

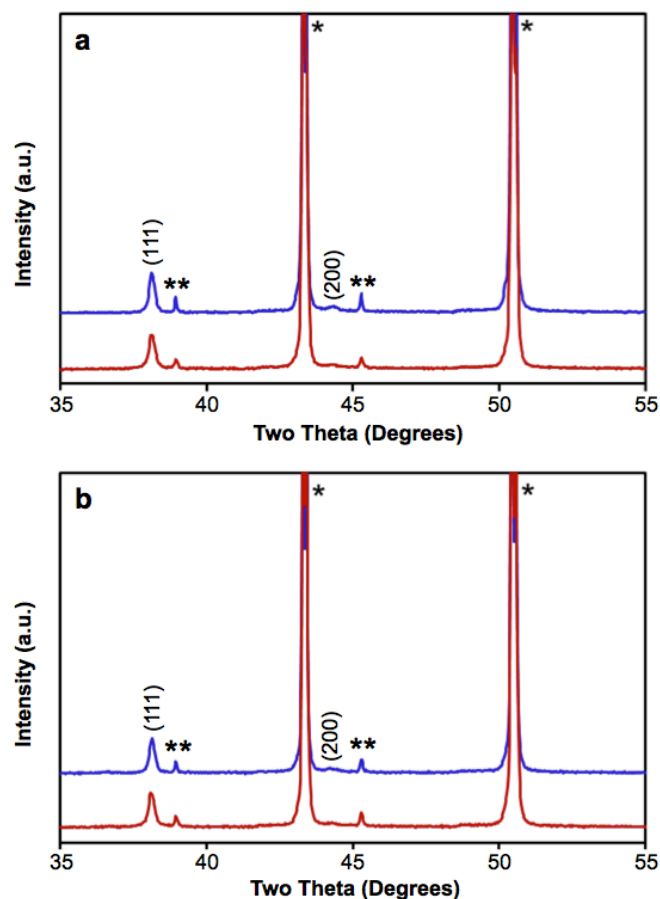
**Efficient and Selective Electrochemical and Photoelectrochemical  
Reduction of 5-hydroxymethylfurfural to 2,5-  
bis(hydroxymethyl)furan Using Water as the Hydrogen Source**

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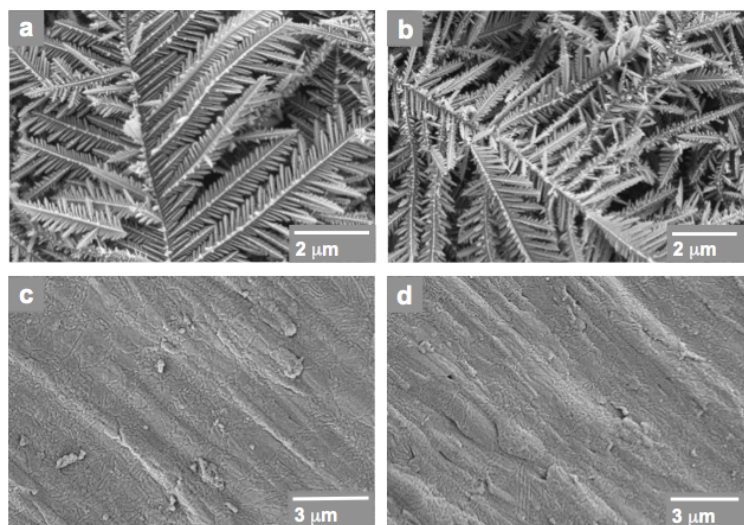
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**Supporting Information**

