Supporting Information for

CO_2 Reduction on Cu at Low Overpotentials with Surface Enhanced In-Situ Spectroscopy

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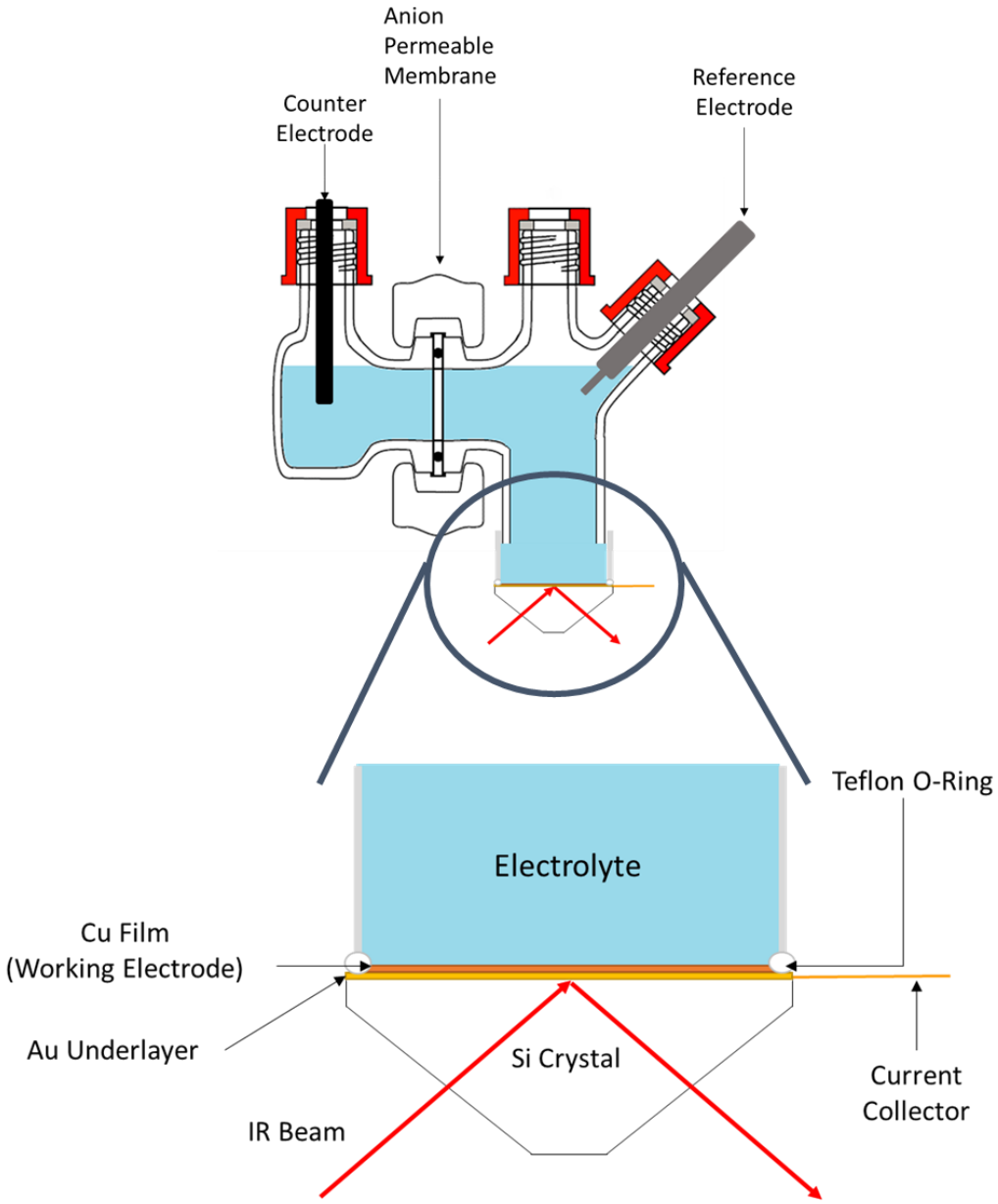

Figure S1. Schematic of the experimental setup used for SEIRAS experiments.

