Electronic Supplementary Information for 

Passivating Surface States on Water Splitting Hematite Photoanodes with Alumina Overlayers

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1. Additional Experimental Details

Fe₂O₃ APCVD Photoanode Preparation: The photoanodes were prepared according to the method developed in our laboratory in 2006¹ which was recently optimized.² To summarize, this method consists of bringing the precursors—iron pentacarbonyl (Fe(CO)₅, Acros, 99.5%) and tetraethoxysilane (TEOS, Aldrich 99.9999%)—to the gas phase by bubbling argon in the liquids put in different vials. The vapor streams are then mixed and diluted in the carrier gas (dry air), which is targeted at a substrate (FTO, TEC 15) heated at ca. 420°C on a titanium block in a closed chamber. The iron oxide film obtained is formed by the agglomeration of small Fe₂O₃ particles (ca. 5 nm) nucleated in the gas phase, resulting in a cauliflower-like nanostructure.

Atomic Layer Deposition: Amorphous aluminum oxide (Al₂O₃) was deposited in a layer-by-layer fashion onto the hematite films by atomic layer deposition (ALD, Cambridge Nanotech S100). Deposition using successive pulses of trimethylaluminum (TMA) and deionized water in a nitrogen carrier gas was performed in a vacuum chamber heated at 200°C. The number of cycles (TMA / vacuum / H₂O pulse / vacuum) applied to the sample was adjusted to be 1, 3, 6, or 13 which corresponds to a thickness of 0.15, 0.45, 0.9 or 1.95 nm as measured by spectroscopic ellipsometry on Si wafer (Sopra GES 5E, fitted to a Tauc-Lorentz function). For samples covered with TiO₂, 6, 33, 66 and 132 cycles (titanium isoproxide pulse / vacuum / H₂O pulse / vacuum) were necessary to give similar thicknesses due to the lower reactivity of the precursor at 200 °C. Control electrodes were subjected to identical conditions but without precursor pulses.

Cobalt Treatment: The ALD-treated electrode was dipped in a 10mM aqueous solution of cobalt nitrate Co(NO₃)₂ for 30 seconds and rinsed with deionized water according to the method developed previously in our laboratory.¹

Photoelectrochemical Characterization: Photocurrent measurements were performed to estimate the solar photocurrent of the photoanodes in a three-electrode configuration with 1 M NaOH (pH 13.6) as electrolyte using Ag/AgCl in saturated KCl as a reference electrode and a platinum wire as a counter electrode. The hematite electrode was scanned at 50 mV s⁻¹ between 0.3 and 0.8 V vs. Ag/AgCl. The potential is reported relative to the reversible hydrogen electrode (RHE). The samples were illuminated at the photoanode/electrolyte interface with simulated sunlight from a 450 W xenon lamp (Osram, ozone free) using a KG3

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filter (3 mm, Schott) with a measured intensity of 1 sun (100 mW cm⁻²) at the sample’s surface. Spectral mismatch factors to estimate the difference of the electrode photoresponse obtained from simulated sun light and real sun light at AM 1.5 G were calculated according to the method described by Seaman et al. (M =0.98).³ The photocurrent transient data were obtained using the same set up with the addition of a computer-controlled light chopper. The potential was set at –0.1, 0.1 and 0.5 vs. Ag/AgCl for 4 seconds with the chopper programmed to switch the light ON and OFF every 2 seconds.

2. Photoelectrochemical Characterization of a Hematite Photoanode Covered with 3 ALD Cycles of Al₂O₃

Figure S1 is analogous to Figure 1 in the main text but for three ALD cycles instead of one. The sample similarly exhibits a resistive behavior after the ALD (red squares) and requires a thermal treatment at 300°C (green triangles) to recover the original photocurrent shape. Annealing at 400°C (blue diamonds) further improves the photocurrent at low bias potentials but decreases its plateau at high potential compared to the control (black circles).

![Figure S1](image_url)

**Figure S1.** Current densities, in mA cm⁻² of the prepared photoanodes in the dark (broken lines) and under simulated solar illumination (AM 1.5G 100 mW cm⁻², solid curves) are shown as a function of the applied potential, V vs. RHE. An APCVD hematite sample covered with 3 ALD cycles of Al₂O₃ has been measured after deposition (red squares), after annealing for 20 minutes at 300°C (green triangles) and after annealing for 20 minutes at 400 °C (blue diamond). The ALD covered photoanode is compared to a control (black circles).

