

Supporting Information for Kinetics of Photoelectrochemical Oxidation of Methanol on Hematite Photoanodes

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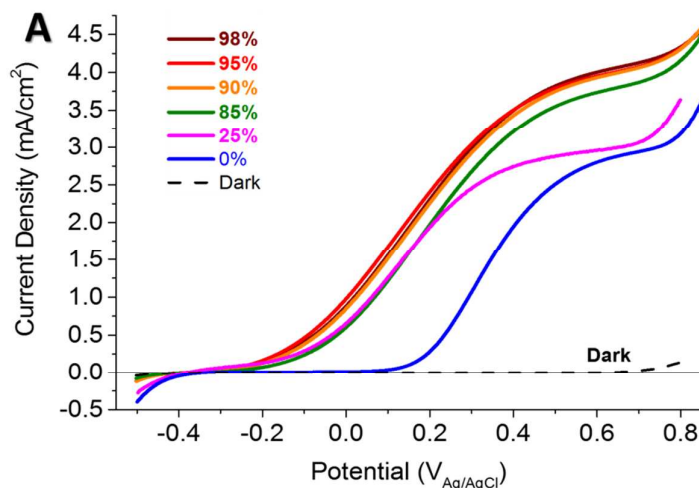
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1. Photoelectrochemistry

The effect of the concentration of methanol is shown in Figures S1.A and S1.B. Figure S1.A shows the increasing plateau photocurrent response for methanol oxidation on a α -Fe₂O₃ photoanode as the concentration of methanol is increased. This constant increasing of the photocurrent may be due to diffusion limitations that are overcome at high concentrations of methanol in the electrolyte. Figure S1.A shows that from 90 to 98% of methanol the plateau photocurrents obtained were constant, this indicates that above 90 % methanol, diffusion is not limiting the reaction. Therefore, a 95% methanol in 0.1 M NaOH electrolyte was selected for our studies on α -Fe₂O₃. Figure S1.B shows that the plateau photocurrent when methanol is oxidized on TiO₂ reaches a saturation point at a concentration of 4% of methanol in 0.1 M NaOH and it remains constant as the concentration of methanol increases up to 50%.



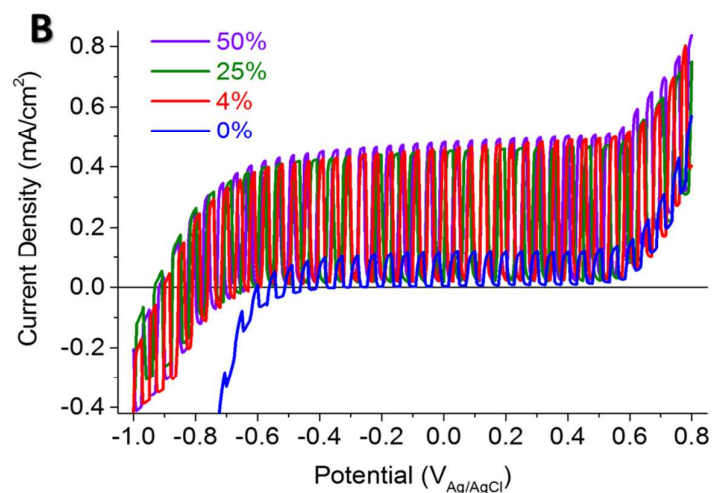


Figure S1. Current/potential response of the measured photoanodes under approximately 1 sun front illumination conditions through electrode/electrolyte (EE) interface, **a)** α - Fe_2O_3 photoanode under dark conditions (black dashed line) and EE illumination, measured in 0.1M NaOH aqueous solution (blue) and 25% methanol (pink), 85% methanol (green), 90% methanol (yellow), 95% methanol (red) and 98% methanol (dark red) in 0.1M NaOH and **b)** TiO_2 photoanode under EE illumination, measured in 0.1M NaOH aqueous solution (blue) and 4% methanol (red), 25% methanol (green), 50% methanol (purple) in 0.1M NaOH.

