**Electronic Supplementary Information**

**Paired Electrocatalytic Hydrogenation and Oxidation of 5-(Hydroxymethyl)furfural for Efficient Production of Biomass-derived Monomers**

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**Table of Contents**

## I.     Product Separation, Identification, and Quantification

Liquid samples were collected and diluted with deionized water for analysis with HPLC (Agilent Technologies 1260) equipped with a variable wavelength detector (VWD, G1314B) at 225 nm and 260 nm for cathode and anode samples, respectively. Additionally, the reactor and components were rinsed in deionized water after completion of the reaction to collect residual species. The column (Phenomenex Inc., Gemini C18, 3μm 110 Å) for analysis of cathode samples was operated at 45 °C with a binary gradient pumping method of water and $CH_3CN$ at 0.6 mL min$^{-1}$ flow rate. The $CH_3CN$ fraction was increased from the initial 15% (v/v) to 30% over the 5 to 8.33 minute period, then was increased from 30% to 50% over the 8.33 to 10 minute period, and then was decreased to 15% from the 10 to 13 minute period. BHMF and HMF eluted around 6.7 and 7.9 minutes, respectively. Two isomers of the HMF dimer, 5,5'-bis(hydroxymethyl)hydrofuroin (BHH), eluded at different retention times (6.2 and 7.0 minutes), and are reported together for simplicity. The column for analyzing anode samples (Bio-Rad Aminex HPX-87H) was operated at 50 °C with a 0.01 M aqueous $H_2SO_4$ mobile phase at 0.5 mL min$^{-1}$. FDCA, HFCA, FFCA, HMF, and DFF eluted around 22.3, 27.0, 31.0, 39.7, 49.2 minutes, respectively. HMF and electrochemical reaction products were identified and quantified by comparison to genuine samples, except for BHH which was identified by fraction collection combined with $^1$H NMR, as described in more detail in **Section III** of the Supporting Information. The reaction profiles shown in **Figure 8c** for ACT-mediated HMF oxidation were produced by sampling the reaction mixtures after 14.4, 28.8, 43.2, and 57.6 C of charge were passed. The data point for 72.2 C was taken from independent experiments conducted without intermediate sampling, identical to the unpaired anode results depicted in **Figure 9.** Evolved $H_2$ was quantified with a gas chromatography (SRI Instrument 8610C MG#3), equipped with HaySep D column and

MolSieve 5 Å columns. The setup and methods were described in detail in our previous publication.[1]

## II.    Calculation of Selectivity and Faradaic Efficiency

The faradaic efficiency (*FE*) of each HMF product $i$ ($i$ = BHMF, BHH, FDCA, DFF, HFCA, or FFCA) was calculated by Equation S1:

$$FE_i = \frac{n_i z_i F}{Q} \times 100\%$$

(S1)

in which $n_i$ is the amount of product $i$ (moles), $z_i$ is the number of moles of electrons transferred per mole of product ($z$ = 2 for BHMF, BHH, HFCA and DFF, 4 for FFCA, and 6 for FDCA), $F$ is the Faraday constant (96485.3 C mol$^{-1}$), and $Q$ is the total charge in coulombs transferred through the external circuit. The combined electron efficiency (*EE*) to desired products (i.e. BHMF and FDCA) was defined by Equation S2:

$$EE = \frac{[2n_{BHMF} + 6n_{FDCA}]F}{Q} \times 100\%$$

(S2)

Product selectivity ($S_i$) was calculated using Equation S3:

$$S_i = \frac{n_i}{n_{HMF}^*} \times 100\%$$

(S3)

in which $n_{HMF}^*$ is the amount of HMF reacted (moles). Product yield was calculated using Equation S4:

$$Y_i = \frac{n_i}{N_{HMF}} \times 100\%$$

(S4)

in which $N_{HMF}$ is the initial amount of HMF (moles). For paired electrolysis, the individual yields for BHMF and FDCA were calculated based on separate values of $N_{HMF}$ for the cathode and anode. Faradaic efficiency for hydrogen gas (FE$_{H2}$) was calculated by the method explained in detail in our previous publication.[1]

### III.    Evaluation of 5,5'-Bis(hydroxymethyl)hydrofuroin

Samples of the HMF dimers (i.e. BHH) were collected using an HPLC (Water Alliance) equipped with an automatic fraction collector (Waters Fraction Collector III). The same column conditions and pumping method were used as described above. The collected fractions were dried in a vacuum oven and reconstituted in acetonitrile-d3 (99.8 atom%, Cambridge Isotope Laboratories, Inc.) for $^1$H NMR and HSQC analysis with a Bruker 600 MHz NMR spectrometer (AVIII-600) (see **Figures S1–S4**). N,N-Dimethyl-formamide (DMF, 99%, Fisher Scientific) was added as an internal standard to allow determination of the BHH concentration. The same samples were analyzed by HPLC (as described in **Section I** of Supporting Information) to acquire quantitative calibration curves based on the concentrations determined by $^1$H NMR. Those calibration curves were used for quantification of BHH.

**BHH-1**

$^1$H NMR (600 MHz, Acetonitrile-d3) δ 6.28 (d, J = 3.1 Hz, 2H), 6.25 (d, J = 3.1 Hz, 2H), 4.84 (dd, J = 3.9, 1.8 Hz, 2H), 4.48 (d, J = 5.9 Hz, 4H), 3.62 (dd, J = 3.9, 1.8 Hz, 2H), 3.34 (t, J = 5.9 Hz, 2H).