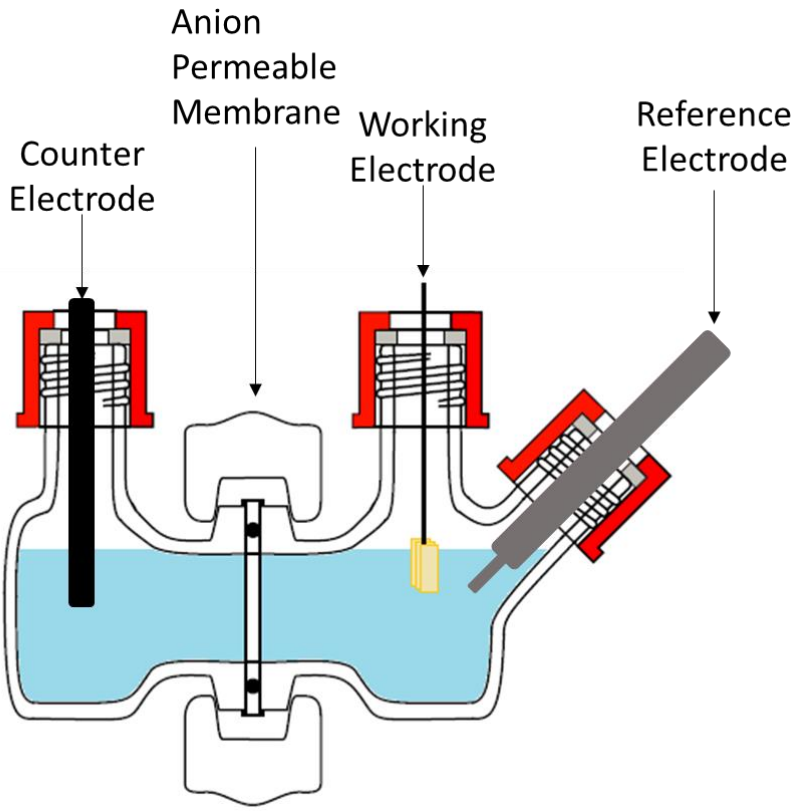

Figure S2. Schematic of the H-cell used for selectivity studies. Not pictured are two additional ports for headspace sampling and purging on the same side of the membrane as the working electrode.

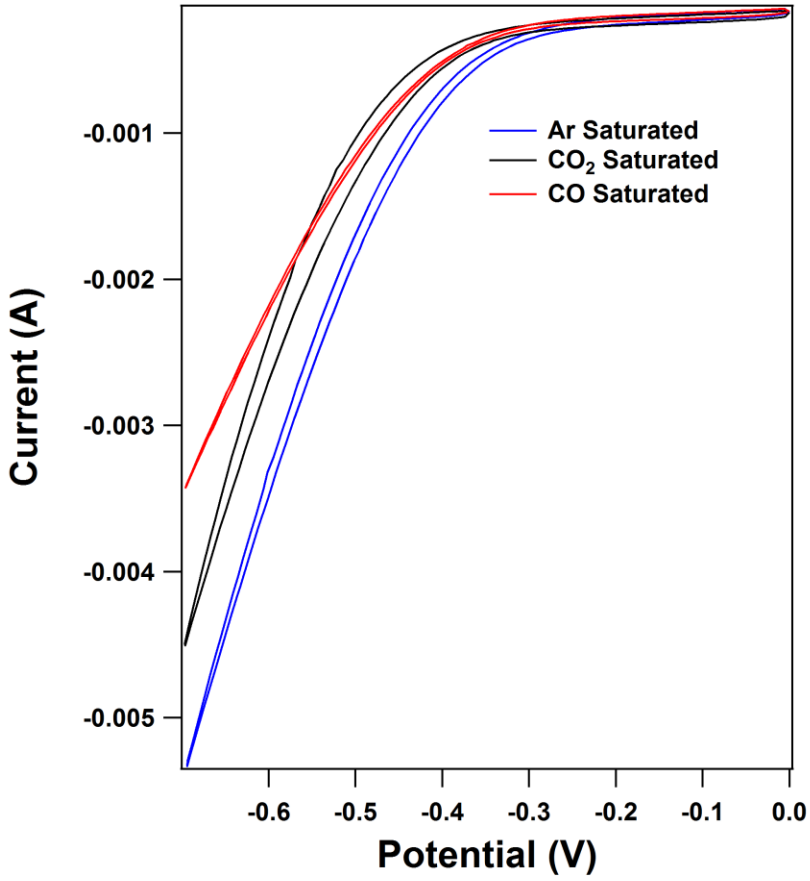

Figure S3. Cyclic voltammogram of 0.5 M $NaHCO_3$ on electrochemically deposited Cu film saturated in Ar, CO_2 and CO. The retardation of HER activity in the CO_2 saturated electrolyte could be a CO_2 reductive intermediate effect. CO similarly retards these reactions by site blocking for HER with a CO_{ad} species.