2. Formaldehyde detection

Formaldehyde generation was performed setting a bulk photoelectrolysis in a 100 mL three electrode photoelectrochemical cell under approximately 1 sun of 365 nm LED light and 0.55V vs Ag/AgCl. In order to quantify formaldehyde, 3 aliquots were extracted at the following times of reaction 13, 31.6 and 47.6 min. The extracted volume (10 mL in the first aliquote, and 5 mL for the two remaining) was mixed with 10 mL of 1M NaOH and 0.1 g of 4-Amino-5-hydrazino-1,2,4-triazole-3-thiol and diluted to 25 mL in water, following the reported procedure.¹ An individual UV-Visible absorption spectrum of the final mixtures was then measured. Using the calibration curve (Figure S2) the amount of produced formaldehyde was quantified. Finally, from the bulk photoelectrolysis (Figure S3) the theoretical amount of formaldehyde was estimated taking into account the total charge measured over the testing period, the Faradaic constant and the number of electrons generated in the reaction, which in this case is 2. The Faradaic efficiency (FE) was estimated as:

$$FE = \frac{\text{mol of detected } CH_2O}{\text{mol of } CH_2O \text{ calculated from the bulk electrolysis}} \times 100 = \frac{3.70 \times 10^{-5}}{3.85 \times 10^{-5}} \times 100 = 96\% \text{ (Figure 2 in the main paper)}$$

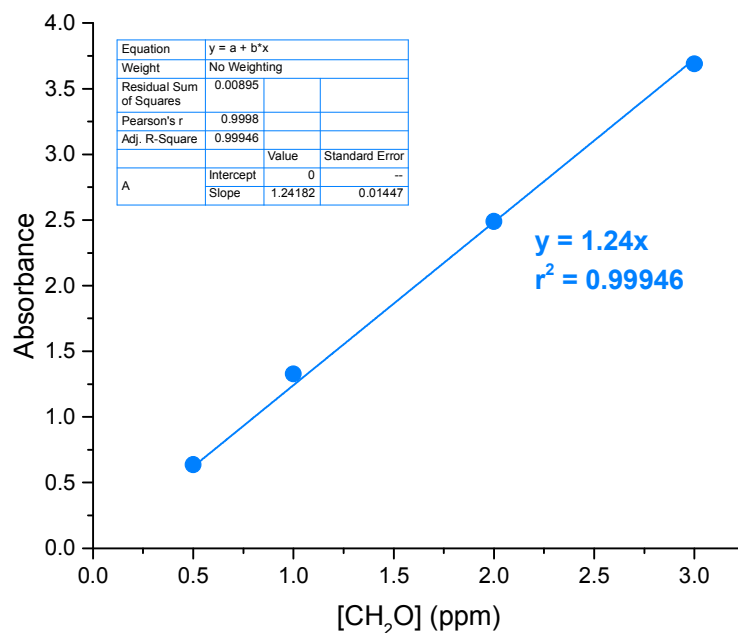


Figure S2. CH₂O calibration curve, prepared following the reported procedure.¹

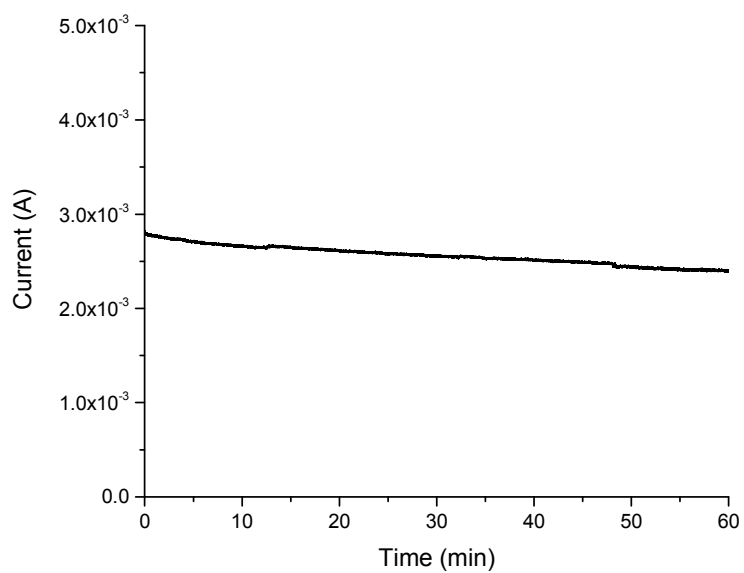


Figure S3. Current-time curve for the Bulk electrolysis applying 0.55V vs Ag/AgCl and approximately 1 sun 365 nm LED irradiation in a 100 mL of 0.1M NaOH in 95% MeOH solution.