**BHH-2**

$^1$H NMR (600 MHz, Acetonitrile-d3) δ 6.19 (d, J = 3.2 Hz, 2H), 6.17 (d, J = 3.3 Hz, 2H), 4.84 (dd, J = 3.0 Hz, 2H), 4.43 (d, J = 5.9 Hz, 4H), 3.87 (dd, J = 2.4 Hz, 2H), 3.28 (t, J = 5.9 Hz, 2H).
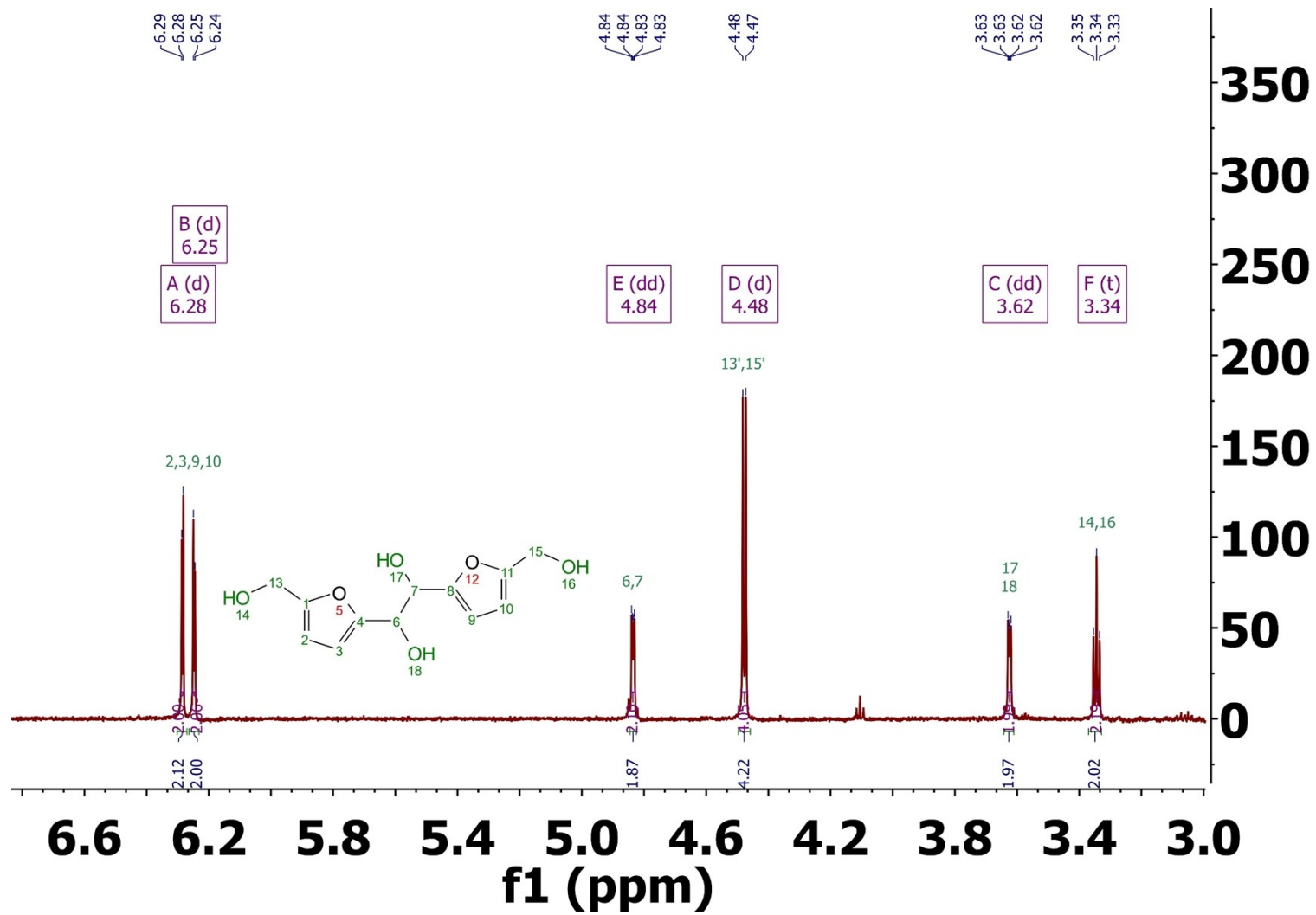
**Figure S1.** ^{1}H-NMR spectra of BHH-1

