Supporting Information

Kinetics *versus* Charge Separation: Improving the Activity of Stoichiometric and Non-Stoichiometric Hematite Photoanodes Using a Molecular Iridium Water Oxidation Catalyst

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Scheme S1 – Preparation of the four hematite thin film samples. Samples A and H (the large samples) were prepared according to the description in the Experimental Section of the manuscript. The iridium functionalization was performed according to Scheme 1 and the Experimental Section in the manuscript.



Figure S1 – UV-vis of the IrCp*(pyalk)OH precursor (1 mM) and the active Ir dimer (0.5 mM) in aqueous solution. Both complexes are shown in Scheme 1 in the manuscript. Path length of UV-vis cell = 1 cm.



Figure S2 – UV-vis spectra of the four thin film samples tested in this study. A peak associated with the iridium catalyst at ~610 nm (see Figure S1) is not observed due to the monolayer coverage of the catalyst. The small peak between 600 and 700 nm for the air-treated samples is due to reflection from the thin films. This peak is not observed when using an integrating sphere.¹ It may disappear following hydrogen treatment due to a change in refractive index of the film, which would account for a change in reflectance.



Figure S3 – ATR-FTIR spectra of all four thin film samples (plus FTO background). While peaks associated with the iridium dimer co-catalyst are not visible due to the monolayer coverage of the homogeneous catalyst, an increase in intensity of the bands from 400 cm⁻¹ to 2000 cm⁻¹ is evident following hydrogen treatment, consistent with our previous results.¹



Figure S4 – Raman spectra of all four thin film samples, plus a bare FTO substrate for comparison. a) Full spectrum showing similar overlap for all five samples. b) Zoom-in of the squared-out area showing the strongest peak for hematite associated with a two-magnon scattering mode.² The peak is absent for the H₂-treated films, consistent with our previous results.¹ However, no peaks could be found for the iridium dimer, which are anticipated in the region from ~400 cm⁻¹ to ~950 cm^{-1.3}



Figure S5 – EDX spectra of a thin film of hematite after air treatment and functionalization with the iridium dimer (sample A-Ir). While peaks associated with iron and nitrogen are present, no peaks associated with iridium could be observed.



Figure S6 – XPS survey spectrum of a thin film of hematite after H₂ treatment and functionalization with the iridium catalyst. The sample was treated under chronopotentiometry conditions (~50 μ A/cm², pH=7.3, Pt wire counter electrode, Ag/AgCl reference electrode) for 1 h before XPS testing. The presence of the Ir4f, N1s and C1s peaks in the high-resolution spectra in Figure S7 are indicative of the stability of the tethered catalyst even after extended electrolysis.



Figure S7 – High-resolution XPS spectra of a thin film of hematite after H₂ treatment and functionalization with the iridium catalyst. a) Fe3p and Ir4f region, b) C1s region, c) N1s region, and d) Fe2p region.



Figure S8 – Forward and reverse CV scans for sample A-Ir, performed in pH 7.3 solution with a Pt wire counter electrode and Ag/AgCl reference electrode. Cycles 1, 3 and 5 were performed in the dark, while cycles 2 and 4 were performed under AM1.5G 1 sun illumination. The forward scan when under illumination (cycles 2 and 4) does not show any appreciable photocurrent at the peak potential, indicating that the decrease in peak current when under illumination is not a result of overlapping cathodic (Ir^{V} reduction) and anodic (photooxidation of water) currents.



Figure S9 – Chronoamperometry of H₂-treated α -Fe₂O_{3-x} samples with (sample H-Ir) and without (sample H) the iridium dimer. Samples were manually illuminated after 60 s with AM1.5G 1 sun illumination.



Figure S10 – Electrolysis performed on sample H-Ir for 22.4 h under AM1.5 1 sun illumination. The sample was held at a potential of 1.12 V vs. Ag/AgCl at a pH of 7.4 (or 1.75 V vs. RHE) in a custom-designed airtight photoelectrochemical cell. Headspace measurements were performed at the times indicated in the figure ($t_0 = 0$ h and $t_1 = 22.4$ h). Following testing under illumination, the sample was tested again at the same potential but in the dark, over a 24 h period. The chronoamperometry results for the dark run are not included in this figure, however the headspace measurements for both light and dark runs are included in Figure S11.



Figure S11 – Rates of O₂ and H₂ evolution during the electrolysis measurements. Only two measurements were taken for each run to minimize leaking through the sampling septum. The lower Faradaic efficiency (FE) for the run under illumination is likely due to a number of contributing factors, including oxidation of the copper tape contacting the sample, slow leakage of O₂ out of the cell (also evident from the low molar ratio of H₂:O₂, which should be theoretically 2:1), and slow oxidation/decay of the sample over time (see decay in photocurrent in Figure S16). This final factor is unlikely to contribute substantially to low Faradaic efficiency, as a quick calculation reveals that full oxidation of a 25 nm film of Fe₂O_{3-x} (where we assume x=1) at a current density of 0.2 mA/cm² would result in complete reoxidation of the film in 79 seconds, assuming all current was originating from the film oxidation.



