Supporting Information for

Title: Characterizing sustained solar-to-hydrogen electrocatalysis at low cell potentials enabled by crude glycerol oxidation

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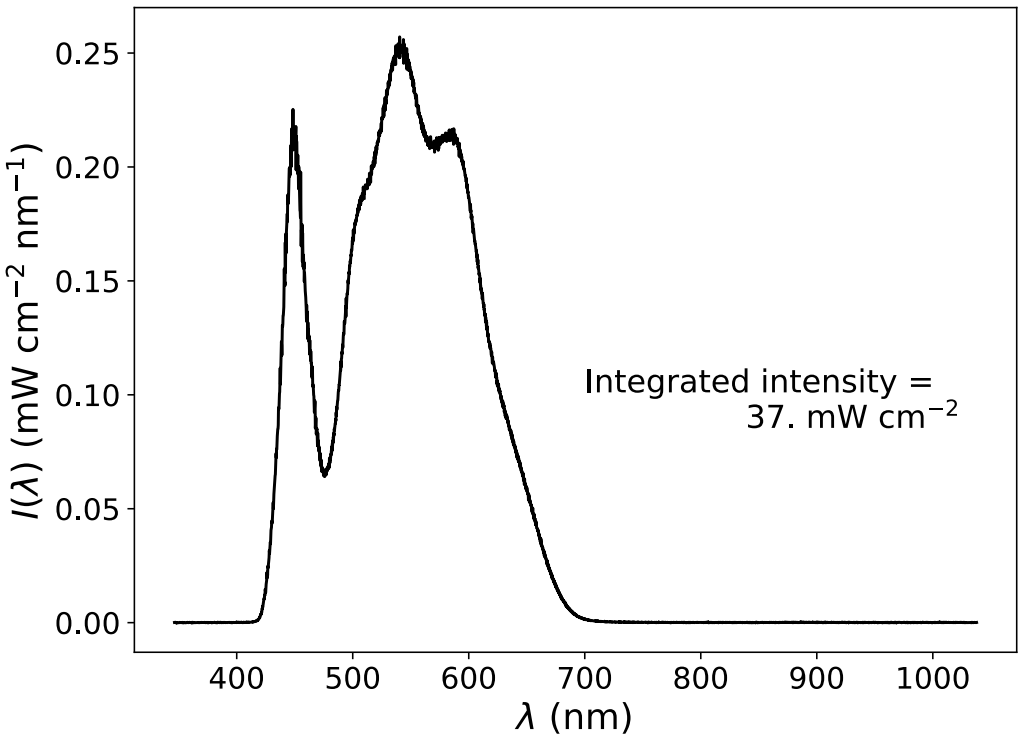

Figure S1 – Absolute spectrum of the Solla COB-LED used for the Si PV electrolysis experiments (Figure 4). The relative spectrum was measured using a UV-Vis spectrometer (USB4000, Ocean Optics). The absolute power was calculated from a measurement of the photocurrent from a calibrated photodiode (FDS1010, Thorlabs) using the integrated product of the relative spectrum of the lamp and the responsivity curve (R(λ), provided by the manufacturer in units of A W^{-1}).