**Figure S2.** HSQC spectra of BHH-1

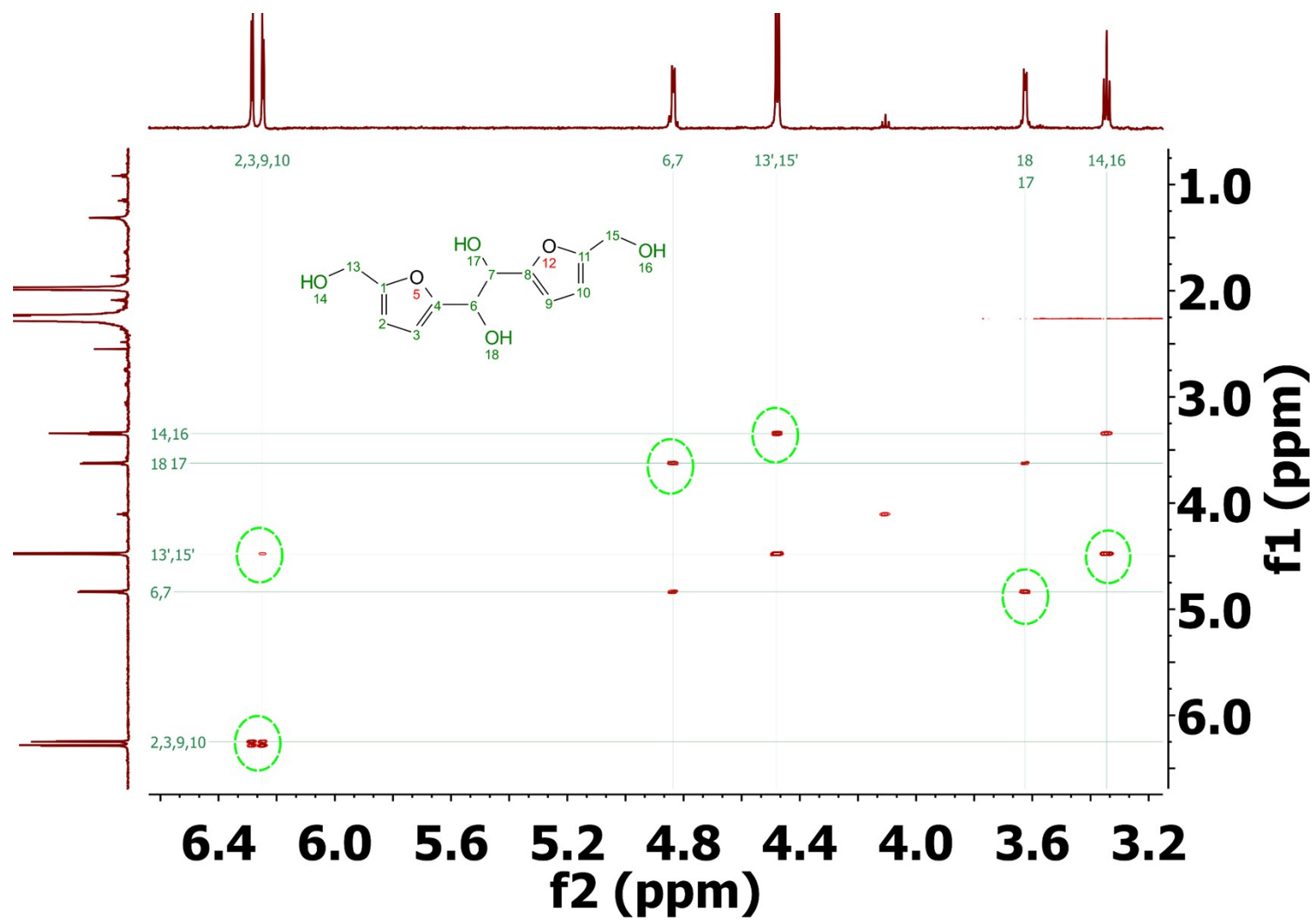**Figure S3.** ¹H-NMR spectra of BHH-2

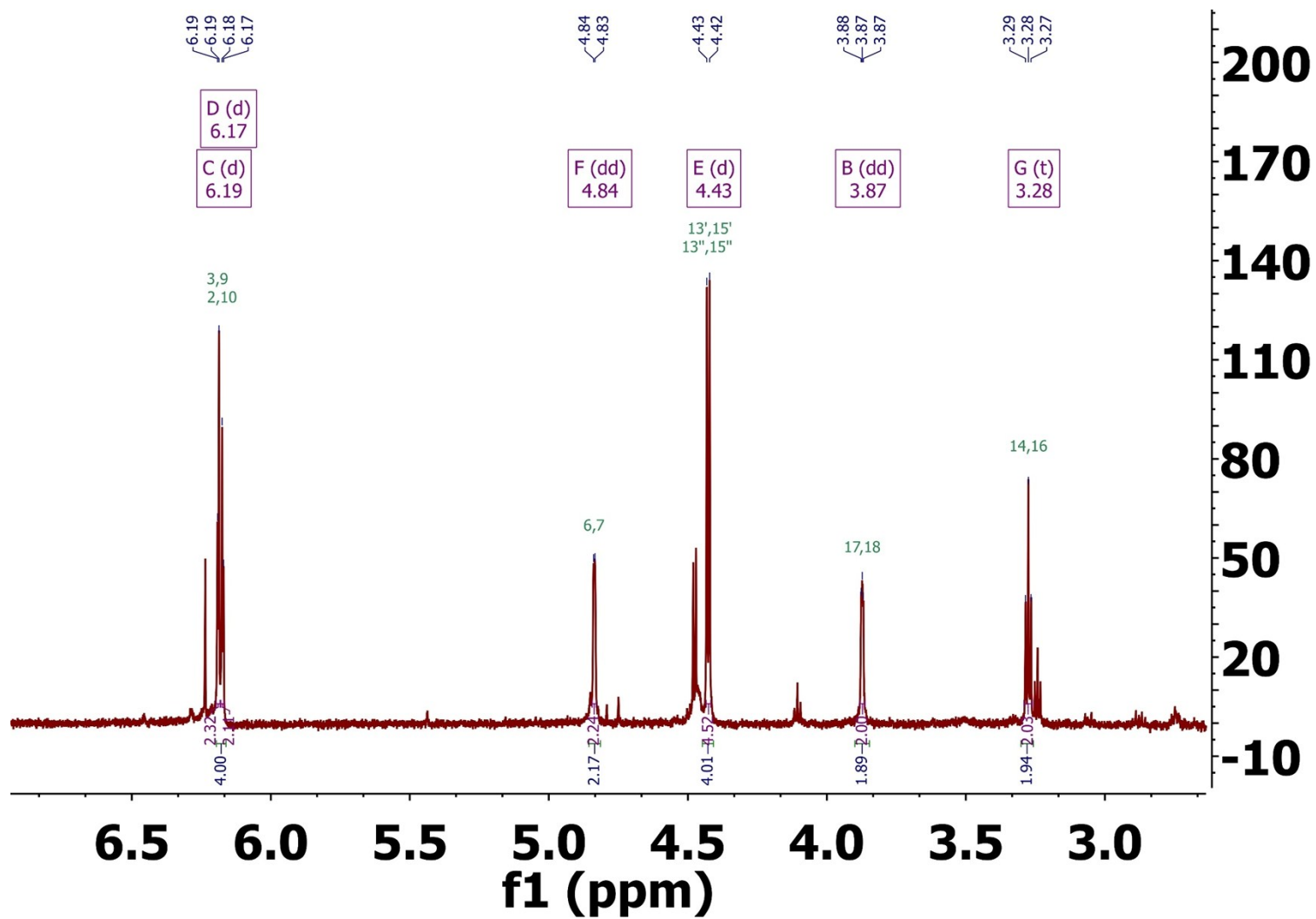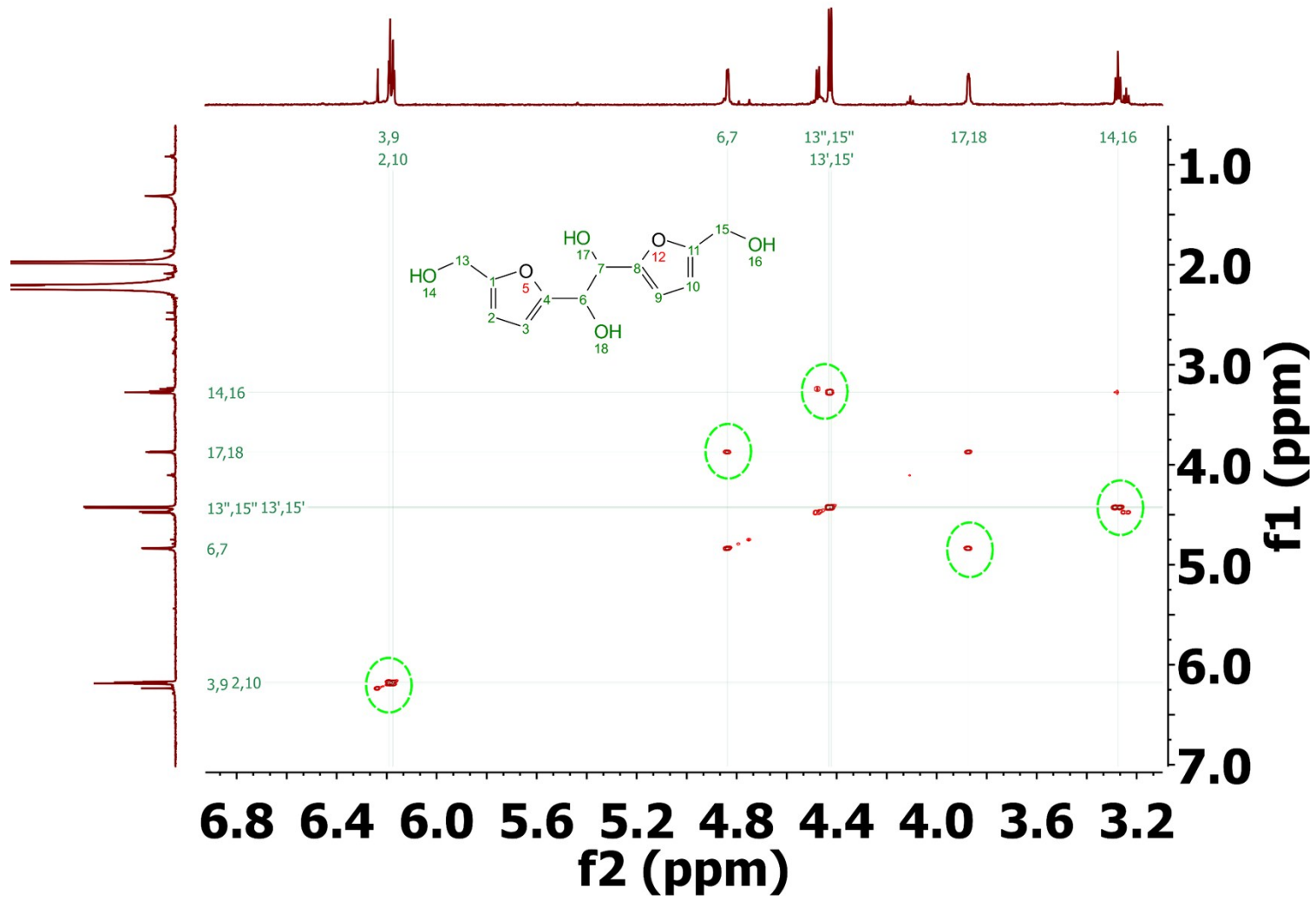