Electrochemical Reductive Amination of Furfural-Based Biomass

Intermediates

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Electronic Supplementary Information

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Experimental

Materials.   Zinc foil (0.25 mm thick, 99.98%), Sn foil (0.025 mm thick, 99.9%), and silver nitrate (99.9+%) was purchased from Alfa Aesar. Copper foil (1 Mil, 0.001 in. thick, 99.9%) was purchased from Nimrod Hall Copper Foil Company. Sulfuric acid (95-98%), methylamine (40 wt%), ethanolamine (> 99%), 5-hydroxymethylfurfural ($\geq$ 99%), 5-methylfurfural (99%), dimethylsulfone,(98%), and sodium acetate ($\geq$ 99.0%) were purchased from Sigma Aldrich. 2,5-diformylfuran (> 98%) and 5-formyl-2-furancarboxylic acid (> 98%) were purchased from TCI. All chemicals were used without further purification.

Preparation of Electrodes. Cu, Sn, and Zn electrodes used in this study were prepared by cutting the foil to pieces with dimensions of 1.5 cm x 2.5 cm. The Zn surface was mechanically polished with sandpaper. The Cu and Sn surfaces were first rinsed with 2-propanol and water, then cleaned by immersing in 1 M HCl for 1 minute to remove surface oxides. After rinsing with DI water and drying, Cu tape was attached to the foil electrodes to enable connection to the potentiostat lead. The backside and top 0.5 cm of the foil electrodes were then covered with Teflon tape to yield a 3.0 cm^2 working area. The cleaning and preparation of electrodes were performed immediately before use in experiments. Ag electrodes were prepared by placing clean Cu foil, cleaned using aforementioned procedures, in a sputter coater (Anatech USA, DC/RF Dual Source Sputtering System) where 100 nm of Ag was sputter-coated onto the Cu substrate. The films were then made into electrodes in the same manner as for the foil electrodes. The Pt working (1.5 cm x 2.0 cm) and counter electrodes (2.5 cm x 2.0 cm) were prepared by sputter coating a 100 nm platinum layer over a 20 nm titanium layer onto cleaned glass slides. Cu and Teflon tapes were then attached to the top of the Pt in the same manner as for the other electrodes. High surface area Ag electrodes (Ag$_{gd}$) were prepared by galvanic displacement by

immersing clean Cu foil electrodes (1.5 cm x 2.0 cm working area), cleaned and prepared just prior to deposition using the aforementioned procedures, into a 50.0 mM solution of AgNO$_3$ for 30 seconds.[1] Following deposition, the film was rinsed gently with water and dried in an air stream. The surface area of the Ag$_{gd}$ electrode was estimated by obtaining cyclic voltammograms using varying scan rates and plotting current densities used for double later charging as a function of scan rate. Since the current density used for double layer charging is proportional to the surface area, this method allows for a comparison of the surface areas of the flat Ag electrode and the Ag$_{gd}$ electrode. The result shows that the surface area of the dendritic Ag electrode is 9.7 times higher than the surface area of the flat Ag electrode.

Solution Preparation and Aldimine Formation. The 0.7 M methylamine buffer solution was prepared by diluting concentrated aqueous CH$_3$NH$_2$ (pK$_a$ = 10.6) with ultrapure water and acidifying to pH 11.0 with concentrated H$_2$SO$_4$. The necessary amount of HMF, 5-MF, DFF, or FFCA was added to make a 0.02 M solution. The same procedure was followed for reaction of HMF with ethanolamine (NH$_2$CH$_2$CH$_2$OH), where the solution was prepared with ethanolamine instead of methylamine. Although the pK$_a$ (9.5) of ethanolamine is lower than that of methylamine, the pH of the ethanolamine solution was adjusted to 11.0 to be consistent with the pH of the methylamine solution used in this study.