Figure S12 – Sample Nyquist plots acquired at 1000 mV vs. Ag/AgCl (~1.63 V vs. RHE). a) Sample A. The inset shows a zoom-in close to the real impedance (Re(Z)) axis. Sample A-Ir exhibited similar Nyquist plots to the ones shown here. b) Sample H-Ir. The inset shows a zoom-in close to the Re(Z) axis. The blue arrow indicates the high frequency shoulder, which was present at all potentials irrespective of the illumination conditions. Sample H exhibited similar Nyquist plots to the ones shown here. All samples were modeled using the Randles' equivalent circuit shown in Figure 4a.



Figure S13 –Capacitance (*C*) vs. potential for all four samples, modeled using a Randles' equivalent circuit. The capacitance was derived from the constant phase element (CPE). a) Measured in the dark. The inset shows the circuit model and element in question. b) Zoom-in close to the potential axis derived from the figure in a). c) Measured under AM1.5 1 sun illumination. d) Zoom-in close to the potential axis derived from the figure in c).



Figure S14 – EIS and cyclic voltammetry measurements acquired in the dark for the reference FTO substrates with and without iridium (all measurements were performed in the dark as no photocurrent could be detected). a) Capacitance (*C*) vs. potential. The inset shows the Randles' equivalent circuit, with the capacitance values derived from the constant phase element (CPE). b) Charge transfer resistance (R_{CT}) vs. potential. The inset shows a zoom-in close to the potential axis. c) Cyclic voltammograms acquired following the impedance measurements. The third scan is plotted in the figure. The inset shows a zoom-in close to the potential axis.



Figure S15 – Logarithmic representation of the photocurrent decay shown in Figure 5a. Fitting a monophasic exponential decay to each linear portion of the curve gives time constants of 0.039 s and 0.54 s. These values are consistent with the values extracted using the Origin biphasic exponential fitting at the same potential ($\tau_1 \approx 0.026$ s and $\tau_2 \approx 0.25$ s).



Figure S16 – Decay time constant τ_2 derived from the biphasic exponential fitting using the Origin software.



Figure S17 – a) Zoom-in close to the potential axis of Figure 5b, showing the decay constant (τ_1) as a function of potential. b) Zoom-in close to the potential axis of Figure 5c, showing the cathodic charge passed (Q) as a function of potential.

	Monophasic Exponential			Biphasic Exponential				
Potential (V	τ	+/- error	R ²	τ ₁	+/- error	τ2	+/- error	R ²
vs. RHE)								
1.0336	0.06129	7.682E-4	0.92424	0.0318	3.03442E-4	0.39287	0.00664	0.9873
1.0836	0.05817	7.66035E-4	0.91645	0.02454	2.6174E-4	0.29368	0.00442	0.98678
1.1336	0.03883	4.86055E-4	0.92592	0.01899	1.62047E-4	0.22951	0.00322	0.99074
1.1836	0.04118	5.0008E-4	0.93046	0.02076	1.71946E-4	0.24196	0.0034	0.99138
1.2336	0.03965	4.17922E-4	0.94584	0.02419	1.80884E-4	0.27067	0.00446	0.99189
1.2836	0.03641	3.98844E-4	0.94366	0.02089	1.45176E-4	0.23077	0.00321	0.99367
1.3336	0.03783	4.55843E-4	0.93214	0.01707	1.41339E-4	0.18329	0.00223	0.99286
1.3836	0.03204	3.37335E-4	0.949	0.01727	1.22295E-4	0.16409	0.00209	0.9948
1.4336	0.02687	2.2916E-4	0.96748	0.01779	1.18973E-4	0.15086	0.00258	0.9952
1.4836	0.02192	1.55328E-4	0.97729	0.01786	1.42052E-4	0.17038	0.00645	0.99043
1.5336	0.01663	1.1804E-4	0.977	3.48189E-5*	5.73899E55*	0.69472*	0.84153*	0.3506*
1.5836	0.0131	1.89359E-4	0.91907	0.01183	2.37439E-4	0.1594	0.02704	0.92482
1.6336	0.01135	4.13055E-4	0.63606	0.01094	5.69093E-4	0.1341*	0.15877*	0.63623*
1.6836	0.00743	8.49433E-4	0.65271	0.00743*	29.92206*	0.00743*	45.44696*	0.64893*

Table S1 – Exponential decay time constants for a biphasic function vs. a monophasic function for sample A. The values marked with an asterisk are likely errors in the fitting process and were omitted from the figures. In most cases, the biphasic exponential function fit the data better than the monophasic exponential function.

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