3. Stability of the Photoanode

As mentioned in the main text, the hematite thin film covered with Al₂O₃ by ALD is stable for the entire duration of the EIS characterization (ca. 30 min) in 1M NaOH electrolyte. This experiment is the longest measurement we performed on a hematite photoanode before and after 3 cycles of Al₂O₃ ALD. We observe in Figure S2 that the photoelectrochemical performance (onset potential, photocurrent plateau) of both the ALD-treated electrode and the control stay unchanged before and after the 30 min required for EIS at potentials in the range of 0.7 – 1.8 V vs. RHE and pH 13.6.
Figure S2. Current densities, in mA cm\(^{-2}\) of the prepared photoanodes in the dark (dotted lines) and under simulated solar illumination (AM 1.5G 100 mW cm\(^{-2}\), solid curves) are shown as a function of the applied potential, V vs. RHE. A hematite control sample was photoelectrochemically characterized before and after the EIS experiment (blue circles and blue squares respectively) and after 3 cycles of Al\(_2\)O\(_3\) ALD (annealed 20 min at 300°C) (red diamonds and orange triangles respectively).

Figure S3 shows the photoelectrochemical performance of a hematite photoanode covered with 2 nm of Al\(_2\)O\(_3\) layer, before and after deposition, and after exposure in 1M NaOH electrolyte under standard illumination and at 1.03 V vs. RHE bias potential for increasing lengths of time (25 and 55 min). The photocurrent onset was found to recover its initial value after 55 min. Since the onset potential did not change upon exposure to electrolyte and bias in the dark (Figure S2), we attribute the recovery of the initial performance in Figure S3 to the photoelectrochemical dissolution of the Al\(_2\)O\(_3\) layer. A subsequent annealing treatment at 300°C for 20 min shows the recovery of the initial (pre ALD deposition) photoelectrochemical characteristics.

Figure S3. Current densities, in mA cm\(^{-2}\) of the prepared photoanodes in the dark (dotted lines) and under simulated solar illumination (AM 1.5G 100 mW cm\(^{-2}\), solid curves) are shown as a function of the applied potential, V vs. RHE. A hematite control sample was photoelectrochemically characterized before and after deposition of a 2 nm thick Al\(_2\)O\(_3\) layer (a, blue circles and b, red squares respectively). The same sample was then held in 1M NaOH electrolyte under AM 1.5 illumination and 1.03 V vs. RHE conditions and characterized after 25 min (c, orange triangles) and 55 min (d, yellow diamonds). A subsequent annealing treatment at 300°C for 20 minutes on the same sample (e, green pentagons) exhibits the recovery of the initial current voltage characteristics.
4. Additional Tests

In order to further decouple the role of trap state filling and catalysis at the SCLJ with the Al$_2$O$_3$ overlayer, we treated a control APCVD Fe$_2$O$_3$ photoanode with Al$^{3+}$ using 10 mM Al(NO$_3$)$_3$ in water with the same dip and rinse technique used for the Co$^{2+}$ catalyst. Figure S3 shows no change in the photoelectrochemical performance after one or two Al$^{3+}$ treatments in contrast to the overpotential decrease observed with the cobalt catalyst (Figure 4). This test confirms that the Al$_2$O$_3$ overlayer does not reduce the overpotential by enhancing the catalysis on the Fe$_2$O$_3$ photoanode.

**Figure S4.** Current densities, in mA cm$^{-2}$ of photoanodes in the dark (dotted lines) and under simulated solar illumination (AM 1.5G 100 mW cm$^{-2}$, solid curves) are shown as a function of the applied potential, V vs. RHE. A control (no ALD treatment) hematite photoanode is shown before (black circles) and after one (blue diamonds) and two (red triangles) Al$^{3+}$(aq) treatments.

In addition, APCVD hematite photoanodes were covered with an amorphous layer of TiO$_2$ by ALD to investigate its role as an overlayer. Figure S4 is analogous to Figure 2 and shows the water oxidation photocurrent density at 1.03 V (yellow triangles), 1.23 V (orange squares) and 1.43 V (red circles) vs. RHE, for a control photoanode and samples covered with different thicknesses of TiO$_2$ (adjusted to correspond to the Al$_2$O$_3$ thicknesses applied).