Reduction of HMF. A three-electrode cell composed of the metal electrode of interest as the working electrode (WE), a Pt counter electrode (CE), and a Ag/AgCl (in 4 M KCl) reference electrode (RE) was used for all reductive amination experiments. All experiments were performed at room temperature. LSVs were performed in a 0.7 M methylamine buffer solution (pH 11.0) with and without 0.02 M HMF in an undivided cell without stirring. The potential was swept from the open circuit potential to the negative direction using a scan rate of 5 mV/s. The

potential of the WE was measured against the Ag/AgCl RE during the LSV experiments but the LSV results contained in this study were presented using the potential of the WE against the reversible hydrogen electrode (RHE) as well as the Ag/AgCl for convenience. Since the thermodynamic reduction potential of water to hydrogen is 0 V vs. RHE regardless of the pH condition, showing the LSV results as a function of the WE potential against the RHE makes it easy to calculate the overpotential required for water reduction for each electrode and also to evaluate the ability for each electrode to reduce aldimines compared with the ability to reduce water. The conversion between potentials vs. Ag/AgCl and vs. RHE is performed using the equation shown below.

$$E \text{ (vs. RHE)} = E \text{ (vs. Ag/AgCl)} + E_{Ag/AgCl} \text{ (reference)} + 0.0591 \text{ V} \times pH$$
$$(E_{Ag/AgCl} \text{ (reference)} = 0.1976 \text{ V vs. NHE at 25 °C})$$

The constant potential reduction of HMF was performed in a divided cell where the cathodic compartment and the anodic compartment were divided by a glass frit. The WE and RE were placed in the cathode compartment while the Pt CE was placed in the anode compartment. The cathodic compartment contained 14 mL of the buffer solution (pH 11.0) with 0.02 M HMF while the anodic compartment contained the same solution without HMF. Reduction was performed by passing 20 C (or the desired coulombs) at various potentials. The FE and selectivity of each reaction were calculated using the following equations, where F is the Faraday constant (96485 C/mol) and n is the number of electrons required for the conversion of the aldimine to an amine, which is 2 for all substrates except DFF, where n=4.

$$\textbf{FE } (\%) = \frac{\textbf{mol of amine formed}}{\textbf{Total charge passed (C)/ (F} \times \textbf{n)}} \times \textbf{100\%} \qquad (1)$$

$$\textbf{Selectivity } (\%) = \frac{\textbf{mol of amine formed}}{\textbf{mol of HMF consumed}} \times \textbf{100}\% \qquad\qquad (2)$$

Product Analysis.   Products were detected and quantified via ^{1}H nuclear magnetic resonance (NMR) spectroscopy using a Bruker Avance III 400 MHz NMR spectrometer.   An internal standard of dimethyl sulfone or sodium acetate was used to determine product concentrations. The HMF signal in the product solution was also compared to that of the initial solution to determine the amount of HMF consumed. The identities of the products were further confirmed by ^{13}C-NMR, and ^{1}H-^{13}C HSQC.   Since the water suppression method used to analyze the sample also results in a suppression of the signals near water (4.7 ppm), the product was extracted with $CDCl_3$ and analyzed to confirm peak assignments and product identification.

