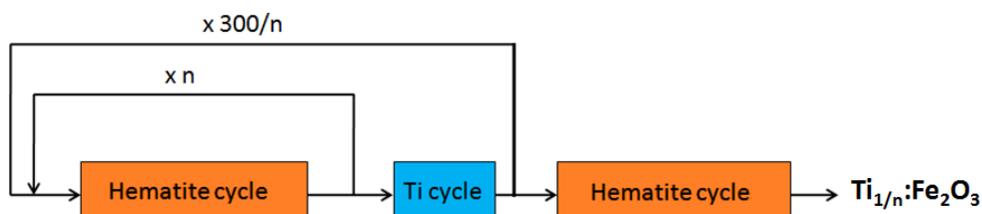


## Supplementary Information

### Highly Photoactive Ti-doped $\alpha$ - $\text{Fe}_2\text{O}_3$ Thin Film Electrodes; Resurrection of the Dead Layer

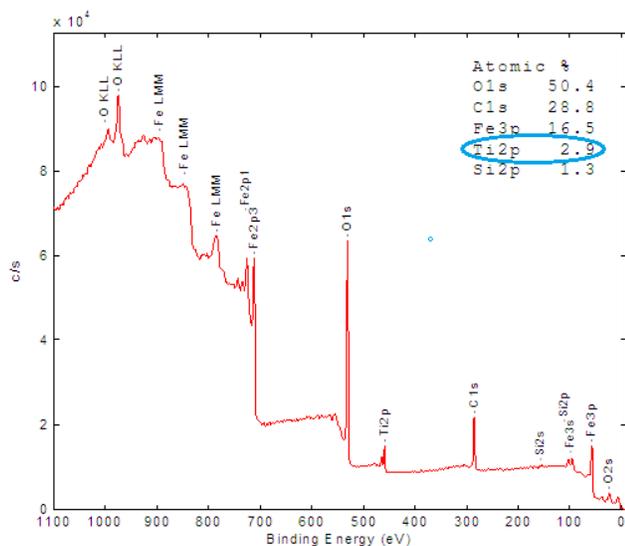
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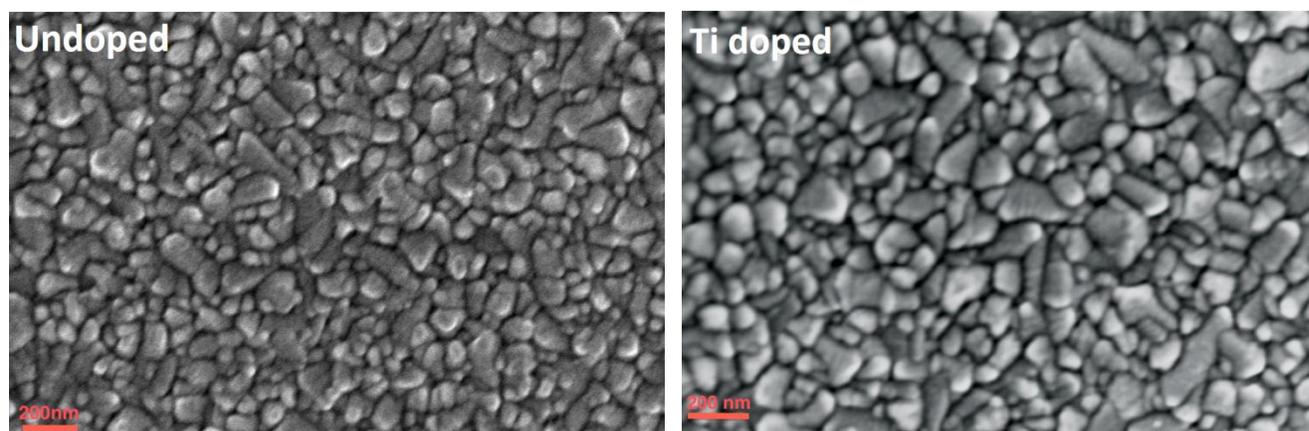


**Figure 1S.** Scheme of the ALD doping procedure employed. A Hematite cycle comprises a pulse of ferrocene followed by a pulsing sequence of water/ozone as an oxidant. A Ti cycle represents a titanium isopropoxide pulse followed by a pulse of water as an oxidant.

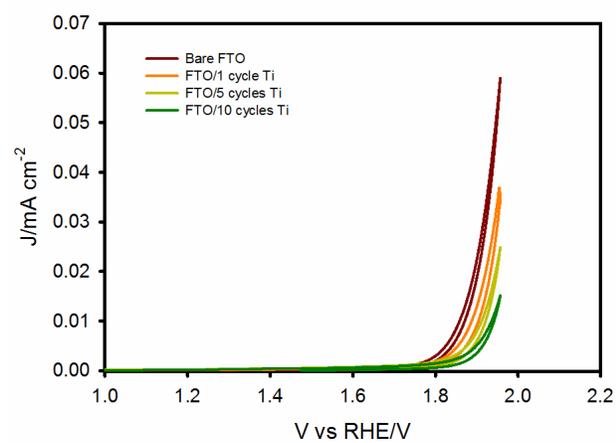
Depth(°A)	Atomic concentration (%)			
	O1s	Ti2p	Fe3p	Sn3d
0	72.3	4.1	23.7	0
13	66.2	3.5	30.2	0
26	64.3	3.3	32.4	0
38	63.5	3.2	33.3	0
51	62.5	3.1	34.3	0
64	61.7	3.2	35	0.1
81	61.2	3	35.5	0.3
98	60.9	2.8	35.5	0.8
115	60.2	2.7	35.5	1.9
132	59.2	2.6	34.1	4
149	58.6	2.4	32.2	6.8
166	58.5	2.2	29.2	10.1
183	58.6	1.9	26.2	13.3
200	58.2	1.6	24	16.3
217	57.8	1.4	22	18.9
234	58	1.2	19.7	21
251	58.2	1.1	17.7	23
268	57.9	1	16.2	24.8
285	57.9	0.9	14.8	26.4
302	57.9	0.8	13.2	28.1
319	57.7	0.7	11.9	29.8
336	57.5	0.6	10.7	31.3
353	57.8	0.5	9.4	32.4
370	58.2	0.4	8.1	33.2
387	58.3	0.4	6.9	34.4
421	58.3	0.3	5.7	35.7
455	57.7	0.3	4.6	37.4
489	57.4	0.3	3.6	38.8
523	57.6	0.2	2.8	39.4
557	57.6	0.1	2.1	40.2
591	57.4	0.1	1.5	41
625	57.2	0	1.2	41.6
659	57.1	0	0.5	42.4



