	4.9	12.5	66.2
	± 0.3	± 2.47	± 0.25	± 0.33	± 0.1	± 0.2	± 0.37	± 0.25	± 0.63	± 3.3
<b>-1.35</b>	14.8	55.1	24.6	29.7	NA	24.2	6.5	16.9	13.0	62.9 3
	± 0.65	± 2.7	± 1.23	± 1.5		± 1.2	± 0.44	± 0.85	± 0.67	± 1.5
<b>-1.45</b>	17.6	51.3	8.2	32.7	NA	35.5	9.0	19.4	21.6	64.2
	± 0.90	± 2.95	± 0.3	± 1.7		± 1.8	± 0.6	± 1.0	± 1.1	± 3.2

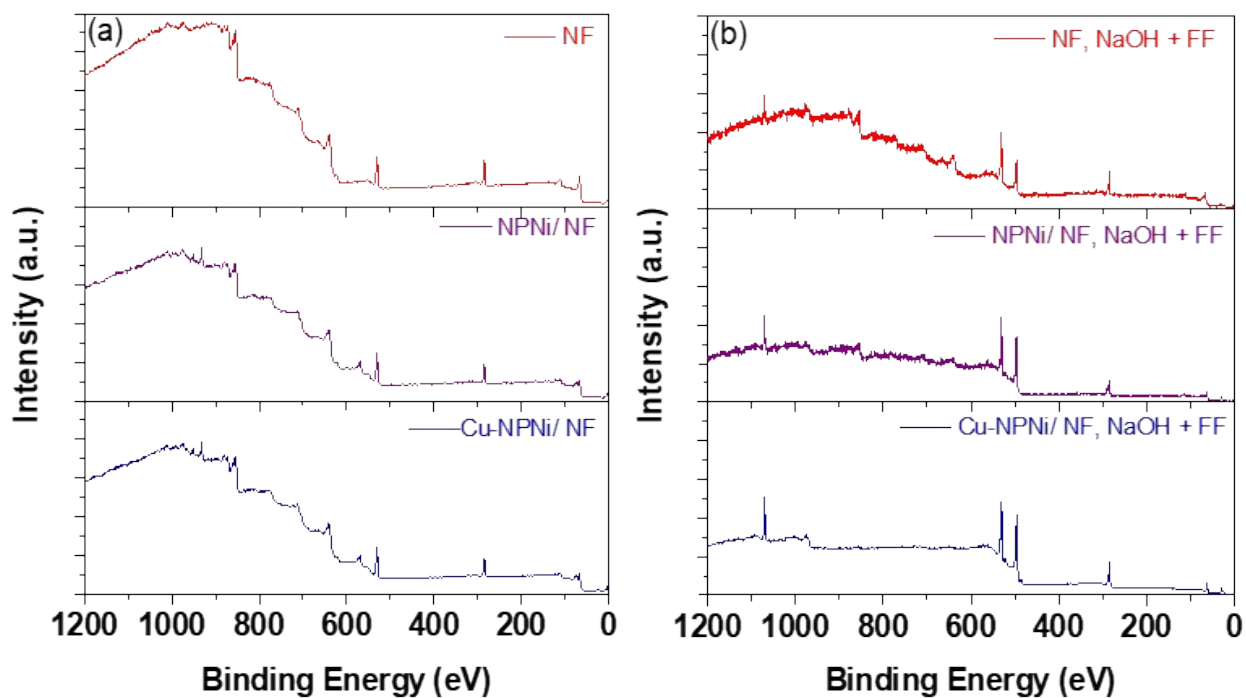
#### 4. Preparation and characterization of ed-Ag/NF:

The silver was deposited at the NF using the electrodeposition method in a 3-electrode electrochemical cell. The working, counter and reference electrode was NF, Pt plate and Ag/AgCl/sat KCl, respectively. A solution of 100 mM AgNO<sub>3</sub>, 7.5 mM citric acid, and 100 mM HNO<sub>3</sub> were used as the electrolyte. For silver electrodeposition, a potential of -0.02 V vs. Ag/AgCl/sat KCl was applied for 2 min. The obtained electrocatalyst was designated as ed-Ag/NF.