References

1. J. J. Roylance, T. W. Kim and K. –S. Choi, *ACS Catal.*, 2016, **6**, 1840-1847.
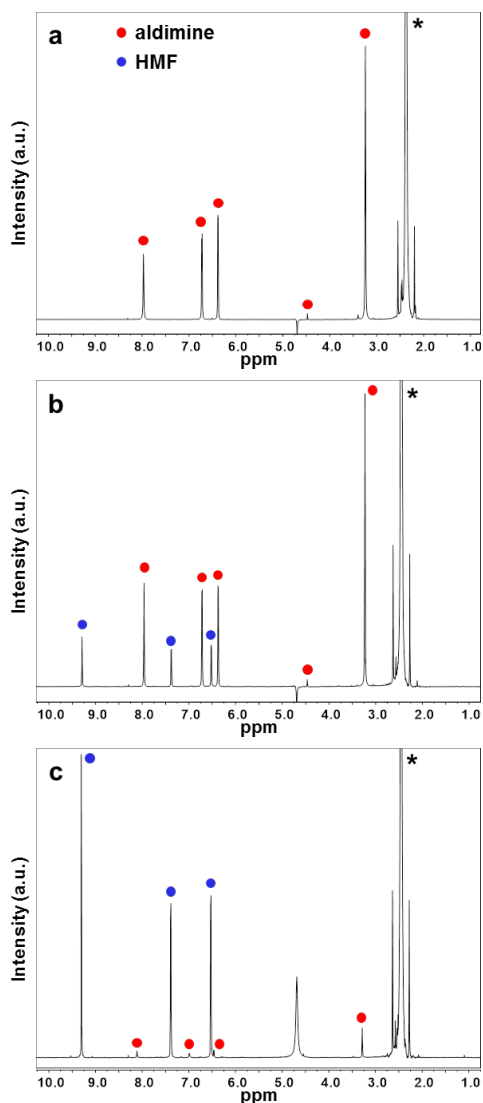
Fig. S1. (a) ^{1}H-NMR spectrum for a 0.02 M HMF solution in 0.7 M methylamine at pH 11.0, ^{1}H NMR (400 MHz, 90% H_2O/ 10% D_2O) δ 7.97 (s, 1H), 6.73 (d, $J = 3.4$ Hz, 1H), 6.38 (d, $J = 3.6$ Hz, 1H), 4.48 (s, 1H), 3.24 (s, 3H), all peaks from aldimine. **(b)** ^{1}H-NMR spectrum for the pH 11 solution acidified to pH 9.0 showing partial recovery of HMF, ^{1}H NMR (400 MHz, 90% H_2O/ 10% D_2O): δ 9.29 (s, 1H), 7.96 (s, 1H), 7.38 (d, $J = 3.8$ Hz, 1H), 6.72 (d, $J = 3.6$ Hz, 1H), 6.52 (d, $J = 3.9$ Hz, 1H), 6.37 (d, $J = 3.5$ Hz, 1H), 4.47 (s, 1H), 3.23 (s, 3H). HMF peaks at 9.29, 7.38, and 6.52, aldimine peaks at 7.96, 6.72, 6.37, 4.47, and 3.23. **(c)** ^{1}H-NMR spectrum for the pH 11 solution acidified to pH 7.0 