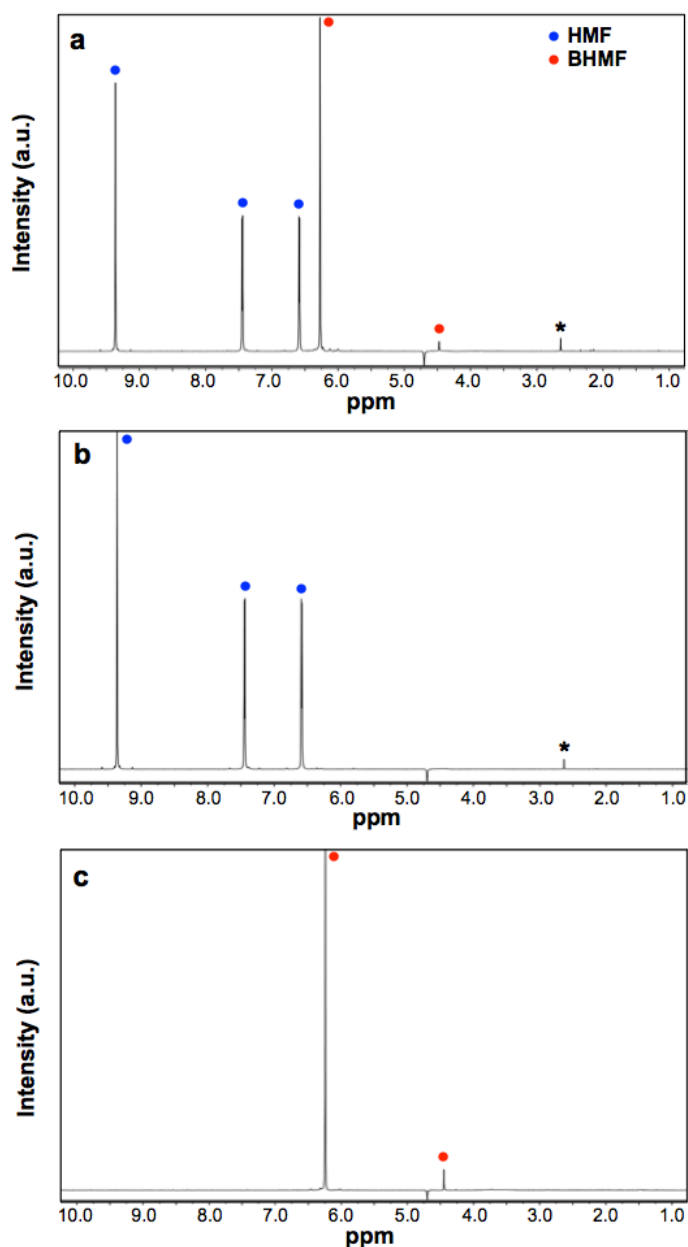
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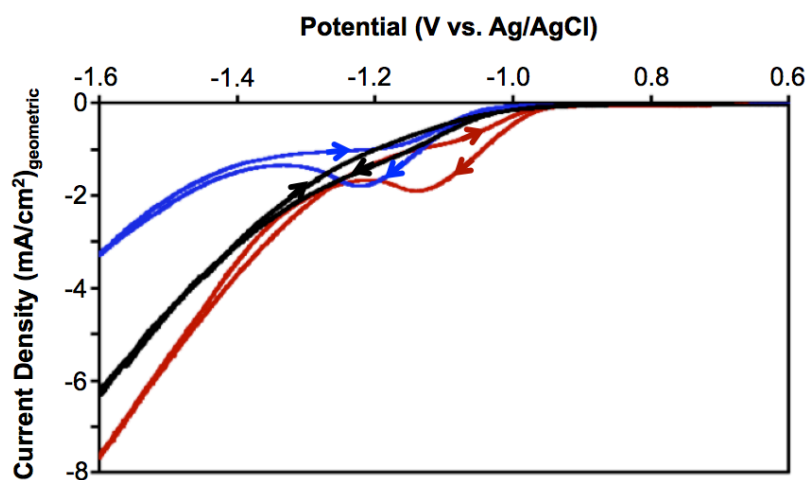
**Figure S1.** XRD patterns of  $\text{Ag}_{\text{gd}}$  (red) and  $\text{Ag}_{\text{sp}}$  (blue) electrodes (a) as-deposited and (b) after passing 20 C at  $-1.3$  V vs. Ag/AgCl for HMF reduction. No changes are observed in the peak shape and height. The peaks from Cu foil are denoted by \* and \*\*. The peaks denoted by \*\* are Cu peaks 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.)



