Electronic Supplementary Material (ESI) for Green Chemistry.

Electrochemical Reductive Biomass Conversion: Direct Conversion of 5-hydroxymethylfurfural (HMF) to 2,5-hexanedione (HD) via Reductive Ring-opening

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Electronic Supplementary Information

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Experimental

Materials. Zinc foil (0.25 mm thick, 99.98%) was purchased from Alfa Aesar. Copper foil was purchased from Nimrod Hall Copper Foil Company. Potassium phosphate, monobasic (≥ 99.0%) was purchased from Electron Microscopy Sciences. Potassium sulfate (≥ 99.0%), sulfuric acid (95-98%), phosphoric acid (≥ 85%), potassium hydroxide (≥ 85%), sodium acetate (≥ 99.0%), acetic acid (≥ 99.7%), 5-hydroxymethylfurfural (≥ 99%), 2,5-hexanedione (≥ 98%), and 5-methylfurfural (99%) were purchased from Sigma Aldrich. All chemicals were used without further purification.

Preparation of Electrodes. Zn and Cu electrodes used in this study were prepared by cutting Zn and Cu foil to pieces with dimensions of 1.5 cm x 2.5 cm. The Zn surface was mechanically polished with sandpaper. The Cu surface was 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 Zn or Cu foil electrodes to enable connection to the potentiostat lead. The backside and top 0.5 cm of the Zn or Cu 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. The Au and Pt working electrodes (1.5 cm x 2.0 cm) and Pt counter electrodes (2.5 cm x 2.0 cm) were prepared by sputter coating a 100 nm platinum or gold layer over a 20 nm titanium layer onto cleaned glass slides.

Reduction of HMF. LSVs were performed in a 0.2 M sulfate buffer solution (pH 2.0) with and without 0.02 M HMF in an undivided three-electrode cell without stirring. The potential was swept from the open circuit potential to the negative direction using a scan rate of 50 mV/s. 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 cathodic compartment contained 14 mL of a 0.2 M sulfate buffer solution (pH 2.0), a 0.2 M sulfate solution with pH adjusted to 1.0, a 0.2 M phosphate buffer solution (pH 2.0 and pH 7.2), or a 0.2 M acetate buffer solution (pH 4.7) commonly containing 0.02 M HMF while the anodic compartment contained the same solution without HMF. Reduction was performed by passing 20 C at various potentials discussed in the main text.

Product Analysis. Products were detected and quantified using a Bruker Avance III 400 MHz nuclear magnetic resonance (NMR) spectrometer. Calibration curves were generated for both HD and HMF by obtaining ^{1}H-NMR spectra for a series of solutions of known concentration for each species and plotting the area obtained for signature HMF and HD peaks for each concentration. The area for HMF and HD peaks of unknown concentrations from the product solution were then plotted against the calibration curves to determine their 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, ^{1}H-^{13}C HSQC, high pressure liquid chromatography (HPLC), and gas chromatography-mass spectrometry (GCMS). HPLC was carried out using a Shimadzu Prominence-i LC-2030C HPLC with an ICSep ICE-COREGEL 87H3 column at 65 °C, 0.1 vol% H_2SO_4 in water mobile phase at 0.5 mL/min flow rate, and photo-diode array (PDA) and refractive index (RID) detectors. GCMS was carried out using a Shimadzu QP2010-Ultra equipped with He carrier gas, Aoc-20i+s autoinjector, split/splitless inlet, and a Shimadzu SHRIX5 column (30 m length, 0.25 mm diameter, 95% dimethylpolysiloxane 5% phenyl stationary phase).