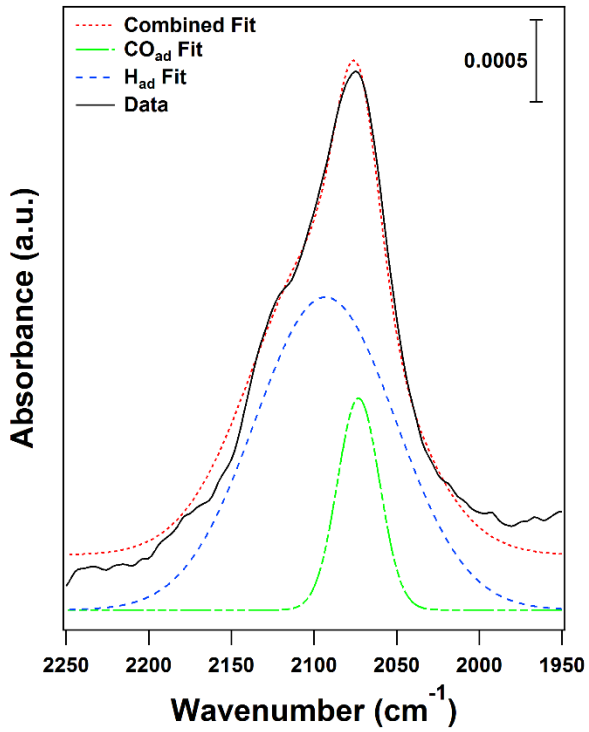

Figure S4. Peak deconvolution of Figure 5a(vii). Similar procedure was conducted for the rest of spectra in Figure 6a. Figure 6c are calculated based on the quantification of these deconvoluted peaks. Peak widths of the Had and CO_{ad} are fixed in the fitting, and similar procedure was employed in the fitting of Figure S5.