Figure                    S4.                    HSQC                    spectra                    of                    BHH-2
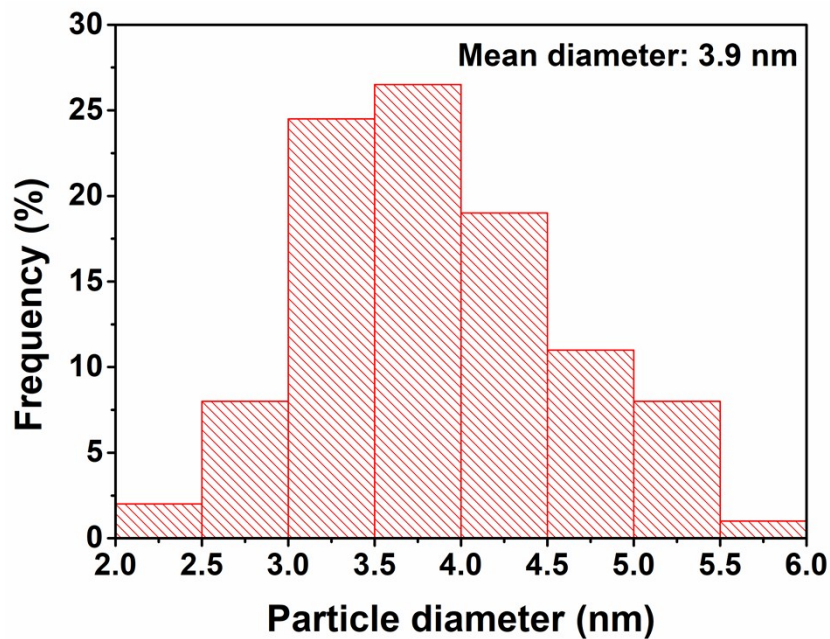
8