**Figure S5.** Current densities, in mA cm$^{-2}$ of the prepared photoanodes at 1.03 V (yellow triangles), at 1.23 V (orange squares) and at 1.43 V (red circles) vs. RHE, are presented for a control and samples covered by different number of cycles of TiO$_2$ ALD (6, 33, 66 and 132 ALD cycles at 200 °C) to obtain thicknesses comparable to that of the Al$_2$O$_3$ overlayers (0.1, 0.5, 1.0 or 2.0 nm as measured by ellipsometry on a Si reference). All samples were measured before and after ALD as well as after annealing at 300°C and 400°C.
5. Mott-Schottky Analysis of Photoanodes

The Mott-Schottky analysis mentioned in the main text was performed on a hematite film before and after Al₂O₃ deposition. The Mott-Schottky (MS) equation links the inverse of the square capacitance with the donor density, \( N_D \), and the flat band potential, \( V_{fb} \), starting from Poisson’s equation coupled with Boltzmann’s distribution to describe the distribution of charges in the space charge region and Gauss’ law relating the electric field at the interface. The MS equation is given by:

\[
\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 A^2 e N_D} \left( V - V_{fb} - \frac{k_BT}{e} \right)
\]

where \( C \) and \( A \) are the interfacial capacitance and area, respectively, \( V \) the applied voltage, \( k_B \) is the Boltzmann constant, \( \varepsilon \) the dielectric constant of the semiconductor, \( \varepsilon_0 \) the permittivity of free space, \( T \) the absolute temperature and \( e \) the electronic charge.

The MS analysis of the space charge capacitance was performed in the linear region of the \( C^{-2} \) plot from 0.7 to 1.3 V vs. RHE. A dielectric constant \( \varepsilon = 80 \) for \( \alpha \)-Fe₂O₃, and an active area of 5.943 cm² (i.e. a geometric area of 0.283 cm² times a roughness factor of 21) were used to extract the flat band potential and the donor density of a hematite photoanode (full blue markers on Figure S5) and a hematite photoanode covered with 3 ALD cycles of alumina (empty blue triangles on Figure S5). Linear regression of the MS plots led to coefficients of determination, \( R^2 \), of 0.994 and 0.965 for the hematite electrode before and after ALD of the Al₂O₃ overlayer, respectively.

Figure S6. Mott-Schottky analysis of a hematite photoanode before (full triangles, plain line) and after (empty triangles, broken line) 3 ALD cycles of alumina. The inverse of the square space charge capacitance is plotted vs. the potential applied during the impedance measurement.

6. EIS Measurement in the Dark and under Illumination of a Photoanode

Figure S7 shows the Nyquist plots of an APCVD photoanode (without alumina overlayer) corresponding to the EIS measurements performed in dark and under illumination conditions at key applied potentials.

Before the onset of the photocurrent by the illuminated sample, the two measurements exhibit the same features: two superimposed semicircles (as shown by the inflection point
observed in the figures below) but with a smaller high frequency arc for the electrode under illumination, resulting in a smaller $R_{SC}$ according to our model and as expected according to the increased conductivity in the semiconductor afforded by illumination. At a potential when photocurrent onsets in the illuminated electrode, two features are still apparent in the Nyquist plots for both conditions but the two arcs are more distinguishable on the light measurement due to the lower value of $R_{CT}$ (current is now flowing through the SCLJ during illumination). Finally, when EIS was performed at high bias potential (when water oxidation current starts to flow also in the dark sample), the same behavior for both conditions was observed (i.e. only the low frequency arc is now noticeable and decreasing as the dark current starts to flow). From these observations we are confident to assign the high frequency arc to processes occurring in the semiconductor and the low frequency arc to charge transfer processes. Overall, no evidence that a distinct process is occurring (e.g. surface intermediates specific to photo-oxidation) in the illuminated sample, which would be evidenced by a third arc.

**Figure S7.** Nyquist plots representing the EIS measurements performed on a hematite APCVD sample (not covered with alumina) in the dark (a - blue markers) and under AM 1.5 illumination (b – red markers) at three key applied potentials: before onset of the photocurrent (squares - 0.9V vs. RHE), when photocurrent is flowing in the illuminated sample (circles - 1.1V vs. RHE) and at the onset of dark current (triangles - 1.6 V and 1.75 V vs. RHE for measurement under dark and illumination respectively). Two different applied potentials are shown for the last condition to enable observation on the disparate scales.

**References**