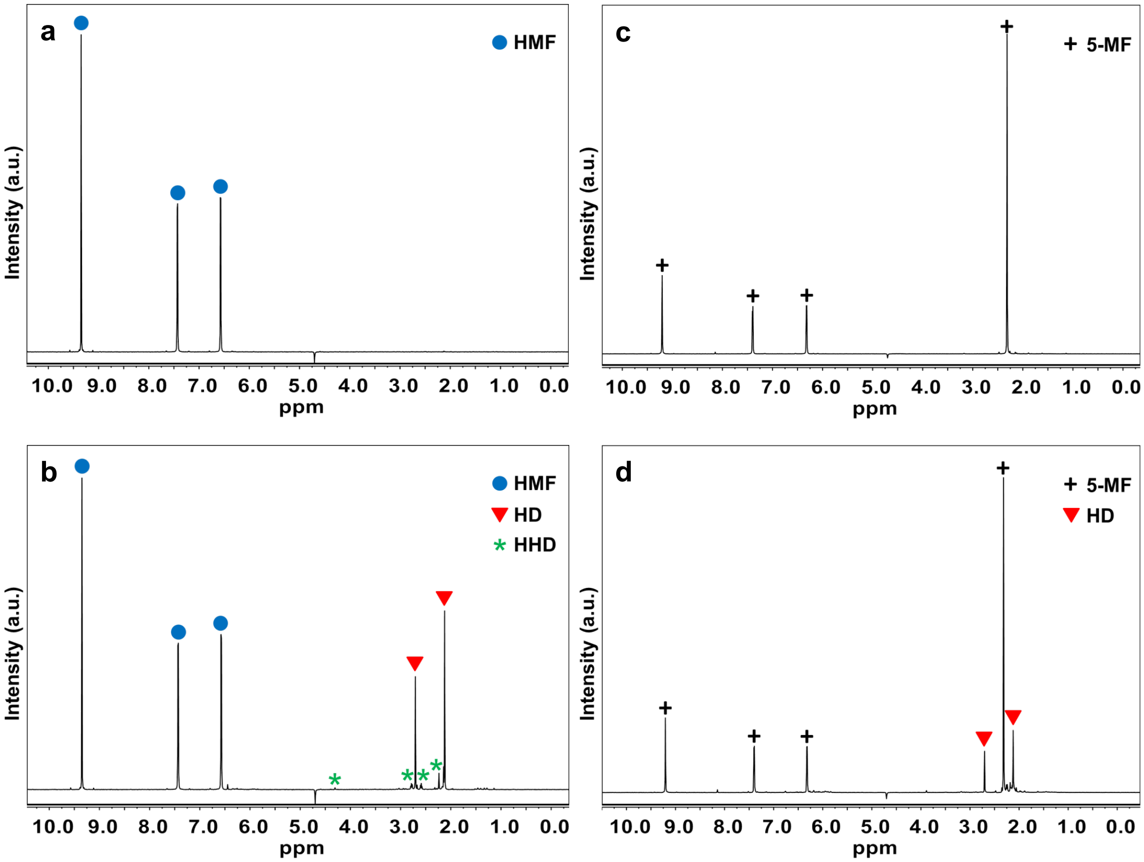

Fig. S1. (a-b) ^{1}H-NMR spectra for a 0.2 M sulfate buffer solution (pH 2.0) containing 0.02 M HMF (a) before and (b) after passing 20 C at −1.2 V vs. Ag/AgCl to the Zn electrode for HMF reduction. ^{1}H NMR (400 MHz, 90% H_2O/ 10% D_2O): δ 9.35 (s, 1H), 7.43 (d, J = 3.9 Hz, 1H), 6.57 (d, J = 3.9 Hz, 1H), 4.31 (s, 2H), 2.78 (t, J = 6.3 Hz, 2H), 2.71 (s, 4H), 2.59 (t, J = 6.3 Hz, 2H), 2.24 (s, 3H), 2.12 (s, 6H); **(c-d)** ^{1}H-NMR spectra for a 0.2 M sulfate buffer solution (pH 2.0) containing 0.02 M 5-MF (c) before and (d) after passing 20 C at -1.2 V vs. Ag/AgCl to the Zn electrode for 5-MF reduction. ^{1}H NMR (400 MHz, 90% H_2O/ 10% D_2O): δ 9.21 (s, 1H), 7.40 (d, J = 3.9 Hz, 1H), 6.32 (d, J = 3.8 Hz, 1H), 2.70 (s, 4H), 2.32 (s, 3H), 2.12 (s, 6H).

(HMF peaks at 9.35, 7.43, and 6.57 ppm. HD peaks at 2.71 and 2.12 ppm. HHD peaks at 4.31, 2.78, 2.59, and 2.24 ppm. 5-MF peaks at 9.21, 7.40, 6.32, and 2.32 ppm. The HHD peak at 4.31 ppm is diminished by water suppression.)