3. Photo-Induced Absorption Spectroscopy and Transient Photocurrent measurements on hematite at 0.00 V_{Ag/AgCl}

Photo-induced absorption spectroscopy and transient photocurrents were measured at different applied potentials in the PEC cell for the oxidation of methanol. Figure S4.A shows the PIA signal corresponding to the photogeneration and accumulation, steady-state and reaction of holes as a function of excitation light intensity for the oxidation of methanol on the α -Fe₂O₃ photoanode at 0.00 V. The corresponding TPC signals are shown in Figure S4.B which gives us information about the electron extraction

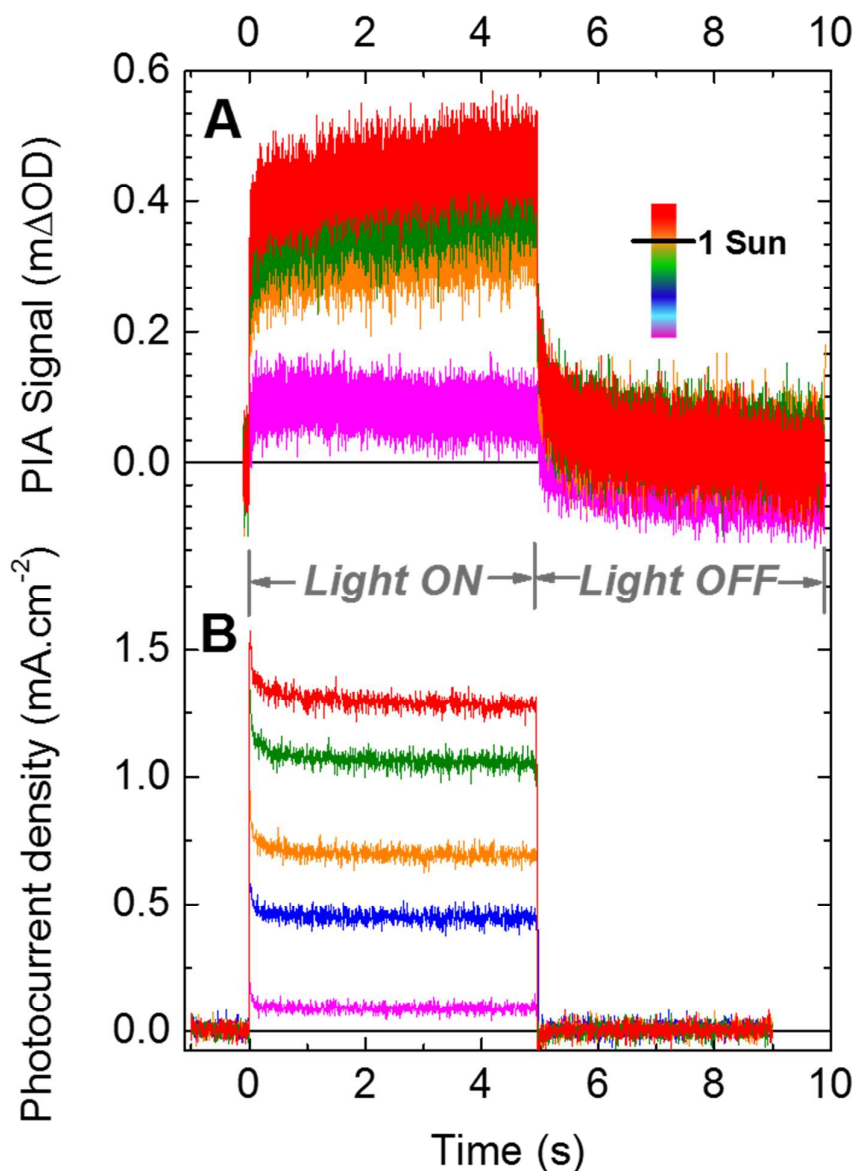


Figure S4. Oxidation of 95% methanol in 0.1 M aqueous NaOH on α -Fe₂O₃ during 5s on/5 s off pulsed 365 nm illumination conditions at 0.00 V, **a)** photoinduced absorption of excited species probed at 650 nm and **b)** transient photocurrent measured simultaneously.

