

Supporting Information

Proton-Induced Trap States, Injection and Recombination Dynamics in Water-Splitting Dye-Sensitized Photoelectrochemical Cells

Nicholas S. McCool,¹ John R. Swierk,² Coleen T. Nemes,² Timothy P. Saunders,^{1,†} Charles A. Schmittenmaer,^{2,*} and Thomas E. Mallouk^{1,3,4,*}

¹Department of Chemistry, ³Department of Biochemistry and Molecular Biology, and ⁴Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802, United States

²Department of Chemistry and Engineering Sciences Institute, Yale University, 225 Prospect Street, P.O. Box 208107, New Haven, Connecticut 06520-8107, United States

Corresponding Authors:

*tem5@psu.edu

*charles.schmittenmaer@yale.edu

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Electrochemical detection of oxygen. Photoelectrochemical water-splitting has been demonstrated in dye-sensitized cells using a variety of colloidal and molecular water oxidation catalysts. Interestingly, Fielden et al. have recently observed water-splitting in a similar system without the deliberate addition of a catalyst.¹ Herein, we also verify oxygen evolution without a deliberately added catalyst by using a Clark-type electrode configuration.¹⁻⁴ Amperometric detection of oxygen was carried out using a Pine Instruments bipotentiostat (Model AFCBP1). Pt electrodes were made by sputtering 10 nm of Ti on FTO glass (Hartford Glass) followed by 200 nm of Pt. Electrical contact was made to the Pt electrodes using a copper wire and silver paste which was then protected using (Loctite Hysol 1C) white epoxy. Approximately 1 μm of additional Pt was electrochemically plated onto the electrodes at 2.5 mA/cm^2 for 20 minutes. Prior to each experiment, the Pt electrodes were electrochemically polished to ensure a clean working surface and the collection efficiency was recalibrated. To calibrate the system, a Pt working electrode was masked to 1 cm^2 using Kapton tape to match the working area of a typical photoanode. A second Pt electrode was sandwiched with the first using a nominally 0.1 mm thick microscope coverslip as a spacer and held together using Parafilm. The electrodes were placed in the anode compartment of an H-cell filled with 0.1 M phosphate buffer at pH 6.8 and purged with nitrogen. Using the bipotentiostat, the collector electrode was biased at -640 mV vs. Ag/AgCl and allowed to reach baseline. Once stabilized, the generator was biased at 1200 mV vs Ag/AgCl to oxidize water while the collector reduced locally generated oxygen. After several minutes, the generator electrode was disconnected and the collector returned to baseline. A linear fit between before and after electrolysis was used to approximate the baseline at a given time point for the collector current. When baseline-corrected, the ratio of collected current to generator current yielded the collection efficiency for this configuration. The two electrodes were separated and the Pt generator was replaced with a photoanode. The photoanode was biased at 100 mV vs Ag/AgCl and both electrodes were allowed to stabilize before being illuminated. The collection efficiency for the experiment was then obtained from the ratio of generator and collector currents using the calibrated collection efficiency.

Two Pt electrodes were used before each collector experiment to calibrate the collection efficiency of the system. The top panel in Figure S1 shows a collection calibration in which the generator electrode was connected at a 1200 mV vs Ag/AgCl bias at 0 s. The calibration was taken at 60 s in order to ensure that there was no non-Faradaic or other transient contribution to the current. These measurements typically resulted in a collection efficiency between 75 and 85%. The Pt electrode was replaced with a standard photoanode, Ru-EtOH, in order to determine the faradaic efficiency for the production of oxygen by water oxidation. The bottom panel in figure S1 shows a collector experiment using either a Pt or an FTO collector electrode. When corrected for the background current at the collector, we found that the electrodes produced oxygen with a $97.8 \pm 4.7\%$ ($n = 3$ samples) faradaic efficiency. The efficiency remains constant within experimental error when other time points along the photoelectrolysis trace were used. An FTO electrode is included in order to rule out the production of hydrogen peroxide. At the cathodic potentials used, Pt should reduce both oxygen and hydrogen peroxide, but the FTO electrode is only sensitive to hydrogen peroxide. The lack of a current response at the FTO collector demonstrates that the photoanodes generate oxygen at unit current efficiency despite the lack of a deliberately added catalyst.