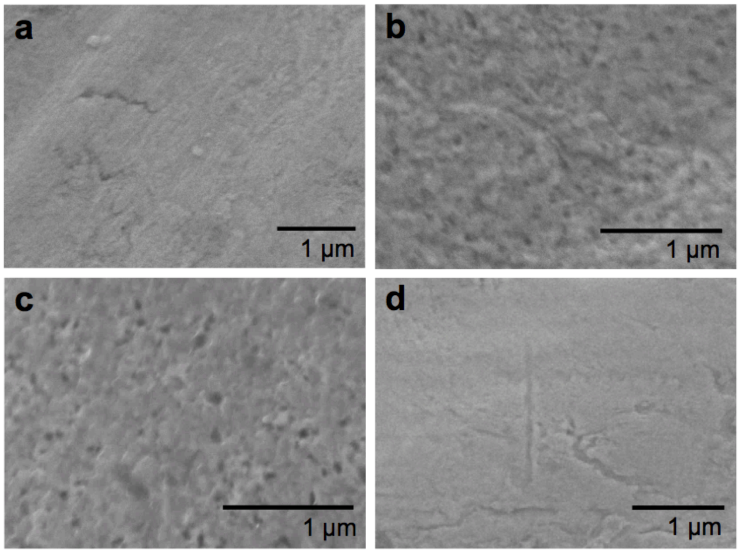

Fig. S2. SEM images of (a) a Zn electrode before electrochemical reduction, a Zn electrode after passing (b) 20 C and (c) 40 C at -1.2 V vs. Ag/AgCl (-0.89 V vs. RHE) in a 0.2 M sulfate buffer solution (pH 2.0) containing 0.02 M HMF, (d) a Zn electrode after passing 20 C at the same potential in the same solution that did not contain HMF. Comparing images shown in (a) and (b) suggests that surface restructuring of Zn occurs during HMF reduction. However, the fact that the surface morphologies of Zn after passing 20 C and 40 C are comparable suggests that after initial restructuring of the surface, continuous alteration of the surface does not occur. The Zn surface after passing 20 C at the same potential without the presence of HMF in solution looks comparable to the fresh Zn surface, confirming that the surface roughening shown in (b) and (c) are due to the interactions between the Zn surface and HMF under reduction conditions and not simply due to the application of potential for reduction or other factors such as water reduction.

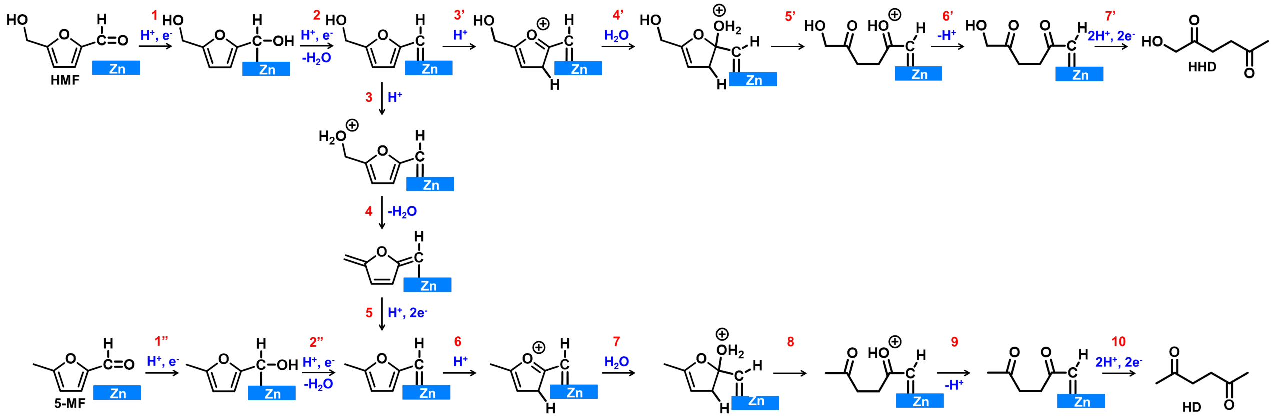

Fig. S3. A plausible mechanism for the electrochemical reduction of HMF to HD on Zn electrodes composed of hydrogenolysis (steps 3-5) and reductive ring opening (steps 6-10). The scheme also shows the reduction of HMF to HHD (top row) and the reduction of 5-MF to HD (bottom row), which involve only reductive ring opening without hydrogenolysis, to demonstrate how these reaction pathways are related to one another.