## ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

## What Do you Do, Titanium? Insight into the Role of Titanium Oxide as Water Oxidation Promoter in Hematite-based Photoanodes

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**Figure S1.** Dark voltammetric measurements of hematite/titania electrodes with different titania doping percentages. The vertical dashed line depicts the thermodynamic potential of the oxygen evolution reaction (1.23 V<sub>RHE</sub>). Inset: Oxygen evolution reaction (OER) overpotential ( $\eta_{OER}$ ) at a current density of 1 mA·cm<sup>-2</sup> and in function of titania doping values, as calculated from:  $\eta_{OER} = E - E_{eq} - IR_u$ , where *E* is the potential for a current density of 1 mA·cm<sup>-2</sup> (V<sub>RHE</sub>),  $E_{eq} = 1.23$  is the thermodynamic (equilibrium) potential for the OER (V<sub>RHE</sub>), and  $IR_u$  is the Ohmic drop of the electrode-electrolyte system (I = 0.002 A;  $R_u$  was estimated from impedance measurements and took values between 14 and 20  $\Omega$ ). Error bars stem from repeated measurements. Electrolyte: 1 M NaOH. Scan rate: 20 mV/s.



**Figure S2.** (Left) Scheme of the illuminated hematite/electrolyte interface and the corresponding photogenerated hole transfer mechanism, direct from the valence band (blue arrow) or indirect through a sequential trapping at surface states (purple arrow) and transfer from surface states (orange arrow). Charge carrier generation by photon absorption is depicted with the green arrow. Relative sizes of electrons (red circle) and holes (blue circle) are related to their effective masses. Note that band bending is included as it corresponds to a generic semiconductor electrolyte interface (SEI); however, in our particular case of mesoporous thin films with full electrolyte permeation, both bands remain flat at the SEI (see Figure S5). (Right) Equivalent circuit (EC) of the charge transfer process at the illuminated hematite/electrolyte interface mediated by surface states.  $R_s$ , resistance associated with the electric contacts of the electrode, electrolyte, etc.  $R_{trapping}$ , resistance associated with charge trapping at surface states.  $C_{bulk}$ , capacitance associated with charge accumulation in the bulk.  $R_{ct, trap}$ , resistance associated with charge accumulation on the surface states.



**Figure S3.** Nyquist (Imaginary vs. Real component of impedance) plots in the dark of hematite/titania electrodes with different titania doping percentages and at 0.8, 1.0, 1.23, 1.4, 1.5 and 1.6  $V_{RHE}$ . Electrolyte: 1 M NaOH. AC amplitude: 10 mV. Frequency range: 100 mHz-1 MHz.



**Figure S4.** Mott-Schottky plots (C<sup>-2</sup> vs. E) for hematite/titania electrodes with different doping levels. Each point was obtained upon fitting the corresponding Nyquist plot at each potential in the dark to a classic Randles circuit (i.e. resistance and capacitance in parallel). Linear fittings (obtained in the 0.7-1.2 V<sub>RHE</sub> potential range) are also depicted on each case. Electrolyte: 1 M NaOH. AC amplitude: 10 mV. Frequency range: 100 mHz-1 MHz. Error bars stem from the goodness of the impedance fittings.

Titania doping / %	$E_{ m fb}$ / ${ m V}_{ m RHE}$	$N_{ m D}$ / $10^{18}$ cm <sup>-3</sup>	$N_{ m ss}$ / $10^{14}~{ m cm}^{-2}$
0	$0.71\pm0.01$	$0.43\pm0.02$	$0.35\pm0.06$
5	$0.68\pm0.01$	$2.40\pm0.10$	$1.43\pm0.30$
10	$0.72\pm0.02$	$2.74\pm0.30$	$1.73\pm0.30$
15	$0.73\pm0.01$	$2.76\pm0.20$	$1.59\pm0.40$
20	$0.81 \pm 0.03$	$1.60 \pm 0.30$	$0.68 \pm 0.10$

**Table S1.** Flat band potential values ( $E_{\rm fb}$ ), (uncorrected for Sn diffusion) bulk donor densities ( $N_{\rm D}$ ) and total surface states density ( $N_{\rm ss}$ ) as a function of titania doping on hematite/titania electrodes.  $E_{\rm fb}$  and  $N_{\rm D}$  values were respectively estimated from the x-intercepts (at C<sup>-2</sup> = 0) and slopes of the Mott-Schottky plots (Figure S3).  $N_{\rm ss}$  values were obtained from integration of their respective fitted Gaussian profiles (Figure 5). Errors stem from the goodness of the linear fittings or curve integrations.



