# Correlating long-lived photogenerated hole populations with photocurrent densities in hematite water oxidation photoanodes

# - Supporting Information

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#### Hematite photoanodes:

Four different types of hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) photoanodes were investigated, detailed as follows; synthetic details are given in the references indicated. PLD: undoped (*i.e.* not intentionally doped) solid (non-porous) hematite deposited by pulsed laser deposition, approximately 600 nm thick.<sup>1</sup> USP: Nb-doped hematite approximately 200 nm thick with mesoporous "leaflet" nanostructure, deposited by ultrasonic spray pyrolysis using a method similar to that already described in the literature,<sup>2</sup> with 0.5% Nb precursor. Fe<sub>2</sub>O<sub>3</sub> CVD is undoped hematite deposited by atmospheric pressure chemical vapour deposition (APCVD), as described in the literature;<sup>3</sup> Si-Fe<sub>2</sub>O<sub>3</sub> CVD the Si-doped version of the this photoanode. The main paper concentrates on results from this last type of photoanode.



**ESI Fig 1:** UV-vis spectra of the different hematite photoanodes discussed in the main paper: solid PLD  $Fe_2O_3$ , Si-doped CVD  $Fe_2O_3$ , undoped CVD  $Fe_2O_3$ , Nb-doped USP  $Fe_2O_3$ .

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**Results:** 



**ESI Fig 2:** Spectra of Si-Fe<sub>2</sub>O<sub>3</sub> CVD (EE 355 nm excitation) on the timescale of 10 ms to 1 s at +0.4 V vs Ag/AgCl/3M NaCl (in 0.1M NaOH, ~pH 12.8), i.e. the spectrum of the photogenerated hole.

Previously we have used 580 nm to probe the photogenerated hole on undoped Fe<sub>2</sub>O<sub>3</sub> CVD photoanodes,<sup>4</sup> but at early timescales there is a strong bleach (negative absorption) at wavelengths <625 nm for Si-Fe<sub>2</sub>O<sub>3</sub> CVD photoanodes (this bleach is the subject of a future publication). However, the photogenerated hole in this type of photoanode also absorbs strongly at longer wavelengths. Hence the photo-hole was probed at 650 nm on Si-Fe<sub>2</sub>O<sub>3</sub> CVD photoanodes for the majority of measurements discussed in the main paper.



**ESI Fig 3:** Normalised transient absorption (TA) decays of the photo-hole in Si-Fe<sub>2</sub>O<sub>3</sub> CVD, excited at 355 nm and probed at 650 nm (EE illumination), as a function of applied bias (vs Ag/AgCl). Normalised at 4  $\mu$ s. NB: there is some variation in the slow phase decay timescale between individual photoanodes of the same type.

The fast phase (1  $\mu$ s-20 ms) of the TA decay is associated with electron-hole recombination. The normalised decays clearly show that the lifetime of this fast phase (equivalent to the apparent recombination rate) increases with increasing positive applied bias until ~0 V<sub>SSC</sub>, when the apparent recombination rate becomes approximately constant. This corresponds to the potential at which electron collection starts to become significant compared to recombination (see main paper).



**ESI Fig 4:** correlation of photocurrent amplitude (left) at +0.4  $V_{SSC}$  with population of longlived photoholes, as measured by the amplitude of the TA signal at 0.2 s under +0.4  $V_{SSC}$  bias (right: 355 nm excitation, 575 nm probe; number of photons absorbed EE and SE approximately equal for all photoanodes).



**ESI Fig 5:** transient photocurrent (355 nm excitation) decays for Si-Fe<sub>2</sub>O<sub>3</sub> CVD photoanode, excited EE ("front side", solid lines) and SE ("back side", dashed lines). Number of photons absorbed matched for SE and EE excitation.

At low applied bias (-0.1  $V_{SSC}$ ) the EE and SE TPC decay dynamics are almost identical, indicating that electron-hole recombination dominates at this potential. At high positive applied bias (+0.4  $V_{SSC}$ ) the EE and SE decay dynamics are significantly different, indicating that electron collection becomes significant compared to recombination at this potential. It is also clear that the TPC decays to zero faster at more positive applied bias.



**ESI Fig 6:** TA decays (355 nm excitation, number of photons absorbed matched EE/SE; 650 nm probe) of the photo-hole probed SE (black line) and EE (coloured line) at 0  $V_{SSC}$  (left) and +0.4  $V_{SSC}$  (right). Normalised decays inset.

At low applied bias (0  $V_{SSC}$ ) the SE and EE TA photo-hole decays have identical decay kinetics, but at high positive bias (+0.4  $V_{SSC}$ ), where there is significant photocurrent, the TA decay kinetics are notably different.



**ESI Fig 7:** *a*) TA decays of the photo-hole, as shown in Fig 5 in the main paper, normalised at 10  $\mu$ s. The recombination rate (decay of fast phase) clearly increases with increasing excitation intensity (charge carrier density), indicated by the arrow. *b*) Ratio of amplitude of fast and slow decay phases of transient absorption as a function of excitation intensity; inset: variation of amplitudes with excitation intensity. At the very lowest excitation intensities (<200  $\mu$ J.cm<sup>-2</sup>) we approach pseudo-first-order recombination behaviour (i.e. within the small perturbation regime).

## Estimation of band-bending in undoped hematite:

Using the method outlined by O'Regan et al:<sup>5</sup>

 $\Delta \varphi_{SC} = \frac{kT}{6e} \left(\frac{r}{L_D}\right)^2$ 

where  $L_D = (\varepsilon_0 \varepsilon kT/2e^2 N_D)^{0.5}$  is the Debye length. The radius of the particle (which we approximate as spherical) is *r*, while the voltage drop across the radius of the particle is  $\Delta \varphi_{SC}$ . Undoped hematite has a donor (electron) density, N<sub>D</sub> ~10<sup>17</sup>-10<sup>18</sup> cm<sup>-3</sup> and dielectric constant,  $\varepsilon$  ~30-60.<sup>6-8</sup> This gives a Debye length of 4.6-21 nm. Nanostructured undoped hematite photoanodes deposited by CVD have feature sizes in the range ~20-250 nm.<sup>3</sup> The estimates of  $\Delta \varphi_{SC}$  for different feature sizes are shown in Table 1 below. These values are a very rough estimate, but do indicate that some degree of band-bending is likely to be present in undoped CVD hematite photoanodes; Si-doped hematite will have a higher donor density (although the dielectric constant will also change) with respect to undoped hematite, so band-bending is expected to be greater in Si-doped photoanodes.

particle radius / nm	$\Delta \varphi_{\rm SC}$ for L <sub>D</sub> = 4.6 nm / mV	$\Delta \varphi_{SC}$ for L <sub>D</sub> = 21 nm / mV
10	20	1
50	500	24
125	32 x 10 <sup>3</sup>	150

ESI Table 1: estimated values of potential drop across radius of spherical nanoparticle

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