4. Effect of Recombination on the Decays

The photo-induced absorption signal probed at 650nm, when the LED light is turned off corresponds to the decay of the photogenerated holes. In the case of the oxidation of methanol at 0.55 $V_{Ag/AgCl}$, where no back electron/hole, or 'surface', recombination² takes place, the decay corresponds to the reaction with methanol of the holes accumulated at the surface of hematite. At lower applied potentials, such 0.00 $V_{Ag/AgCl}$ and matched surface hole density compared to 0.55 $V_{Ag/AgCl}$ (approximately 0.3 holes.nm⁻²), the PIA signal decays with faster kinetics. In these conditions of low applied potential where no water oxidation occurs, we assign this faster decay to the presence of back electron/hole recombination taking place, with kinetics competitive with methanol oxidation.

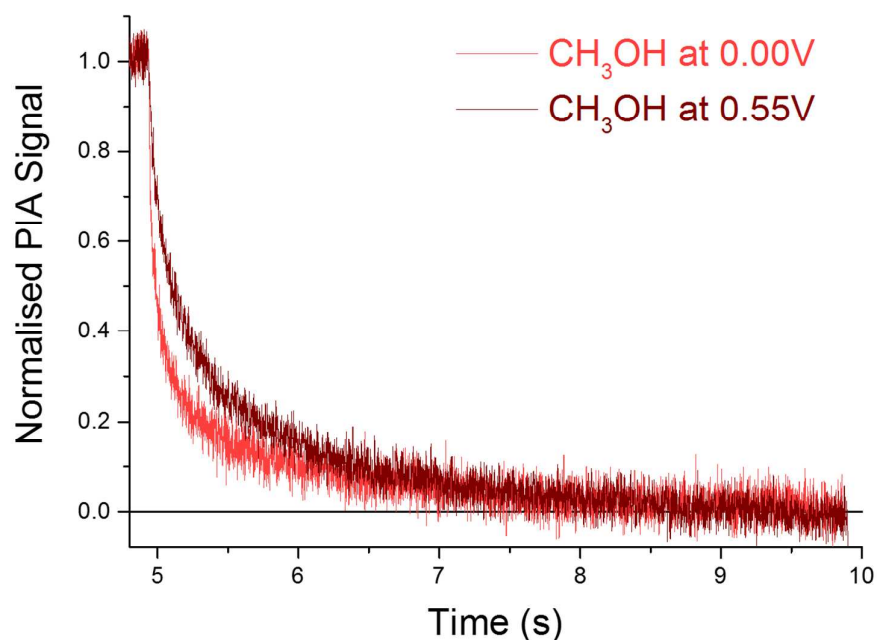


Figure S5. Normalised surface hole absorption, probed at 650nm when the PEC cell was held at 0.00 V (light red) and 0.55 V (dark red)

5. Photo-Induced Absorption Spectroscopy and Transient Photocurrent measurements on titania at -0.80 V_{Ag/AgCl}

Figure S6.A shows the PIA signal corresponding to the photogeneration and accumulation, steady-state, and reaction of holes as a function of excitation light intensity for the oxidation of methanol on the TiO₂ photoanode at -0.80 V. The corresponding TPC signals are shown in Figure S6.B.