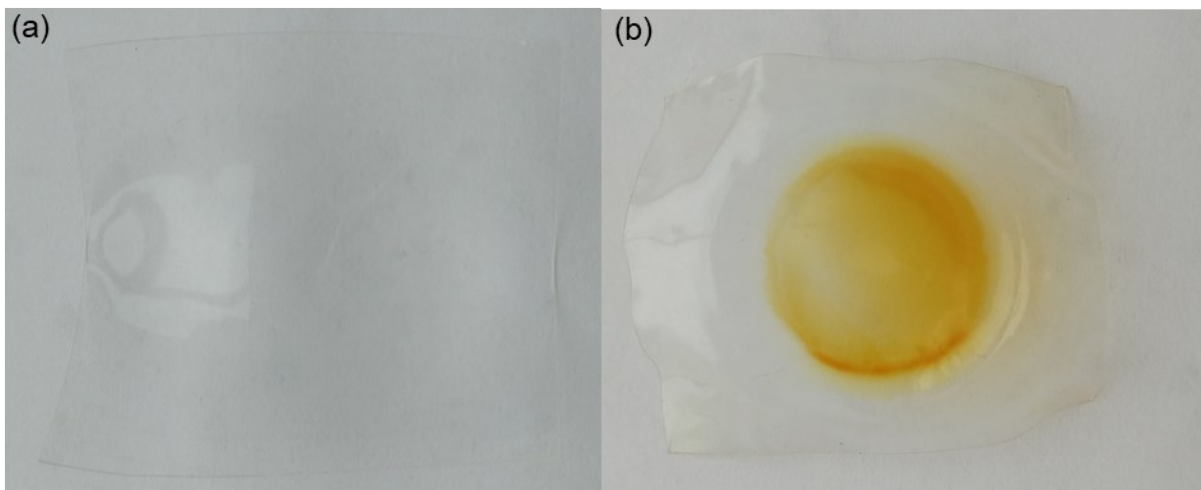
The XRD revealed the characteristic features of Ag and Ni metals. The features were indexed with the (111), (200), (220), and (311) planes of face-centered cubic Ag (JCPDS:65-2871) as shown in Figure S6a. The SEM image depicted the nanoplates type morphology of Ag deposited on the NF surface (Figure S6b) indicating a large number of active sites, which facilitated the high reaction rate of FF ECH. The EDXS mapping depicted the uniform distribution of Ag all along the NF surface (Figure S6c). The EDXS spectra further confirmed the presence of Ag and Ni on the surface (Figure S6d).



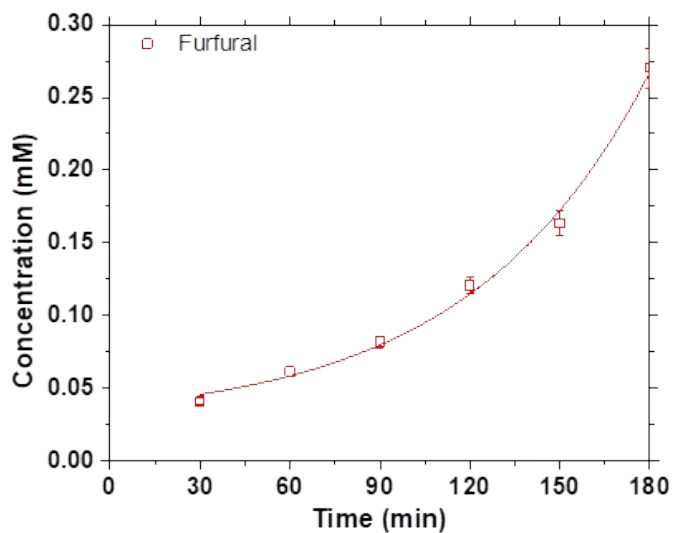
**Figure S6.** (a) XRD spectra, (b) SEM image, (c) EDXS mapping, (d) EDXS spectra of ed-Ag/NF.



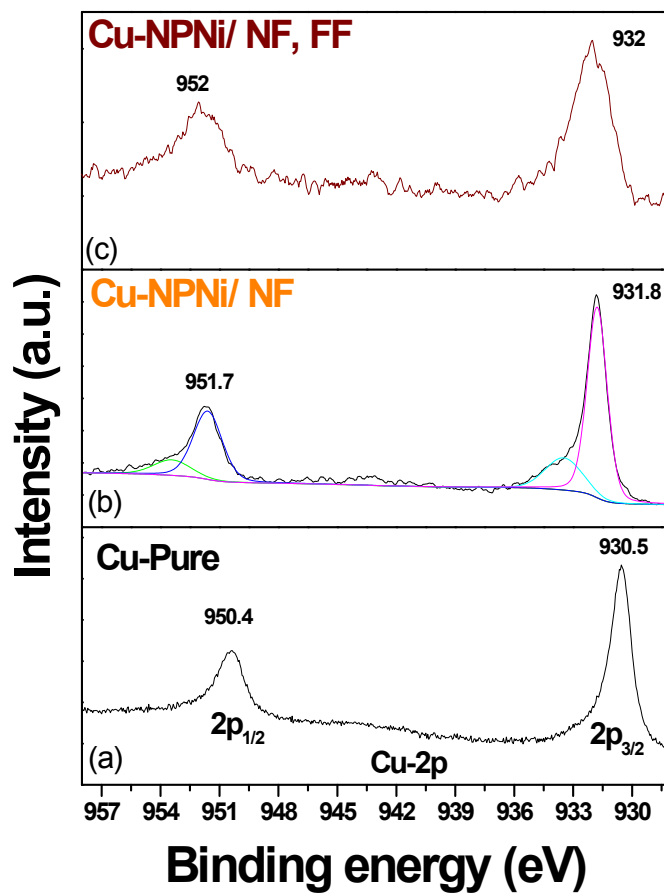
**Figure S7.** XPS Survey scan of Ni foam, NPNi/NF and Cu-NPNi/NF (a) before furfural reduction, (b) after furfural reduction. Electrolyte: 0.5 M NaOH + 50 mM Furfural, electrolysis duration: 1 h, potential:  $-1.45$  V.



