Supporting Information

Tunable, light-assisted co-generation of CO and H_2 from CO_2 and H_2O by Re(bipy-tBu)$(CO)_3$Cl and p-Si in non-aqueous medium

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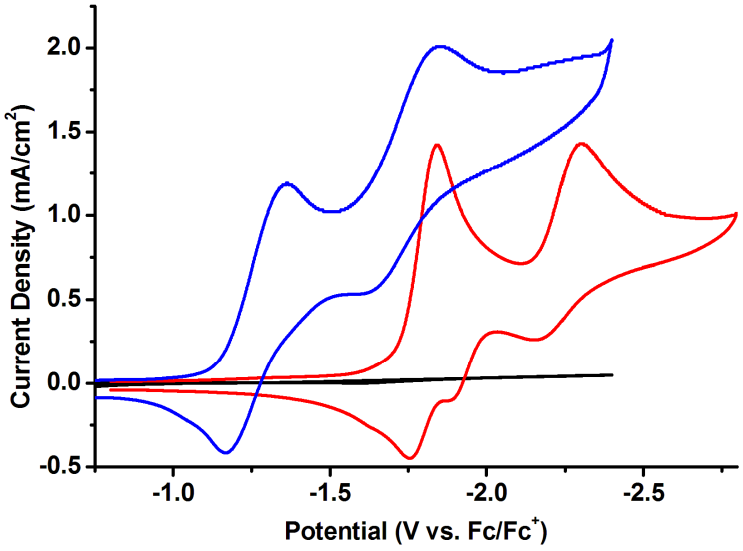

Figure S1. Re(bipy-tBu)$(CO)_3$Cl at Pt (red), illuminate p-Si (blue), and dark p-Si (black). All three scans are 6 mM catalyst, 0.1 M TBAH electrolyte, at 100 mV/s. Pt is used as the counter electrode and a silver wire was used as a pseudo reference with Fc added as an internal reference.[1]

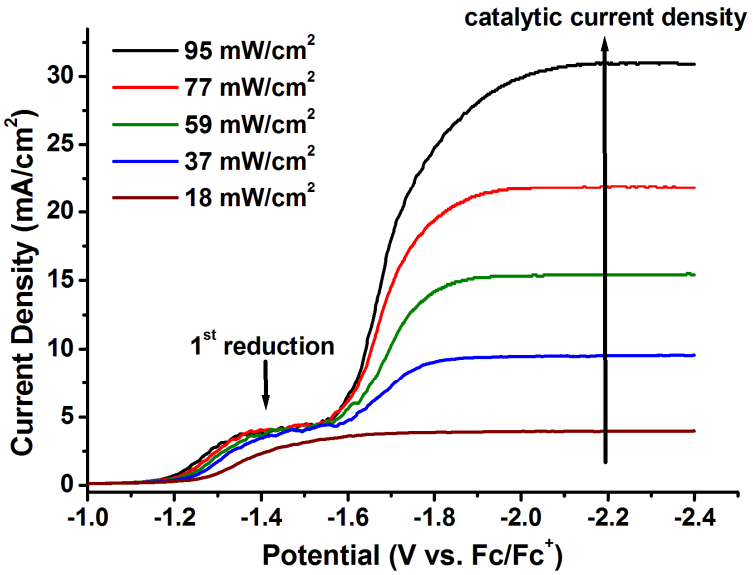

Figure S2. Light intensity dependence of the catalytic current density for Re(bipy-tBu)$(CO)_3$Cl (5 mM) under an atmosphere of CO_2 with monochromatic light (661 nm) illumination of p-type H-Si photocathode.[1]

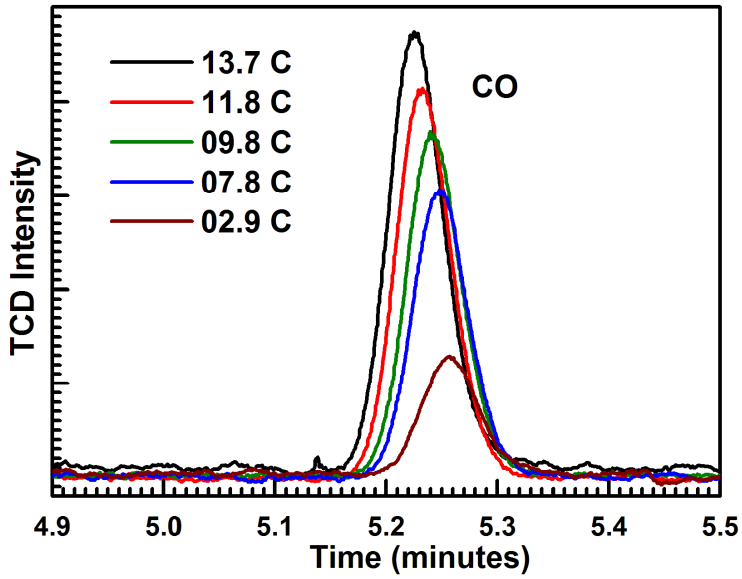

Figure S3. Growth of the carbon monoxide peak with increased charge passed over the course of a bulk electrolysis experiment with 0.5 mM Re(bipy-tBu)$(CO)_3$Cl at p-Si under an atmosphere of CO_2 with 2.6 M water.