showing nearly complete recovery of HMF, ^{1}H NMR (400 MHz, 90% H_2O/ 10% D_2O): δ 9.30 (s, 1H), 7.39 (d, $J = 3.8$ Hz, 1H), 6.53 (d, $J = 3.8$ Hz, 1H), 6.37 (d, $J = 3.5$ Hz, 1H). HMF peaks at 9.30, 7.39, and 6.53 ppm. Minor aldimine peaks at 8.11, 6.99, 6.47, and 3.28. The aldimine peak near 4.48 ppm is diminished by water suppression, which is present as the peak (or inverted peak in **c**) at 4.70 ppm. The peak denoted by * is from methylamine.
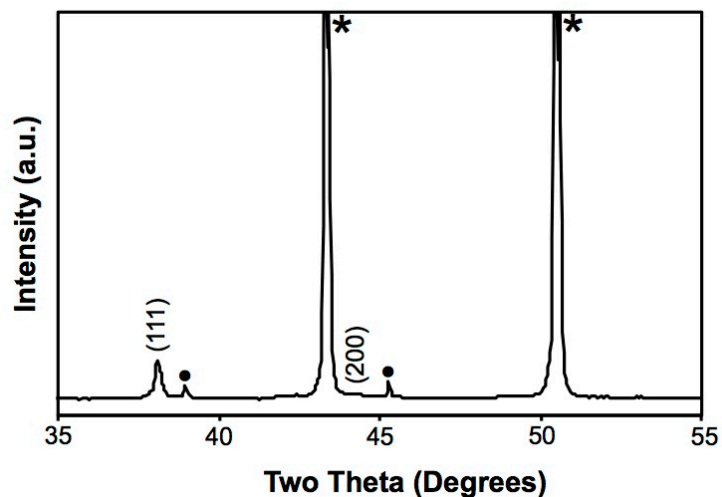
Fig. S2. XRD pattern of an as-prepared Ag$_{gd}$ electrode.   The peaks from Cu foil are denoted by * and •. The peaks denoted by * are generated by Cu K$_\beta$ radiation and the peaks denoted by • are generated by Cu K$_\beta$ radiation, which could not be completely removed by the Ni filter. (When slow scanning conditions were used to collect Ag peaks from thin Ag