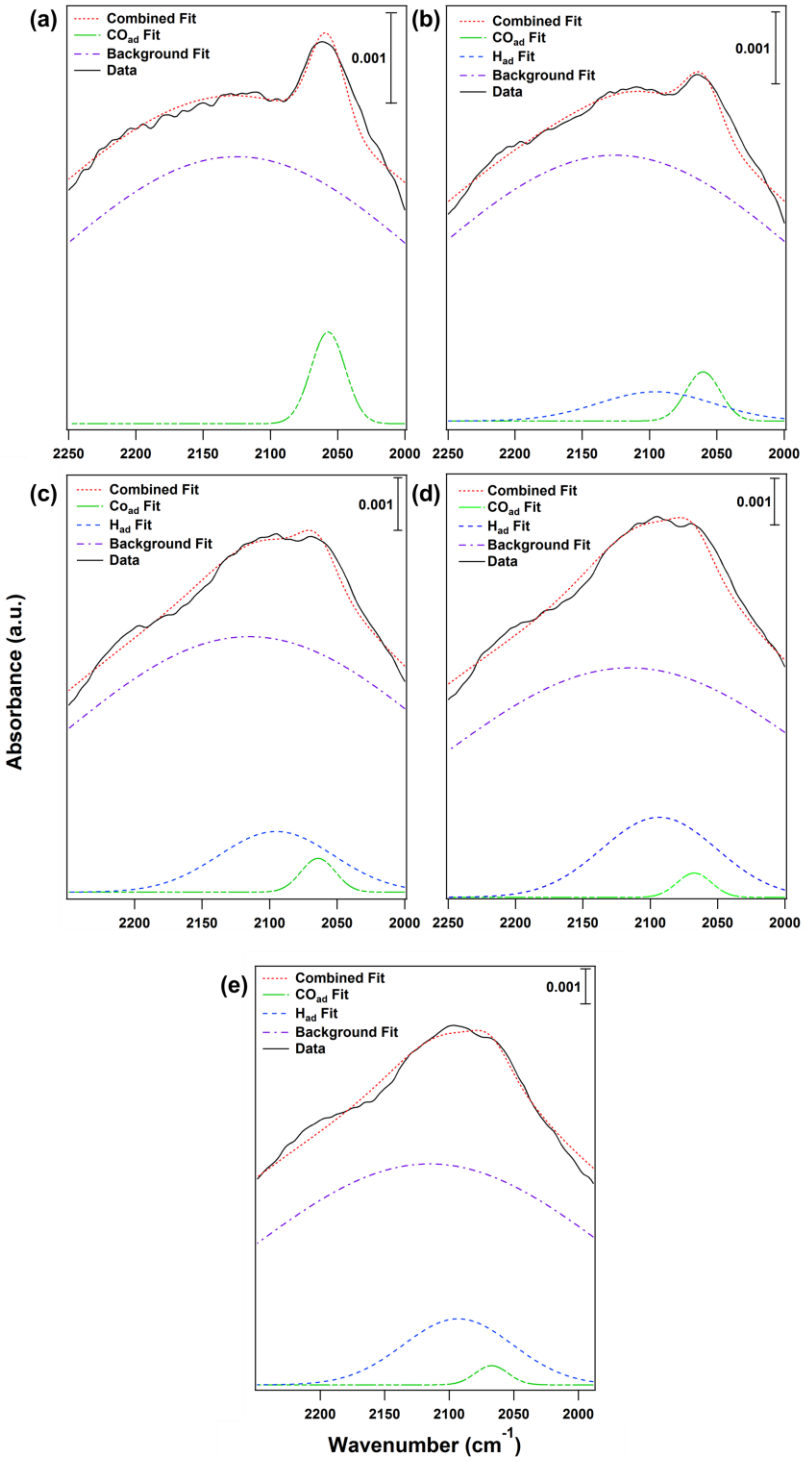

Figure S5. Fitting of spectra in Figure 5b at times: 0 min (a), 5 min (b), 15 min (c), 25 min (d). Background fit is attributed to broad water character seen in Figure S6. Note that the broad envelope from 2200-1975 cm^{-1} in Figure 6 is due to water rather than the H_{ad} or CO_{ad} band, which is confirmed by the spectrum of pure water. This broad band was removed in the peak deconvolution and quantification.

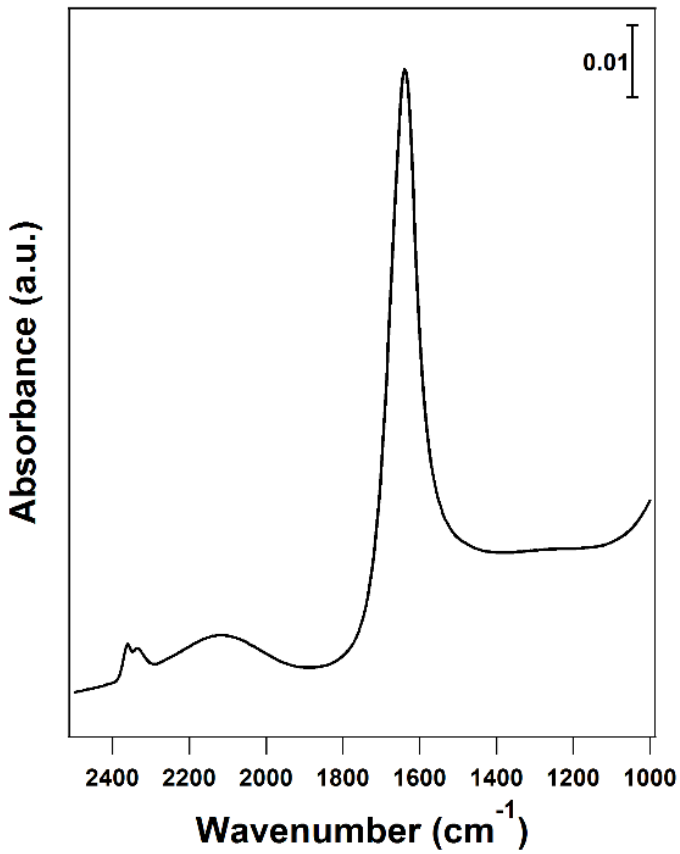

Figure S6. Single reflectance ATR-FTIR spectra of H_2O on ZnSe prism, 4 cm^{-1} resolution. Peak centered at approx. 2350 cm^{-1} is ambient CO_2 present in apparatus.