**Figure S8.** Nafion 117 membrane (a) pristine, (b) after 3 h of furfural adsorption at the intersection of anode and cathode compartment of H-cell.

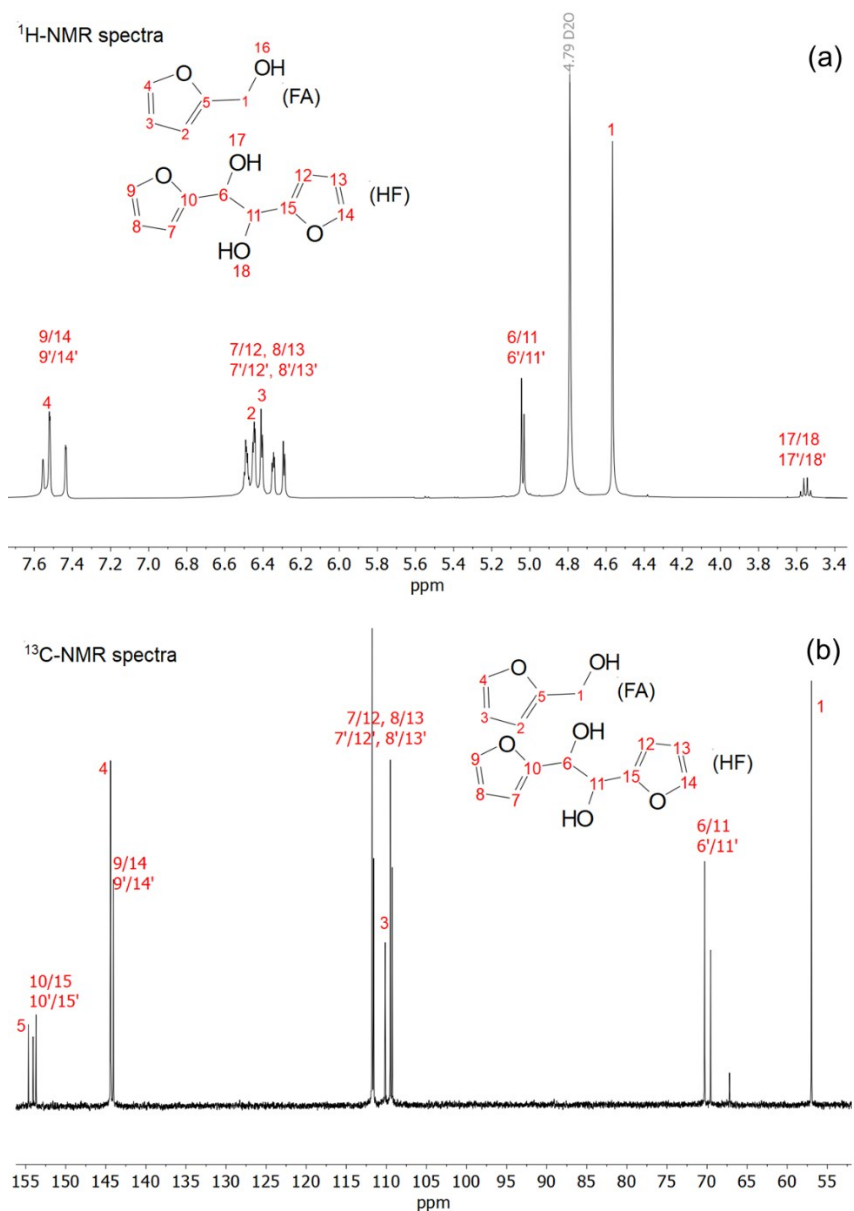


**Figure S9.** Change in furfural concentration in anode compartment with respect to time.



**Figure S10.** XPS spectra of Cu-2p for (a) Cu-pure from Cu sheet (b) Cu-NPNi/ NF before reaction (c) Cu-NPNi/ NF after FF reduction (Cu-NPNi/ NF, FF).