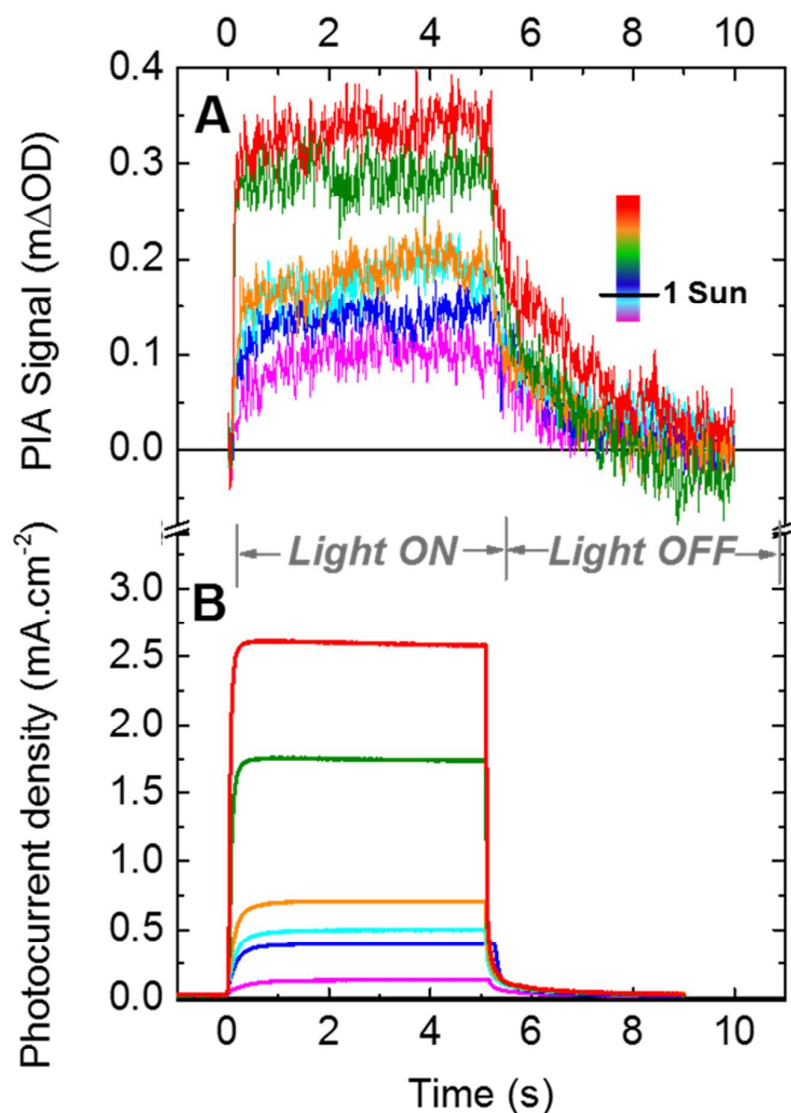


Figure S6. Oxidation of 4% methanol in 0.1 M aqueous NaOH on TiO₂ during 5s on/5 s off pulsed 365 nm illumination conditions at -0.80 V, **a)** photoinduced absorption of excited species probed at 500 nm and **b)** transient photocurrent measured simultaneously

Signals corresponding to TPC measurements do not show any indication of back electron/hole recombination described by Le Formal *et. al.*,³ therefore, for the kinetic model described in section 4 the flux of photogenerated holes towards the surface of the photoanode is equivalent to the photocurrent measured.

6. Initial Rates Analysis of methanol oxidation on hematite

The rate law analysis is based on the kinetic model described by Le Formal et. al.,³ in which the photogeneration, accumulation and reaction of the holes within the time ($\frac{dp_s}{dt}$) in any photoanode (followed by PIAS) in absence of back electron/hole recombination can be described by eq 1.

$$\frac{dp_s}{dt} = J_{holes}^{sur} - k_{H_2O}^{obs} \cdot p_s^\beta - k_{MeOH}^{obs} \cdot p_s^\alpha \quad (1)$$

Where J_{holes}^{sur} is the flux of photogenerated holes to the surface, $k_{H_2O}^{obs}$ and k_{MeOH}^{obs} are the rate constants for water and methanol oxidation respectively. β and α are the orders of water and methanol oxidation reactions, with respect to the density of accumulated holes. The term $k_{H_2O}^{obs} \cdot p_s^\beta$ accounting for water oxidation as side or competitive reaction⁴ is taken into account in this model. At steady-state conditions, where the rate law analysis is reported, $\frac{dp_s}{dt}$ is zero and J_{holes}^{sur} is equivalent to the photocurrent, $j_{(V)}$. Therefore, eq 1 can be rewritten as

$$0 = j_{(V)} - k_{H_2O}^{obs} \cdot p_s^\beta - k_{MeOH}^{obs} \cdot p_s^\alpha \quad (2)$$