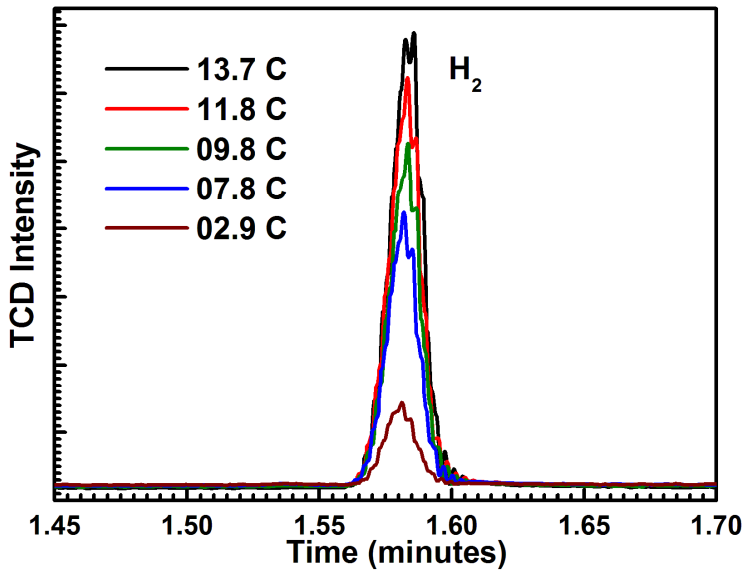

Figure S4. Growth of the hydrogen peak with increased charge passed over the course of the same bulk electrolysis experiment as above in Figure S3 with 0.5 mM Re(bipy-tBu)$(CO)_3$Cl at p-Si under an atmosphere of CO_2 with 2.6 M water.

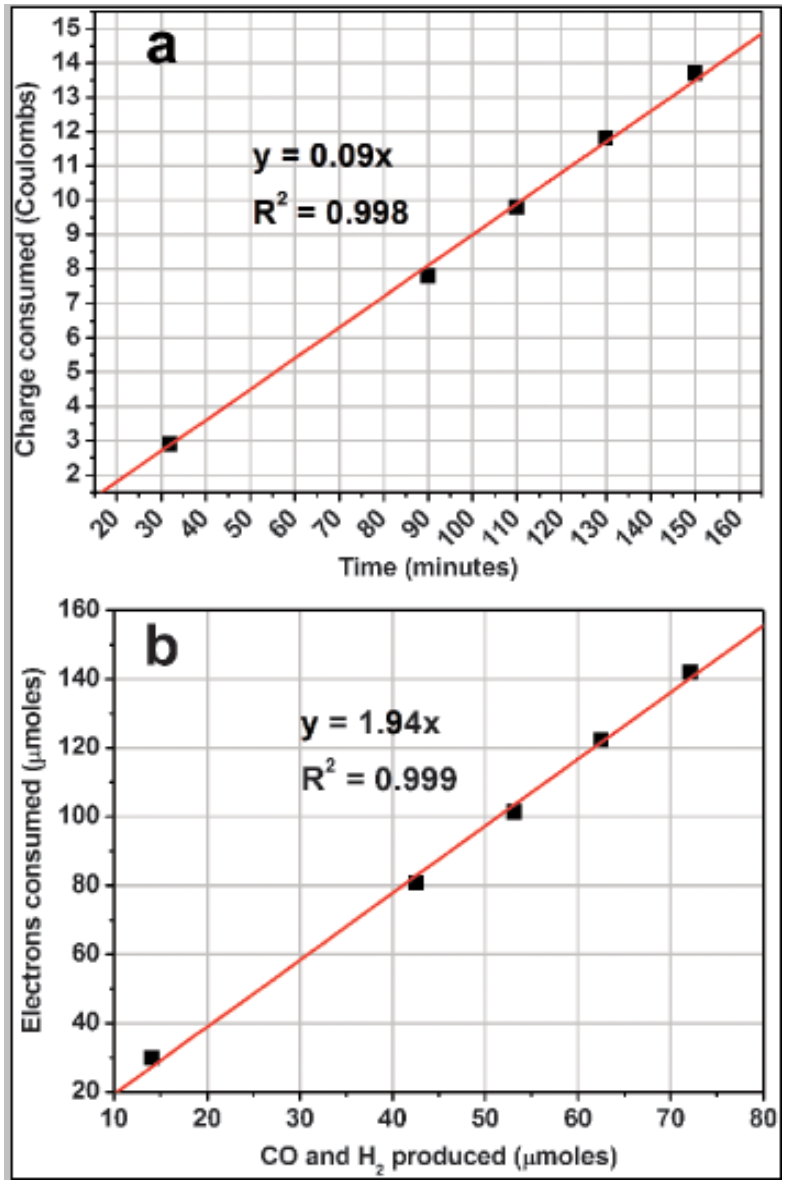

Figure S5. (a) Plot of charge consumed over time showing consistency (lack of degradation) over a period of nearly three hours and (b) a plot of electrons consumed *versus* gases produced ($CO + H_2$). The slope of nearly two represents the two electron processes for both CO_2 to CO and $2H^+$ to H_2 reductions and a Faradaic efficiency of 102 ± 5% for the overall process.

Reference:

1. B. Kumar, J. M. Smieja and C. P. Kubiak, *Journal of Physical Chemistry C*, 2010, **114**, 14220-14223.