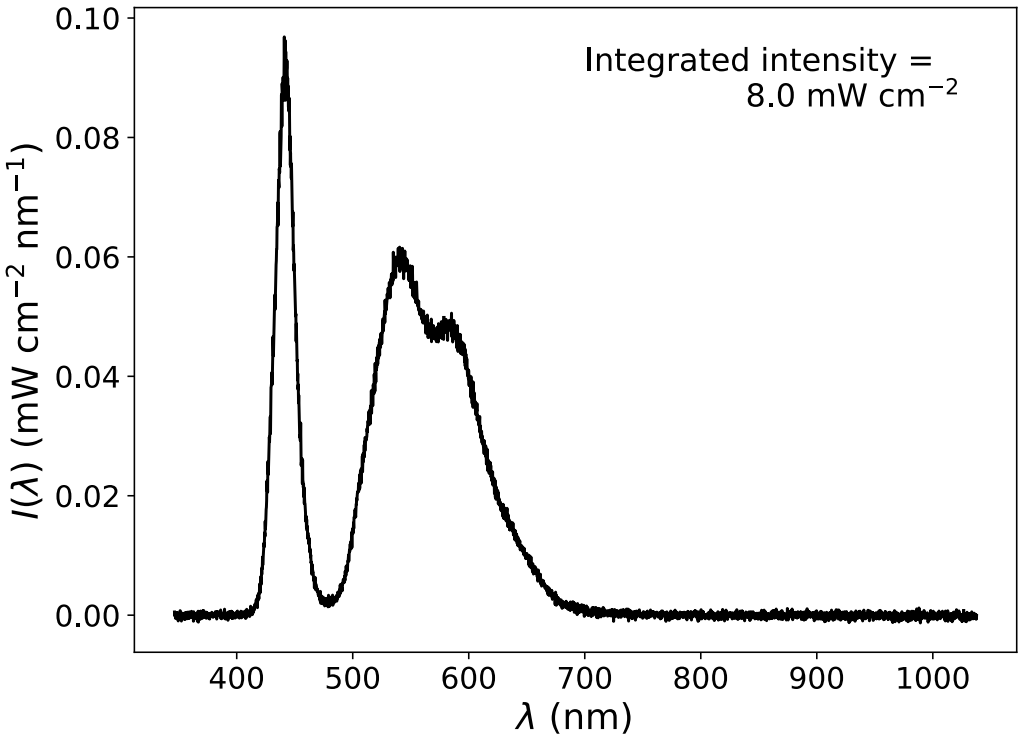

Figure S2 – Absolute spectrum of the Boruit COB-LED used for the GaAs PV electrolysis experiments (Figure 4), calculated from spectroscopic and photodiode measurements in the same manner as in Figure S1.

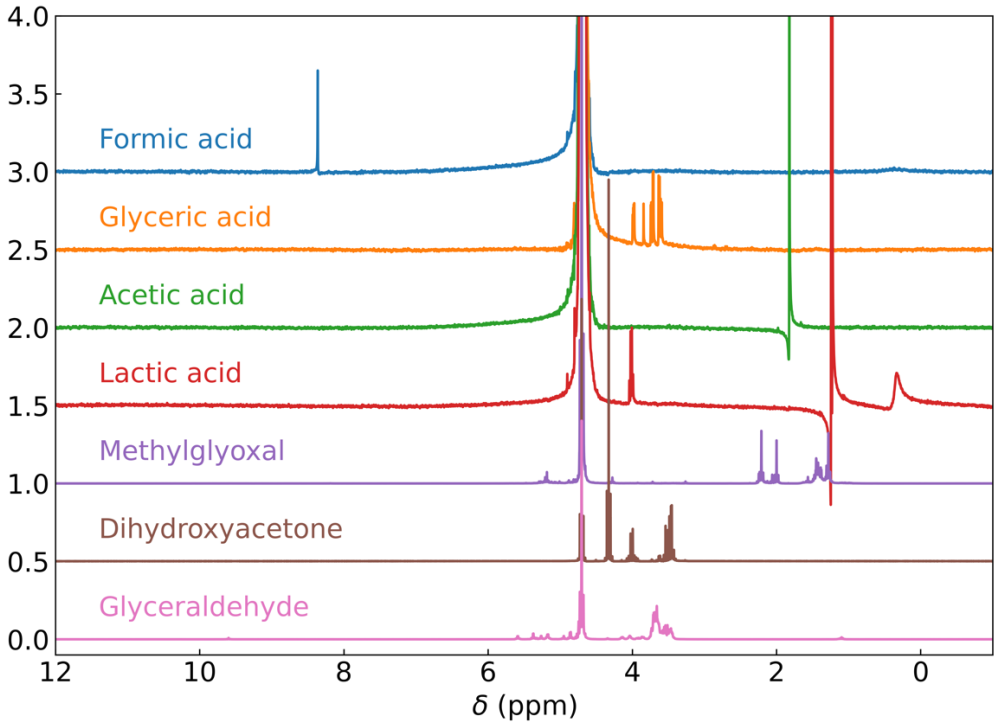

Figure S3 - ^{1}H NMR spectra for standards of compounds relevant to NMR studies in the main text (formic acid, glyceric acid, acetic acid, lactic acid, methylglyoxal, dihydroxyacetone, and glyceraldehyde). These standards are measured in D_2O with no added KOH to show the chemical shifts distinct to the electrolyte in alkaline (Figure 6) and neutral conditions. Each solution has 100 mM of the standard compound. The methylglyoxal, dihydroxyacetone, and glyceraldehyde spectra were scaled by a factor of 0.1 compared to the other compounds for easier comparison.