At potentials where no water oxidation can occur i.e., 0.00 V_{Ag/AgCl} for hematite and -0.80 V_{Ag/AgCl} in the case of anatase (shown in Figure 4), according to the J-V curves shown in Figure 1.a in the main text and Figure S1.b, respectively, the rate law analysis from eq 2 can be rewritten in logarithmic base as

$$\log(j_{(V)}) = \alpha \cdot \log(p_s) + \log(k_{MeOH}^{obs}) \quad (3)$$

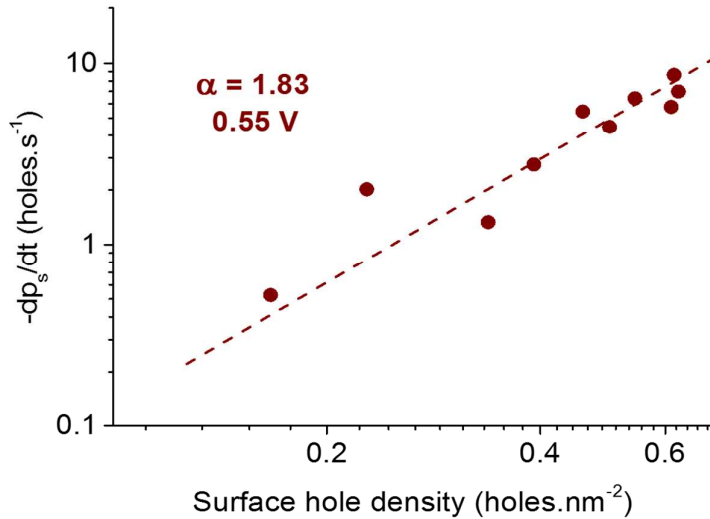


Figure S7. Initial rates analysis, gradient of PIA signal within the first 30 ms, $\frac{dp_s}{dt}$ versus surface hole density, dp_s , of the oxidation of methanol at 0.55 V_{Ag/AgCl} applied potential on α -Fe₂O₃.

An initial rates analysis can also be made taking into account the decay of the photogenerated holes accumulated at the surface of the photoanodes. When the LED illumination is turned off, the flux of photogenerated holes towards the surface of the hematite (J_{holes}^{sur}) is zero and where no water oxidation takes place, the rate law analysis from eq 1 can be rewritten in logarithmic base as

$$\log\left(-\frac{dp_s}{dt}\right) = \alpha \cdot \log(p_s) + \log(k_{MeOH}^{Obs}) \quad (4)$$

Figure S7 shows the initial rates analysis, within the first 30ms of decay, for the oxidation of methanol at 0.55 $V_{Ag/AgCl}$, where a second order of reaction (α) is extracted from the gradient of the $\log(p_s)$ - $\log\left(\frac{dp_s}{dt}\right)$ plot which is in agreement with the analysis done in quasi steady-state conditions and shown in Figure 4.

We now turn to the observed rate constants shown in Figure S7, where k_{MeOH}^{Obs} calculated from the data collected at 0.55 $V_{Ag/AgCl}$, where no back electron / hole recombination takes place, is ~ 20 holes⁻¹nm²s⁻¹, which is in accordance with the observed rate constant calculated from the quasi steady-state analysis (33 holes⁻¹nm²s⁻¹).