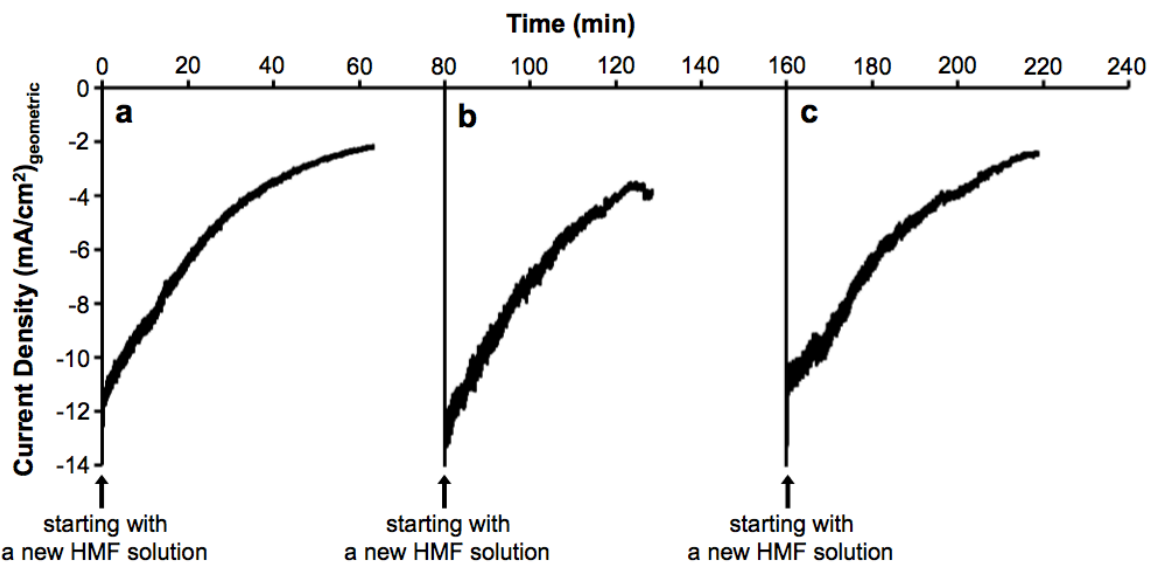
**Figure S2.** SEM images of  $\text{Ag}_{\text{gd}}$  electrodes (**a**) as-deposited and (**b**) after passing 20 C at  $-1.3$  V vs. Ag/AgCl for HMF reduction. SEM images of  $\text{Ag}_{\text{sp}}$  electrodes (**c**) as-deposited and (**d**) after passing 20 C at  $-1.3$  V vs. Ag/AgCl for HMF reduction.



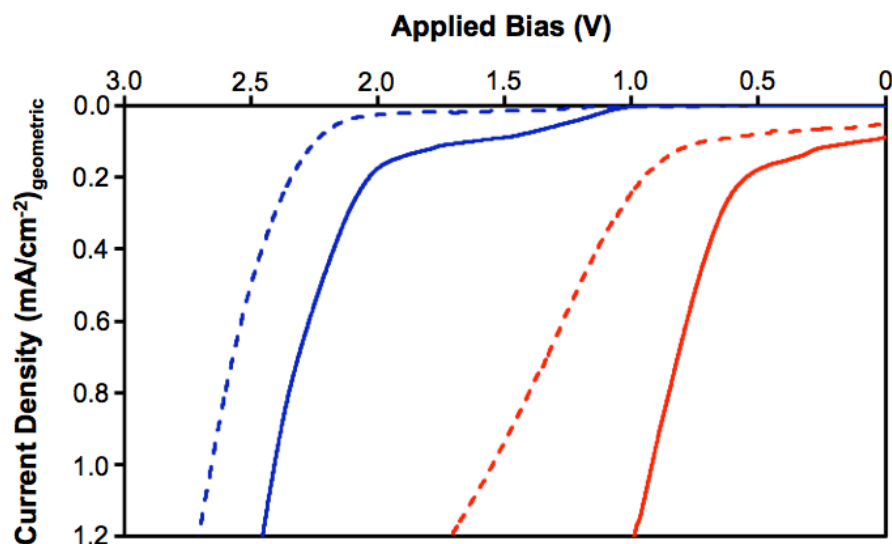
**Figure S3.**  $^1\text{H}$ -NMR spectra for (a) an HMF solution after passing 20 C at  $-1.3$  V vs. Ag/AgCl to the  $\text{Ag}_{\text{gd}}$  electrode for HMF reduction, (b) a fresh HMF solution, and (c) a fresh BHMF solution:  $^1\text{H}$  NMR (400 MHz, 90%  $\text{H}_2\text{O}$ / 10%  $\text{D}_2\text{O}$ )  $\delta$  9.36 (s, 1H), 7.45 (d,  $J = 3.9$  Hz, 1H), 6.59 (d,  $J = 3.9$  Hz, 1H), 6.24 (s, 2H), 4.45 (s, 4H). HMF peaks at 9.36, 7.45, and 6.59 ppm. BHMF peaks at 6.24 and 4.45 ppm. The BHMF peak at 4.45 ppm is diminished by water suppression. The peak marked with \* is from a dimethylsulfoxide impurity present in the as-purchased HMF.