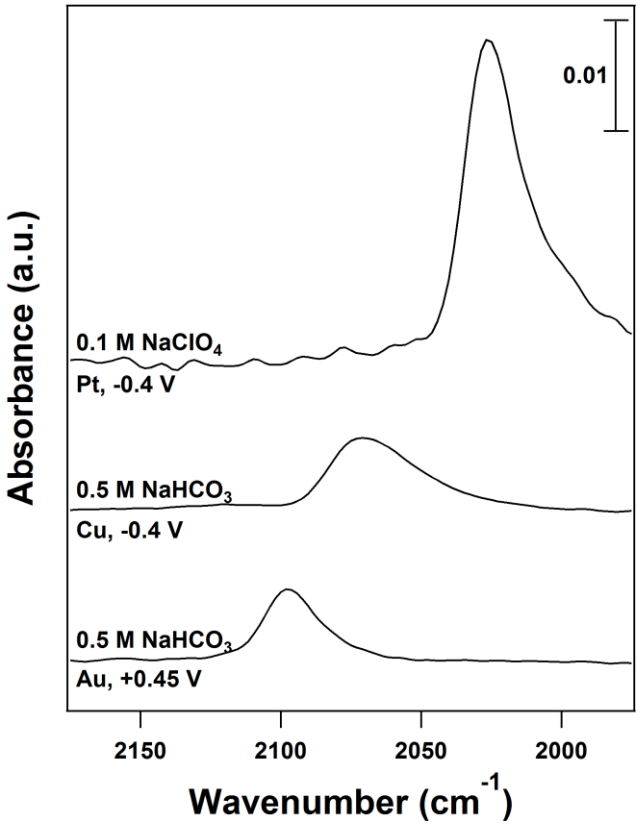

Figure S7. SEIRAS spectral comparison of CO_{ad} on Pt, Cu, and Au surfaces at indicated potentials.

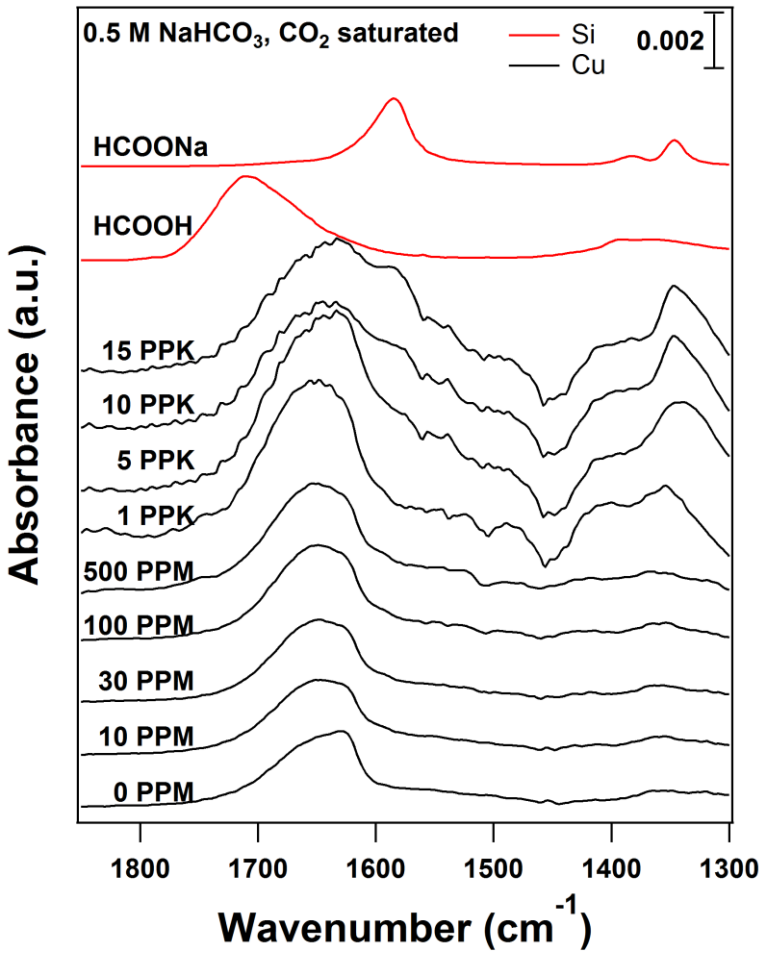

Figure S8. SEIRAS spectra (black traces) of 0.5 M $NaHCO_3$ on Cu film with varying amounts of introduced formic acid at -0.4 V, with reference taken at -0.1 V in 0.5 M $NaHCO_3$ prior to the introduction of formic acid. Concentrations are indicated by volume. ATR spectra of 0.1 M HCOONa and HCOOH on a Si crystal (red traces) are included for comparison.