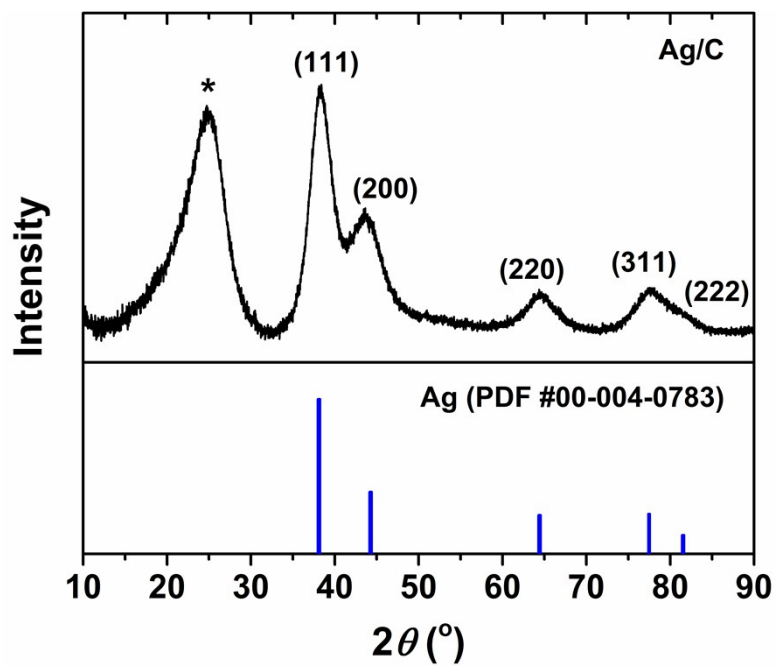## IV. Ag/C Catalyst Characterizations

**Figure S5.** Ag particle size histogram for Ag/C from TEM measurements.

**Figure S6.** XRD pattern for Ag/C. The asterisk denotes the (002) peak from carbon black.
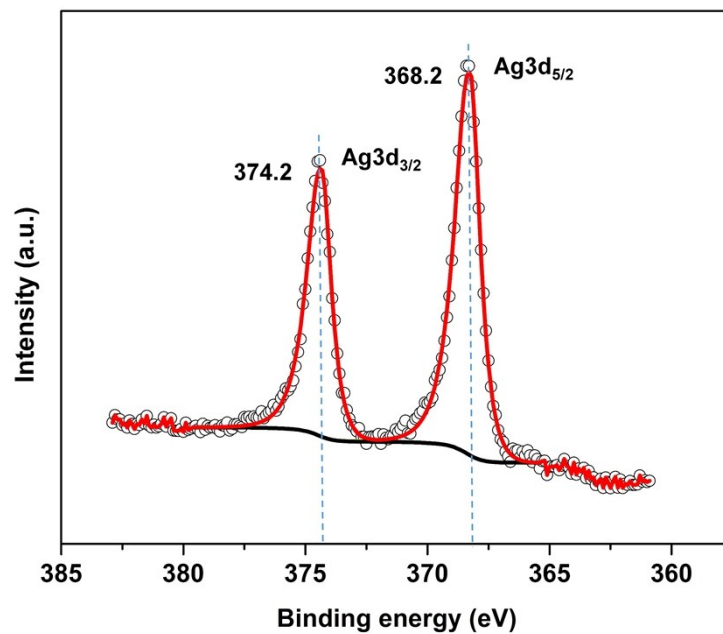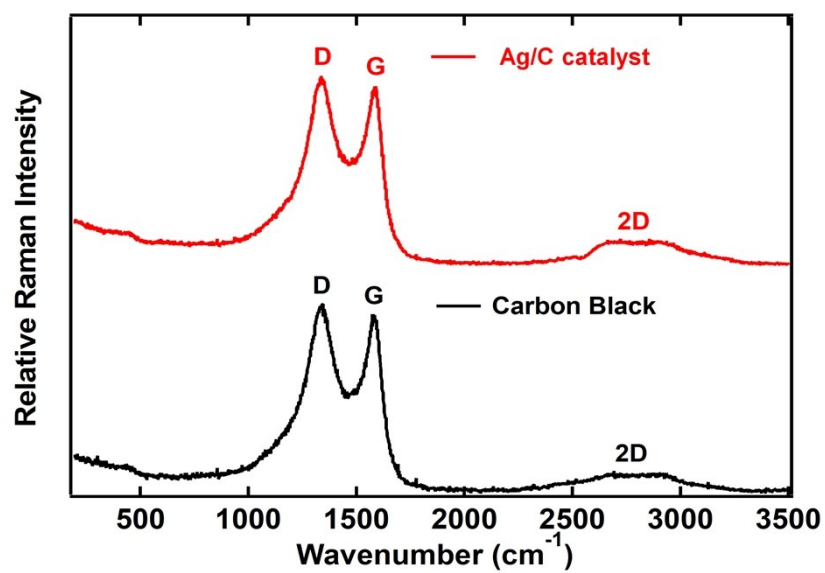
**Figure S7.** XPS spectra of Ag/C catalyst.