**Figure S5.** Depletion region width (*W*) as a function of titania doping and the applied potential ( *E*), as obtained from:  $w = \sqrt{2\varepsilon\varepsilon_r(E - E_{fb})/(e^2N_D)}$ , where  $\varepsilon$  is the vacuum permittivity (8.85 × 10<sup>-12</sup> F·m<sup>-1</sup>),  $\varepsilon_r$  is the hematite relative dielectric constant (60), *e* is the electron charge (1.602 × 10<sup>-19</sup> C),  $N_D$  is the charge donor density (cm<sup>-3</sup>) and  $E_{fb}$  is the flat band potential (V).  $N_D$  and  $E_{fb}$  were obtained from Mott-Schottky plots (Figure S3). Error bars stem from the goodness of the fittings. The *w* values are compared with the particle radius (*r*), where the dashed line represents the minimum particle radius ( $r_{min} = 10$  nm) below which hematite is capable of sustaining a sizable space charge region at any applied potential and titania doping value, evincing a charge transport mechanism governed both by drift and diffusion.



**Figure S6.** SEM micrograph (top) and EDX spectrum (bottom) of a hematite / titania 10% electrode. SEM acquisition conditions: working voltage, 5 kV; working distance, 5.6 mm; magnifications, 50,000; signal, InLens. Ti and Fe atomic percentages (from EDX): 10.39% Ti, 89.61% Fe.



**Figure S7.** Absorptance (left), absorbance (center) and light penetration depth (right) of all hematite/titania electrodes. The first graph was obtained from transmittance (T, %) and total reflectance (R, %) measurements of the films. The absorbance  $(A(\lambda))$  of the second graph (center) was calculated from:  $A = \alpha d = ln \left(\frac{1-R}{T}\right)$ , where d is the electrode thickness and  $\alpha(\lambda)$  its

(center) was calculated from:  $T = \alpha e^{-\alpha} (T)$ , where *d* is the electrode thickness and  $\alpha(\lambda)$  its absorption coefficient. The graph on the right was obtained using the electrode thicknesses as obtained from profilometry. The horizontal dashed line represents the average electrode thickness (200 nm) and informs about the wavelength range of optimum light absorption (i.e. 63% of the incident light intensity,  $I_0/e$ ) by the films (501-550 nm), whereas the vertical dashed line represents the bandgap wavelength (*ca.* 590 nm, 2.1 eV) and informs about the optimum electrode thickness range (0.7-1.2 µm) for optimum light absorption (i.e. 63% of the incident light intensity below the wavelength absorption limit of the material,  $\lambda \leq \lambda_g$ ).



**Figure S8.** Grazing incidence XRD (GI-XRD) patterns of all hematite/titania electrodes. The FTO glass pattern is also included for comparison. Reference line patterns for peak assignation: tin oxide (JCPDS 41-1445, blue), pseudobrookite (JPCDS 41-1432, orange), maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, JPCDS 39-1346, magenta) and hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, JCPDS 33-0664, red). Crystallographic Fe<sub>2</sub>O<sub>3</sub> polymorph and plane (2 $\theta$ ): 30.0°,  $\gamma$  (220); 32.3°,  $\gamma$  (221); 35.7°,  $\alpha$  (110). Gray squares refer to FTO main peaks, while the white square is related with Fe<sub>2</sub>SnO<sub>5</sub> peaks (2 $\theta$  = 36.2°, (222) plane, JCPDS 71-0695).