7. Kinetic Isotopic Effect

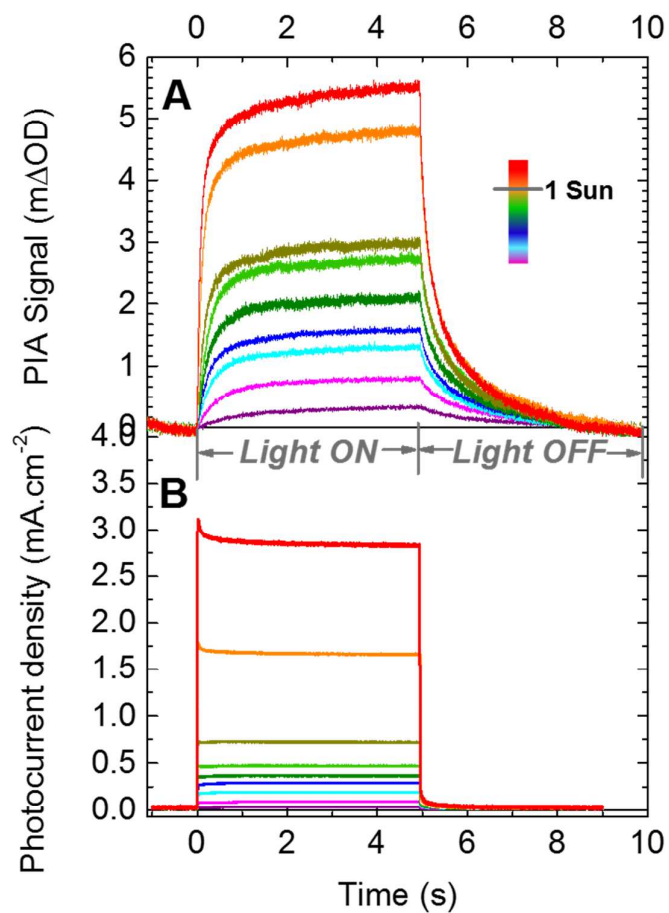


Figure S8. Oxidation of 95% CD₃OD in 0.1 M NaOD in D₂O α -Fe₂O₃ during 5s on/5 s off pulsed 365 nm illumination conditions at 0.55 V, a) photoinduced absorption of excited species probed at 650 nm and b) transient photocurrent measured simultaneously.

Figure S8 shows the photo-induced absorption (PIA) signals (Figure S8.A) and their corresponding transient photocurrents (Figure S8.B) for the oxidation of d₄-methanol in 0.1 M NaOD in deuterated water.

8. Rate Law Analysis of water compared to methanol oxidation on hematite

Turning to potentials where water oxidation might compete with methanol oxidation reaction, i.e. 0.55 V_{Ag/AgCl}, the rate law analysis would be described by eq 2 as $k_{MeOH} \gg k_{H_2O}$, observed graphically in Figure S9, validating the rate law analysis at high applied potentials with no competition of water oxidation reaction.

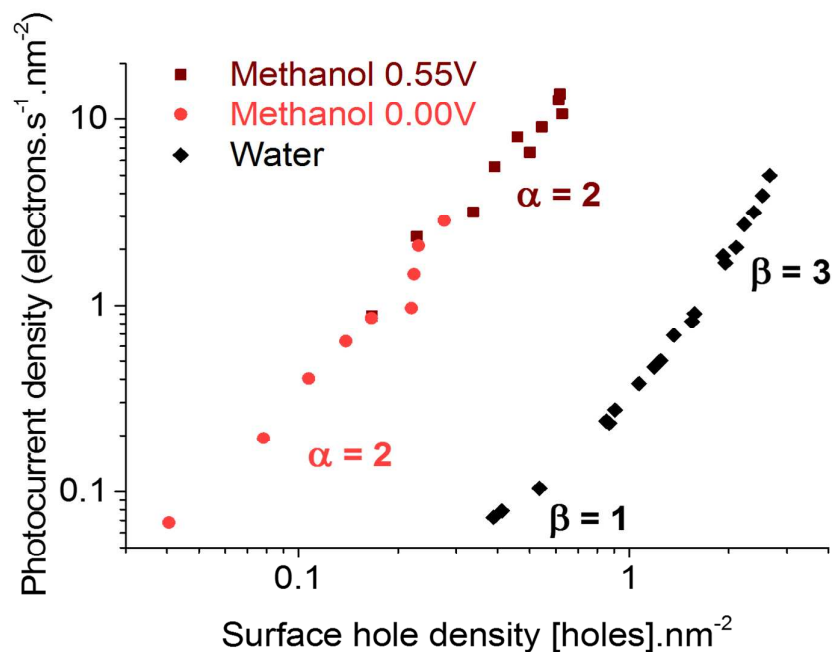


Figure S9. Rate law analysis: photocurrent density, $j_{(V)}$ versus surface hole density, dp_s , for the oxidation of methanol at 0.55 V (dark red) and 0.00 V (light red), and water at 0.55 V (black) on α -Fe₂O₃. The PIA signal was converted to surface hole density using the reported molar extinction coefficient of 640 M⁻¹ cm⁻¹ for α -Fe₂O₃.³ Water oxidation data has already been published by Le Formal *et. al.*³

9. References

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