**Additional information**



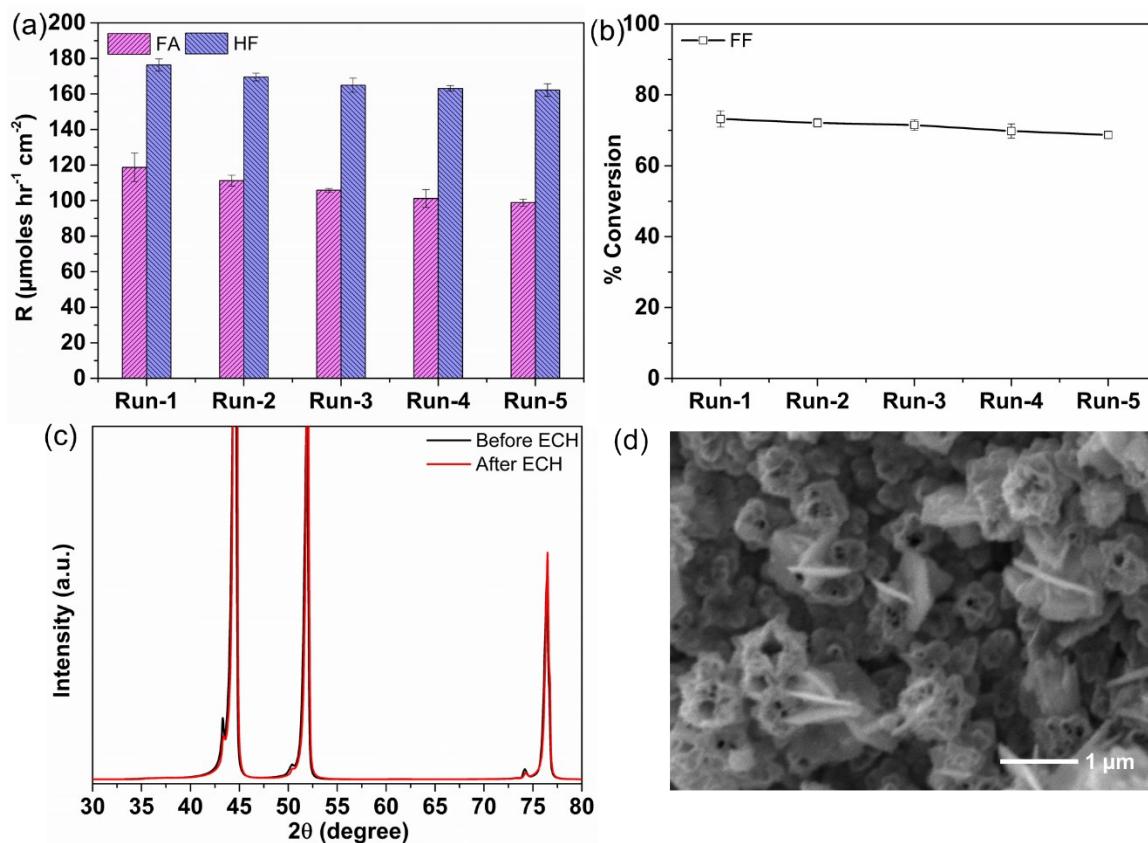
**Figure S11.** (a)  $^1\text{H-NMR}$  spectra, (b)  $^{13}\text{C-NMR}$  spectra of FA and HF. HF was present in the form of enantiomeric mixture which is represented by atom numbers without prime (') and with prime



(') in the spectra. Applied potential: -1.45 V, electrolysis duration: 3 h, Electrolyte: 0.5 M NaOH + 50 mM FF.

**Table S4.** FF ECH analyzed using Nafion<sup>®</sup> coated Cu-NPNi/NF.

<b>Cathode</b>	<b>Electrolyte</b>	<b>Potential/current density and electrolysis duration</b>	<b>Furfuryl alcohol</b>	<b>Hydrofuroin</b>	<b>% Furfural Conversion</b>
Nafion <sup>®</sup> / Cu- NPNi/NF	0.5 M NaOH 50 mM FF	-1.45 V vs. Ag/AgCl/sat KCl 1 h	$R_{FA} = 77.0$ $\pm 9.8$ $\% S_{FA} = 16.7$ $\pm 1.0$	$R_{HF} = 155.2$ $\pm 6.6$ $\% S_{HF} = 67.25$ $\pm 2.3$	$61.5 \pm 5.0$



**Figure S12.** (a)  $R_{FA}$  and  $R_{HF}$ , (b) % Conversion of FF for 5-consecutive runs of FF ECH. (c) XRD analysis before and after 5-consecutive runs of FF ECH. (d) SEM image of electrocatalyst after 5-consecutive runs. Electrocatalyst: Cu-NPNi/NF, applied potential: -1.45 V, electrolysis duration of each run: 1 h, electrolyte: 0.5 M NaOH + 50 mM FF.

## References

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