**Figure S9.** Raman spectra of all hematite/titania electrodes (left), with a magnification of the 600-700 cm<sup>-1</sup> region (right). Raman band assignation (hematite vibrational modes, see refs. 69 and 70 from the manuscript):  $A_{1g}$  (223 and 491 cm<sup>-1</sup>);  $E_g$  (243, 289, 404 and 608 cm<sup>-1</sup>); LO (longitudinal optical)  $E_u$  (660 cm<sup>-1</sup>); magnon scattering (1318 cm<sup>-1</sup>).



**Figure S10.** Ti 2p, Fe 2p and O 1s XPS spectra of all hematite/titania electrodes. Peak contributions: Ti  $2p_{3/2}$  (458 eV), Ti  $2p_{1/2}$  (464 eV), Fe  $2p_{3/2}$  (710.9 eV), Fe  $2p_{1/2}$  (724.8 eV), O 1s lattice oxygen (O<sup>2–</sup>, 529.7 eV) and O 1s surface oxygen (OH<sup>–</sup>, 532.5 eV).

Titania doping / %	Fe / at. %		O / at. %		Ti / at. %	
	XPS	Theoretical	XPS	Theoretical	XPS	Theoretical
0	37.90	40.00	61.53	60.00	0.56	0.00
5	35.10	37.62	62.10	60.40	2.54	1.98
10	26.31	35.29	63.00	60.78	10.69	3.92
15	26.17	33.01	63.47	61.17	10.34	5.83
20	28.16	30.77	62.44	61.54	9.25	7.69

**Table S2.** (Surface) Atomic percentages of Fe, O and Ti as a function of the titania doping level. The XPS values (experimental) were obtained from XPS signals (Figure S10) while the calculated values (theoretical) were obtained assuming the hematite/titania composite is equivalent to Ti(mol%)/[Ti(mol%) + Fe(mol%)], where x = 0, 0.05, 0.10, 0.15 and 0.20. The experimental atomic percentage error stems from the Ti signal in the 0% sample.



**Figure S11.** HR-TEM micrograph of the hematite / titania 20% sample showing several crystallites with different compositions. Details of the left (red) and right (green) squared regions and their corresponding power spectra corresponding respectively to hexagonal Fe<sub>2</sub>O<sub>3</sub> and orthorhombic Fe<sub>2</sub>TiO<sub>5</sub>, the latter with lattice parameters of a = 0.3732 nm, b = 0.9810 nm and c = 0.9950 nm as visualized along the [010] direction.



**Figure S12.** HR-TEM micrograph of the hematite / titania 20% sample showing *ca.* 35 nm spherical-polyhedral nanocrystallite. Detail of the red squared region (right, up) and its corresponding SAED spectrum (right, down) revealing that the nanocrystallite mostly consists of  $Fe_2O_3$  phase measured along the [11-2] growth direction.



**Figure S13.** Low magnification TEM image of an agglomerate (hematite / titania 20% sample) and its corresponding EEL spectrum. Notice that in the TEM image there is carbon contamination, which quickly increased upon beam exposure. Due to the contamination, EELS intensity was quite low. A small peak at 485 eV and a prominent shoulder just before the O edge (532.0 eV) could also be attributed to the presence of Sn.



**Figure S14.** EELS chemical composition maps obtained from the red square area of the STEM micrograph of another agglomerate from the hematite / titania 20% sample (right). Individual Fe (red), Ti (green) and O (blue) maps and their respective composites Fe-O, Ti-O and Fe-Ti are shown. The scale bar is the same for all composition maps. In all cases, the brighter the color is, the larger the amount of the element or composite.



**Figure S15.** EELS chemical composition maps obtained from the red square area of the STEM micrograph (left) of an agglomerate from the hematite / titania 20% sample. Individual Fe (red), Ti (green) and O (blue) maps and composites of Fe-O, Ti-O and Fe-Ti are shown. The scale bar is the same for all composition maps. In all cases, the brighter the color is, the larger the amount of the element or composite.