**Figure S4.** CVs of Cu (black), Ag<sub>sp</sub> (blue), and Ag<sub>gd</sub> (red) electrodes in 0.5 M borate buffer (pH 9.2) with 0.02 M HMF (scan rate: 5 mV/s). The current profiles on the reverse scan show that the reduction of HMF to BHMF is not reversible on these electrodes under the given conditions.



**Figure S5.**  $J-t$  plots obtained for three consecutive HMF reduction experiments labeled as (a), (b), and (c) using the same  $\text{Ag}_{\text{gd}}$  electrode. For each trial, a freshly prepared 0.02 M HMF solution in 0.5 M borate buffer (pH 9.2) was used and 60 C were passed for the complete conversion of HMF to BHMF. The slight difference in current density and time required to pass 60 C among these trials is due to the slight difference in the electrode locations in the cell.



**Figure S6.** LSVs obtained using a two-electrode cell composed of a  $\text{Ag}_{\text{gd}}$  cathode and a  $\text{BiVO}_4/\text{OEC}$  anode in the dark (blue) and under AM 1.5G,  $100 \text{ mW}/\text{cm}^2$  illumination (red) in a 0.5 M borate buffer (pH 9.2) with (solid) and without (dashed) 0.02 M HMF. When HMF was not present, water reduction occurred at the  $\text{Ag}_{\text{gd}}$  electrode instead of HMF reduction. The anode reaction was always water oxidation. Since HMF reduction is more favorable than water reduction on the  $\text{Ag}_{\text{gd}}$  electrode, LSVs shift to the right both with and without illumination when HMF is present, meaning that smaller applied biases were required to generate the same level of current for HMF reduction. Compared to currents generated in the dark, currents generated under illumination for both water reduction and HMF reduction require significantly decreased applied biases due to the photovoltage gained by the  $\text{BiVO}_4$  photoanode under illumination. The results show that in order to achieve a current density of  $1 \text{ mA}/\text{cm}^2$  for HMF reduction in the dark, an application of 2.41 V between the  $\text{Ag}_{\text{gd}}$  cathode and the  $\text{BiVO}_4/\text{OEC}$  anode was necessary. This voltage requirement is smaller by 0.35 V than that of the electrochemical cell discussed in the main text where a Pt anode was used instead of a  $\text{BiVO}_4/\text{OEC}$  anode. This is because the OEC (i.e.  $\text{FeOOH}$  and  $\text{NiOOH}$ ) coated on the  $\text{BiVO}_4$  surface is more catalytic than Pt for water oxidation. When a PEC was used under AM 1.5G,  $100 \text{ mW}/\text{cm}^2$  illumination,  $1 \text{ mA}/\text{cm}^2$  was achieved at a potential of 0.92 V between the  $\text{Ag}_{\text{gd}}$  cathode and the  $\text{BiVO}_4/\text{OEC}$  anode, saving about 1.5 V.

**Table S1.** Changes in FE and selectivity for BHMF production during electrochemical HMF reduction by a Ag<sub>gd</sub> electrode in a 0.5 M borate buffer (pH 9.2) containing 0.02 M HMF after every 10 C passed.

Charge passed (C)	Average current density (mA/cm <sup>2</sup> )	HMF consumed (μmol)	BHMF formed (μmol)	Rate for BHMF production (μmol/h/cm <sup>2</sup> )	FE (%)	Selectivity (%)
10	9.20	51.6	49.6	164	96	96
20	6.90	104	102	127	99	99
30	5.55	155	154	103	99	> 99
40	5.73	206	204	105	98	> 99
50	4.86	238	237	83.0	92	> 99
60	5.27	279	278	87.7	89	> 99

**Table S2.** Changes in FE and selectivity for BHMF production during electrochemical HMF reduction by a Ag<sub>gd</sub> electrode in a 0.5 M borate buffer (pH 9.2) containing 0.10 M HMF after every 50 C passed.

Charge passed (C)	Average current density (mA/cm <sup>2</sup> )	HMF consumed (μmol)	BHMF formed (μmol)	Rate for BHMF production (μmol/h/cm <sup>2</sup> )	FE (%)	Selectivity (%)
50	9.54	426	203	139	78	48
100	8.98	697	418	135	81	60
150	7.72	931	627	116	81	68
200	5.90	1.07 x 10 <sup>3</sup>	813	86.3	80	76