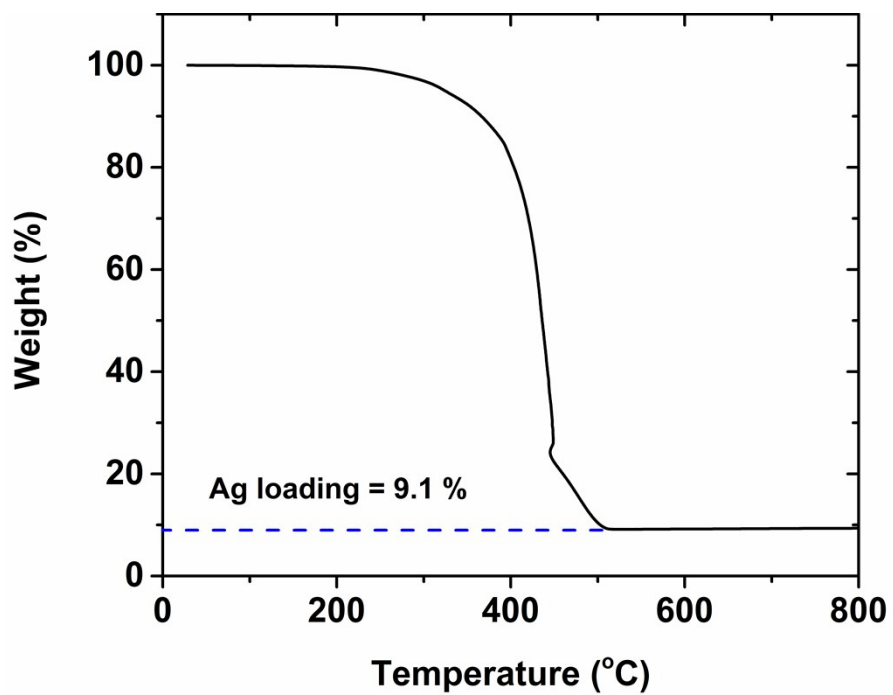**Figure S8.** Raman spectra of Ag/C and Vulcan XC-72R carbon black.

10

**Figure S9.** TGA of Ag/C catalyst to determine Ag loading.
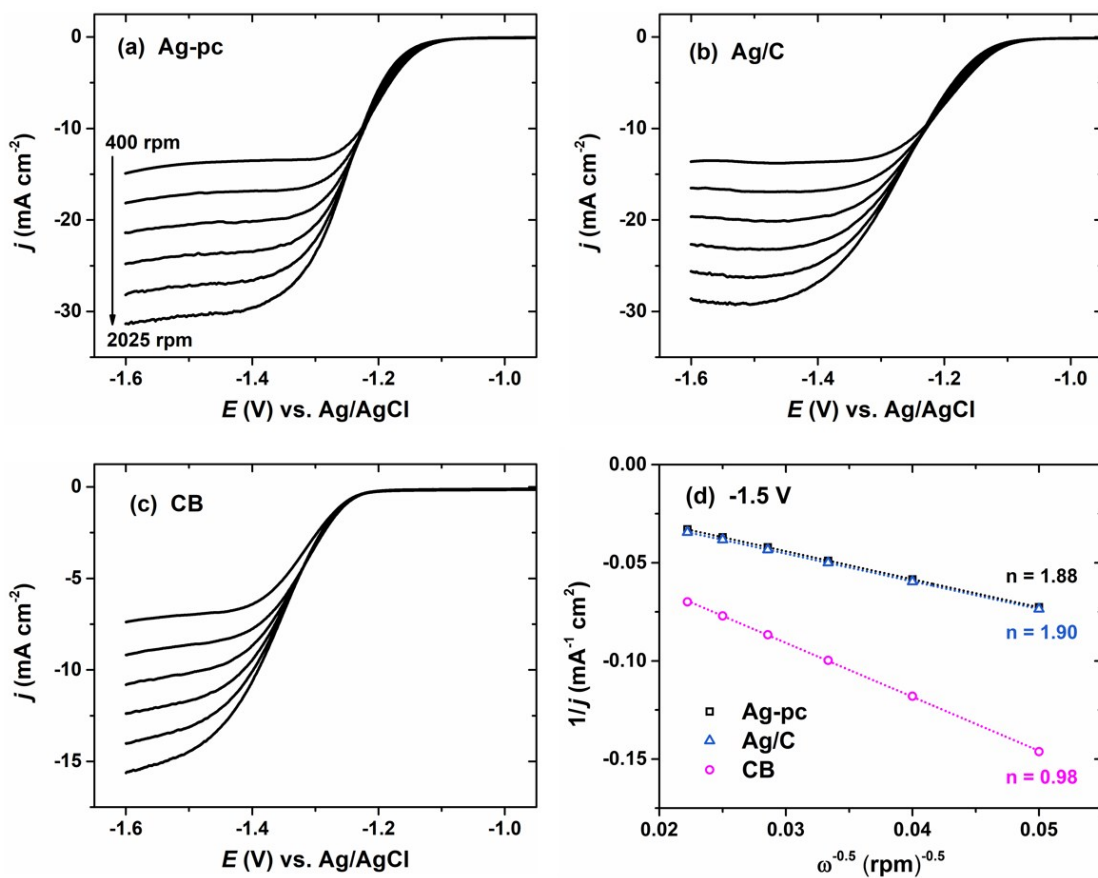
## V.        Koutecký-Levich Analysis



**Figure S10.** Cathodic linear sweep voltammograms for (a) Ag-pc, (b) Ag/C, and (c) CB collected at 50 mV s$^{-1}$ and rotation rates of 400, 625, 900, 1225, 1600, and 2025 rpm, and (d) corresponding Koutecký-Levich plots. The number of electrons transferred (*n*) was calculated from the value of the slope. Electrolytes contained 20.0 mM HMF.