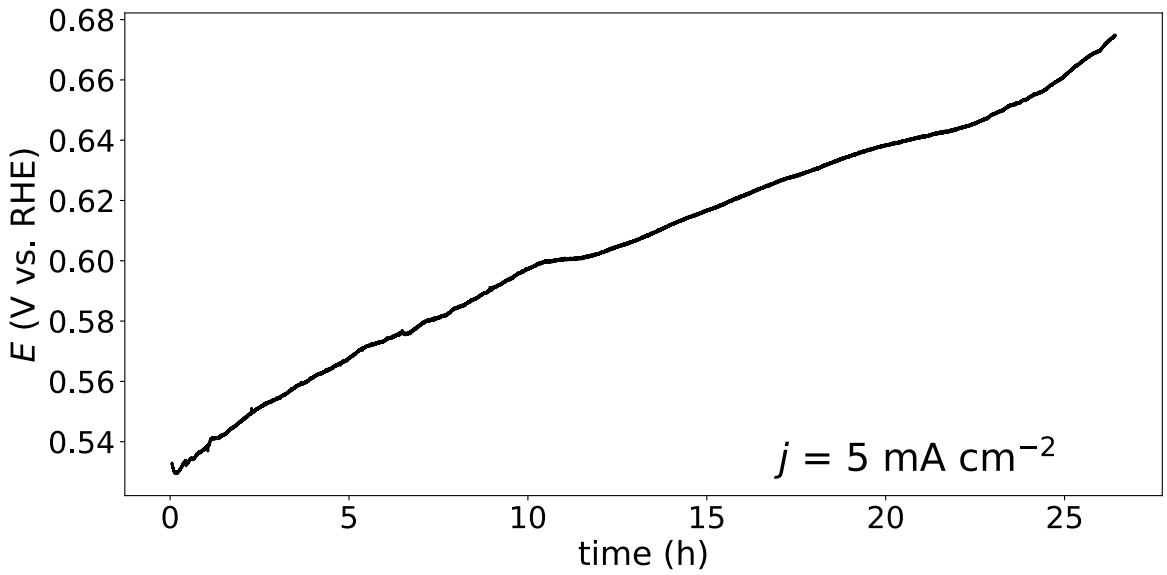

Figure S4 – Chronopotentiometry for the AuPtBi-Ni anode run (A_{geo} = 1 cm^{-2}, mesh electrode) for > 24 hrs in model crude glycerol solution (20% (w/w) glycerol in 2 M KOH, Figure 8). The electrolyte was prepared with D_2O rather than water to facilitate the NMR analysis shown in Figures 8b, 8c, and S3.

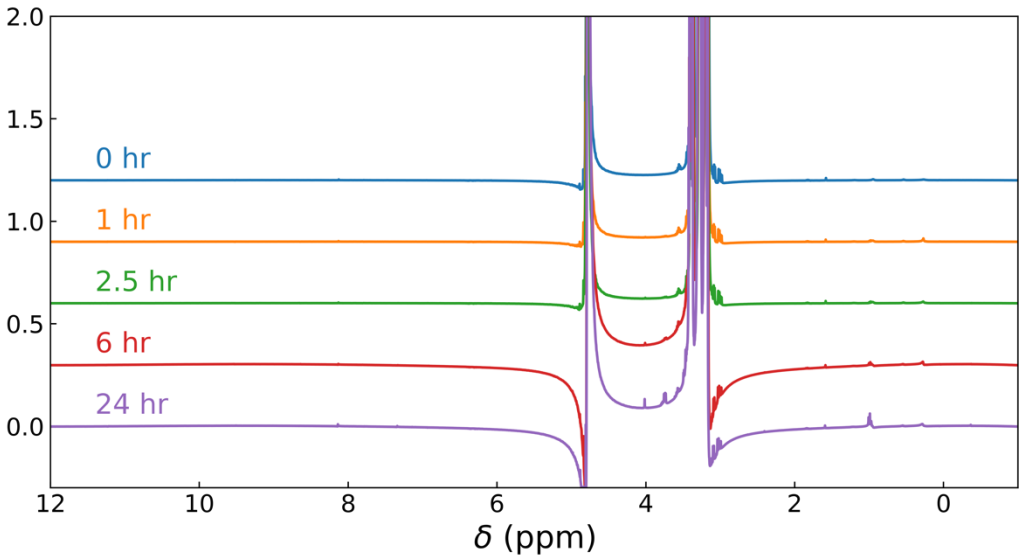

Figure S5 – Full-field ^{1}H NMR spectra for the time series of glycerol electrooxidation experiments shown in Figures 8b and 8c in the main text.