electrodes, the intensities of the Cu peaks from strongly diffracting Cu foil generated by Cu K$_\beta$ radiation were too strong to be completely removed by the Ni filter.)
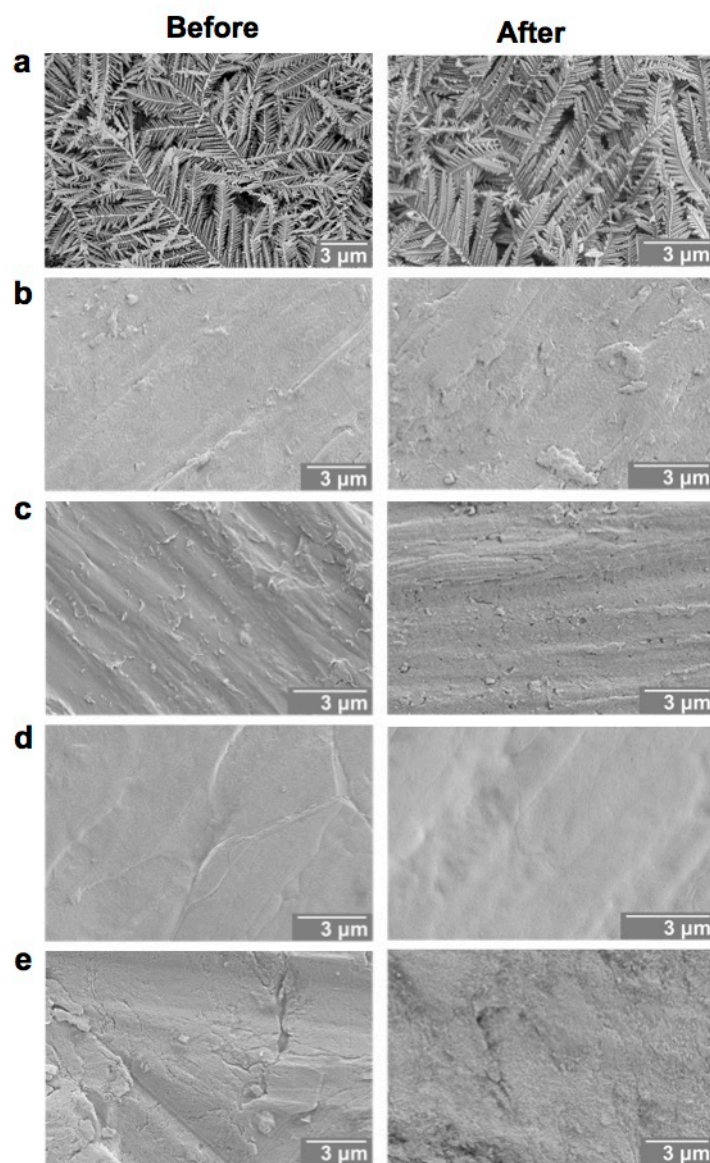
Fig. S3. SEM images of electrodes before and after passing 20 C for HMF reductive amination. (**a**) Ag$_{gd}$ (at −1.1 V vs. Ag/AgCl), (**b**) Ag (at −1.2 V vs. Ag/AgCl), (**c**) Cu (at -1.2 V vs Ag/AgCl), (**d**) Sn (at -1.4 V vs Ag/AgCl), and (**e**) Zn (at -1.4 V vs Ag/AgCl).
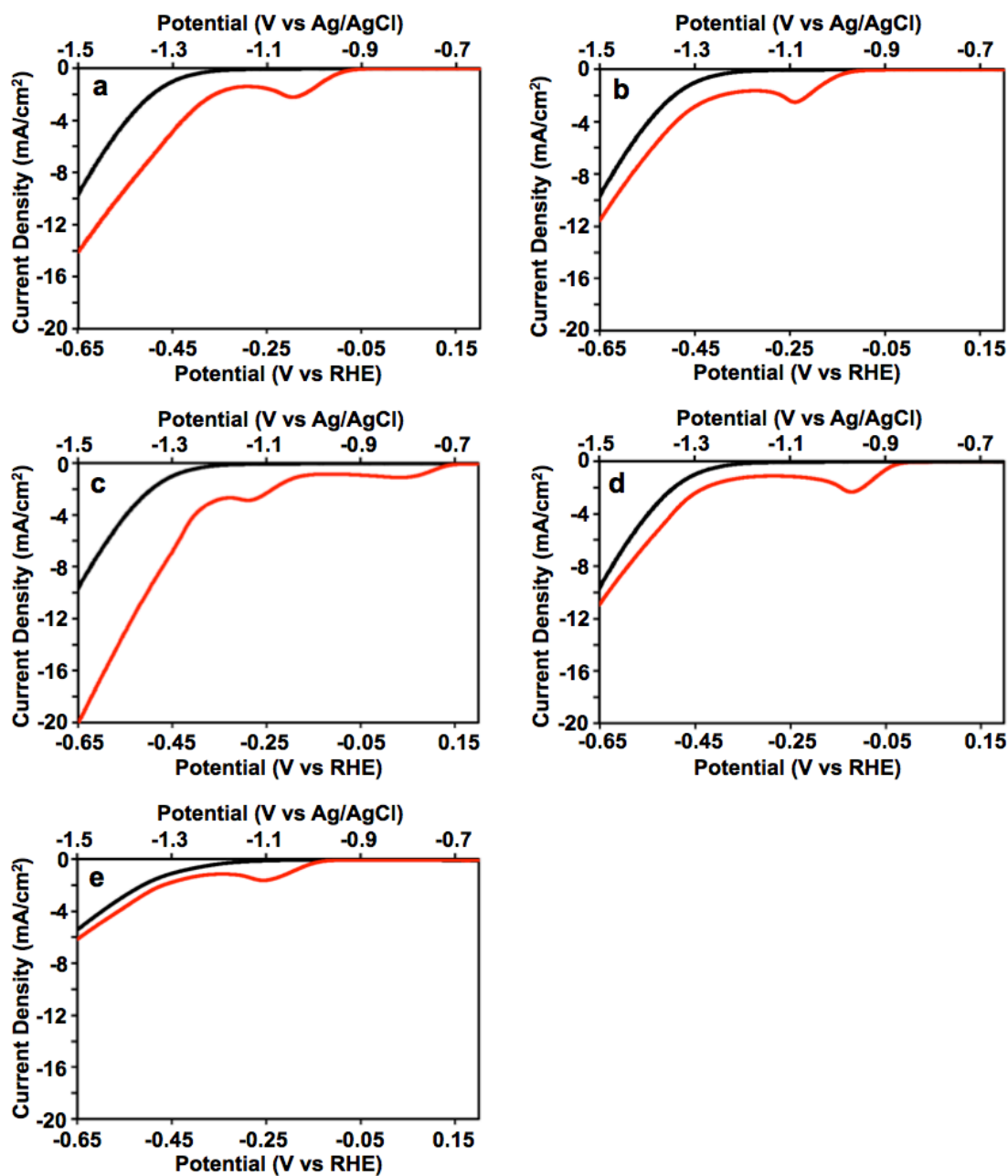
Fig. S4. (**a-d**) LSVs of a Ag$_{gd}$ electrode in 0.7 M methylamine buffer solution (pH 11.0) with (red) and without (black) 0.02 M (**a**) HMF, (**b**) 5-MF, (**c**) DFF, (**d**) FFCA. (**e**) LSVs of a Ag$_{gd}$ electrode in a 0.7 M ethanolamine solution (pH 11.0) with (red) and without (black) 0.02 M HMF (scan rate 5 mV s^{-1}).