## VI.  Additional Electrolysis Results

**Table S1.** Electrocatalytic HMF reduction with Ag-pc electrodes.[a]

| [HMF] (mM) | Duration (min) | Q (C) | Conversion (%) | $S_{BHMF}$ (%) | $S_{BHH}$ (%) | $FE_{BHMF}$ (%) | $FE_{BHH}$ (%) | $FE_{H2}$ (%) |
|---|---|---|---|---|---|---|---|---|
| 5 | 30 | 3.42 | 19.7 | 80.9 | 9.6 | 89.3 | 5.3 | 2.0 |
| 20 | 30 | 7.85 | 13.2 | 57.1 | 30.2 | 75.0 | 19.9 | 0.0 |
| 50 | 30 | 12.1 | 9.1 | 40.7 | 49.5 | 57.8 | 35.3 | 0.0 |
| 20 | 300 | 26.5 | 44.6 | 55.8 | 31.3 | 72.7 | 20.4 | 0.0 |

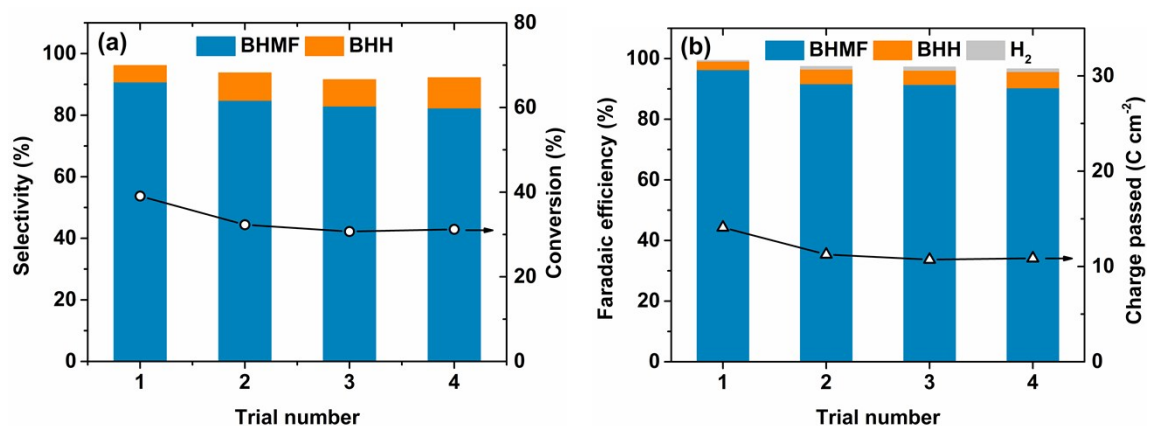[a] Conditions: 0.5 M pH 9.2 borate buffer solution. $E = -1.2$ V vs Ag/AgCl.



**Figure S11.** (a) HMF conversion and product selectivity and (b) faradaic efficiency and total charge transferred for electrochemical reduction of HMF using one Ag/C electrode for four consecutive trials. The Ag/C electrode was rinsed with DI water between trials. Conditions: pH 9.2 electrolyte, 20.0 mM HMF, $E = -1.3$ V, 30 minute reaction each trial.
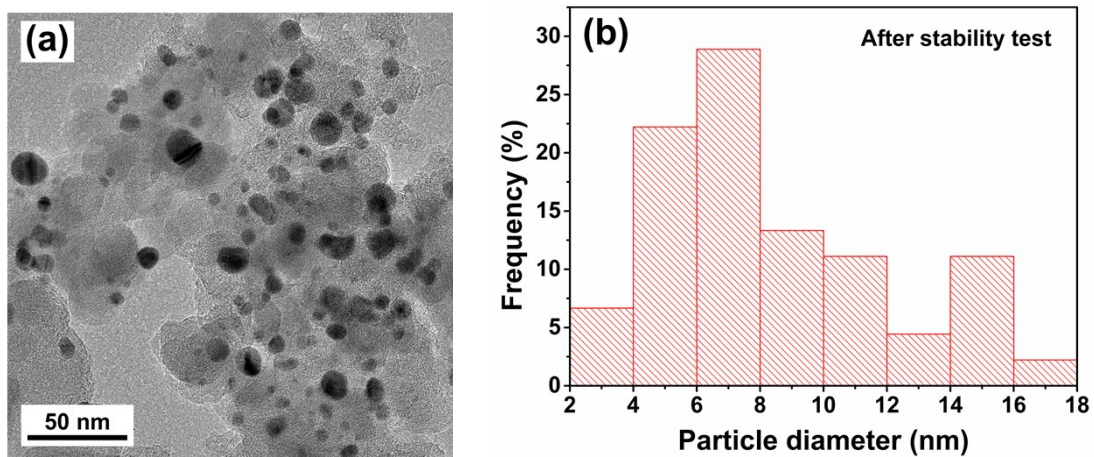
13

**Figure S12.** (a) TEM image of Ag/C after stability test (i.e. reusing one Ag/C electrode for four consecutive trials) and (b) corresponding Ag particle size histogram.