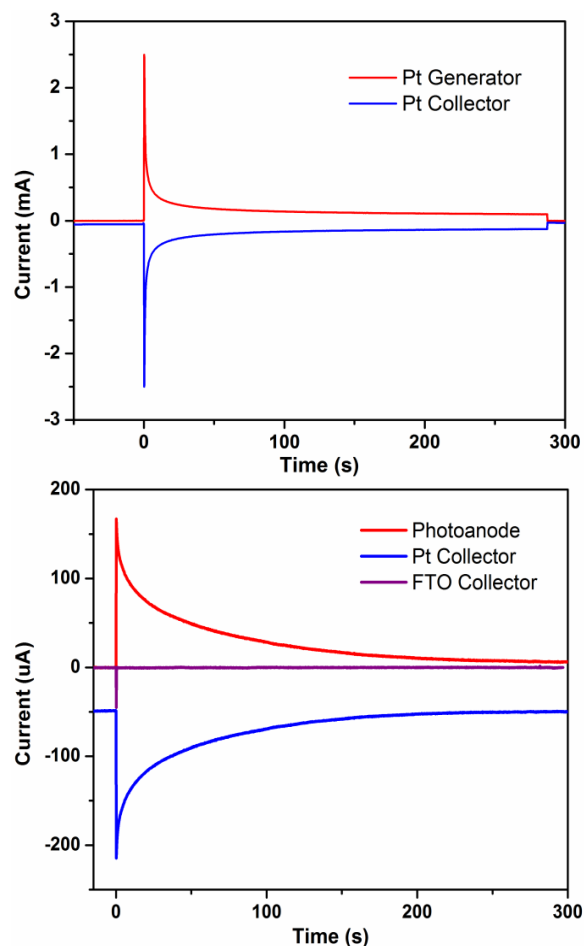


Figure S1. Clark-type measurement for photoanodes prepared with dye from ethanol in pH 6.8 0.1 M sodium phosphate buffer. (Top) Calibration using two Pt electrodes biased at 1200 mV and -640 mV vs. Ag/AgCl as the generator and collector, respectively. The generator electrode was connected at 0 s. (Bottom) Collection experiment using a Ru-EtOH photoanode biased at 100 mV vs Ag/AgCl and a Pt collector or bare FTO electrode collector biased at -640 mV vs. Ag/AgCl, with light on at 0s.

Table S2. Fitting parameters for TA traces in Figure 3

	A (mOD)	τ (ns)	β
Ru-EtOH	-9.46 ± 0.23	607 ± 13	0.51 ± 0.02
Ru-HClO ₄	-14.49 ± 0.06	447 ± 2	0.85 ± 0.01
Ru-HClO ₄ -HV	-9.98 ± 0.07	586 ± 4	0.73 ± 0.01

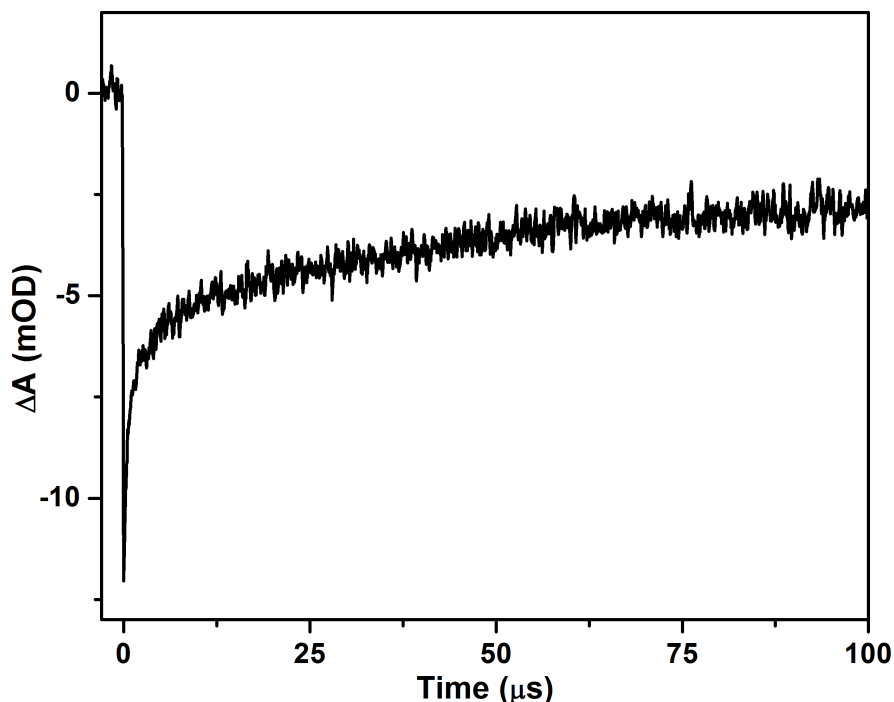


Figure S2. Transient absorption trace at 420 nm for a TiO₂ electrode sensitized with Ru(II)phos from ethanol. Spectrum was collected in N₂-purged 100 mM pH 6.8 potassium phosphate buffer. Data was smoothed using a 5-point moving average.

Table S2. Fitting parameters for TRTS traces in Figure 4

	A_1^a	τ_1 (ps)	A_2^a	τ_2 (ps)	A_3^a	τ_3 (ps)	A_4^a	τ_4 (ps)
Ru-EtOH	0.46	<0.5	0.33	19.1	0.21	231.1		
Ru-HClO ₄	0.20	0.8	0.80	460.1	-1.13	2348		
Ru-HClO ₄ -HV	0.19	<0.5	0.19	16.5	0.62	402.3	-0.94	1960.6

^aA₁, A₂, A₃, and A₄ are normalized amplitudes

References

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