## VII.    Paired Electrochemical HMF Oxidation and Reduction

**Table S2.** Comparison to paired electrochemical HMF oxidation and reduction in literature.[a]

| Anode | | | Cathode | | | EE (%) | Reference |
|---|---|---|---|---|---|---|---|
| Catalyst | Product | FE (%) | Catalyst | Product | FE (%) | | |
| TEMPO | FDCA | 96 | Ag/C | BHMF | 91 | 187 | Present work |
| Vanadium[b] nitride (VN) | FDCA | 84 | Pd/VN[b] | DHMTHF | 86 | 170 | [2] |

[a] At the time of writing, these are the only reports of paired electrochemical HMF oxidation and reduction. [b] In Ref [2], high pH alkaline electrolyte and low pH acid electrolyte was used in anode and cathode, respectively. The electrolyte used in the present work is near neutral pH. All other reports of electrochemical HMF conversion only converted HMF at one electrode, and therefore by definition have a maximum combined electron efficiency (EE) for HMF conversion of 100%.
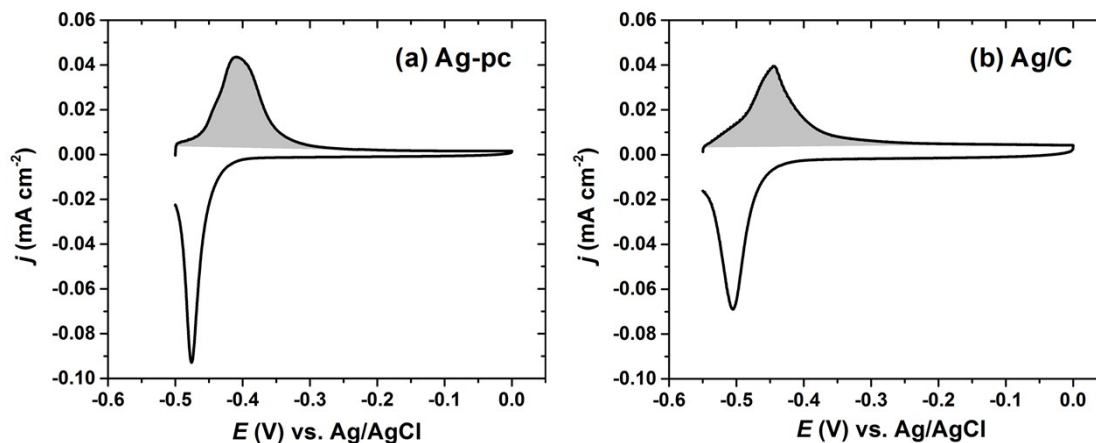
## VIII. Pb stripping and Ag ECSA



**Figure S13.** Voltammograms of $Pb_{UPD}$ for (a) Ag-pc and (b) Ag/C. The anodic stripping peaks (shaded regions) were integrated to determine the charge associated with $Pb_{UPD}$ stripping ($Q_{strip}$), which were then used for calculation of Ag ECSA according to Equation 9. Conditions: 0.5 M pH 9.2 borate buffer solution containing 125 μM lead nitrate. Potential sweep rate was 20 mV s$^{-1}$.
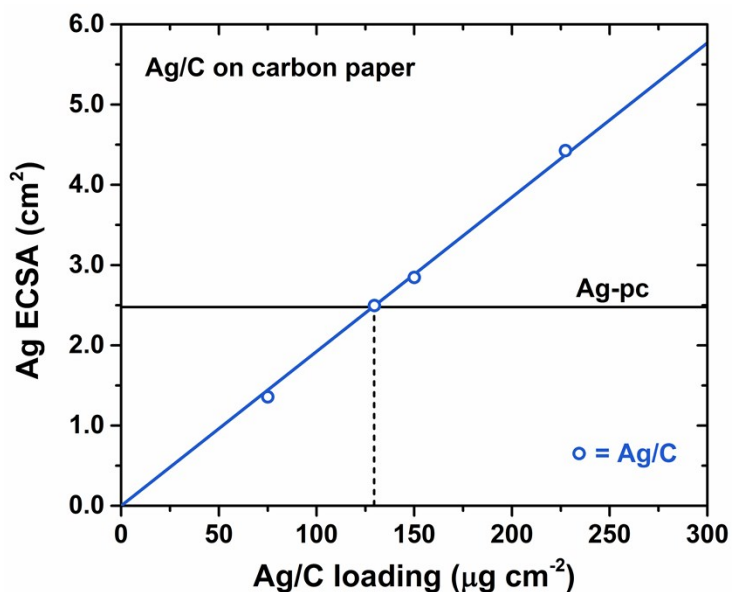


**Figure S14.** Electrochemically-active surface area (ECSA) of Ag/C determined by $Pb_{UPD}$ stripping as a function of catalyst loading, compared to ECSA for Ag-pc. The dashed vertical line indicates the Ag/C loading on carbon paper that was used for HMF electrolysis experiments.

**Table S3.** Summary of electrodes used for HMF reduction.

| electrode | geometric area* (cm$^2$) | Pb$_{UPD}$ anodic stripping charge (mC) | Ag ECSA (cm$^2$) |
| --- | --- | --- | --- |
| Ag-pc foil | 2.0 | 0.652 | 2.51 |
| Ag/C on carbon paper | 2.0 | 0.654 | 2.52 |
| CB on carbon paper | 2.0 | - | - |
| Ag-pc disk | 0.196 | 0.102 | 0.391 |
| Ag/C on GCE | 0.196 | 0.092 | 0.354 |
| CB on GCE | 0.196 | - | - |

* Geometric area of surface exposed to electrolyte. Both front and back sides of the foil and carbon paper electrodes are included.

## IX.    References

[1] Chadderdon, X. H.; Chadderdon, D. J.; Matthiesen, J. E.; Qiu, Y.; Carraher, J. M.; Tessonnier, J. P.; Li, W., Mechanisms of furfural reduction on metal electrodes: distinguishing pathways for selective hydrogenation of bioderived oxygenates. *J. Am. Chem. Soc.* **2017,** *139*, 14120-14128.

[2] Li, S.; Sun, X.; Yao, Z.; Zhong, X.; Cao, Y.; Liang, Y.; Wei, Z.; Deng, S. Zhuang, G.; Li, X.; Wang, J., Biomass valorization via paired electrosynthesis over vanadium nitride-based electrocatalysts. *Adv. Funct. Mater.* **2019**, 1904780.