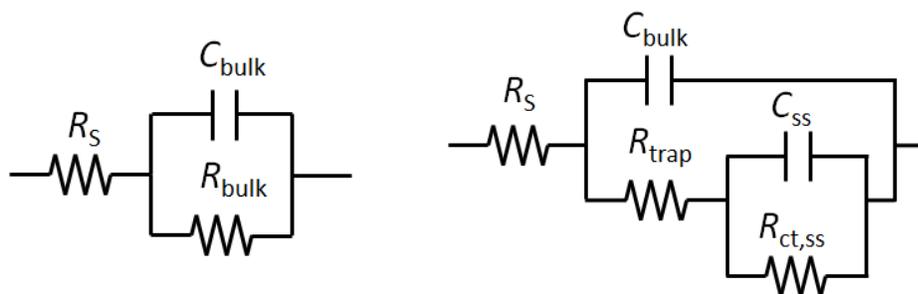
**Figure 2S.** Table of atomic concentration values of XPS depth profiling and a XPS surface survey spectrum of Ti doped hematite thin film.



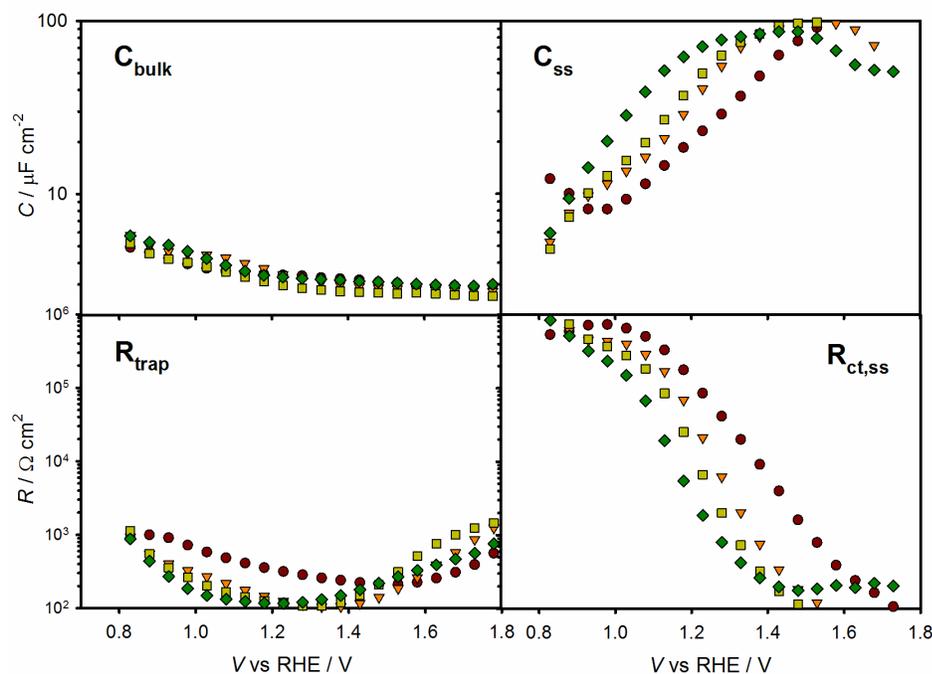
**Figure 3S.** The SEM images of undoped and Ti doped hematite films.



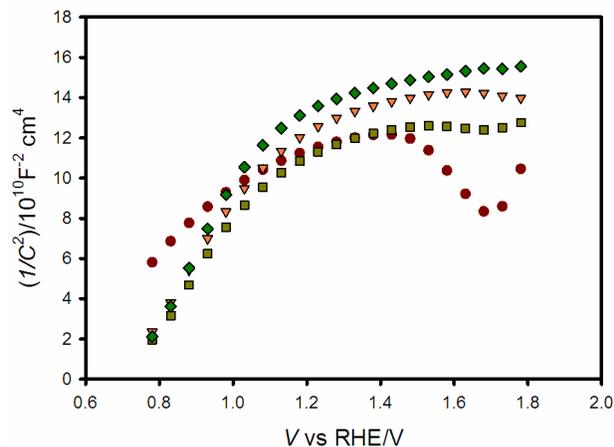
**Figure 4S.**  $J$ - $V$  curves of FTO electrode coated with different cycles of Ti.



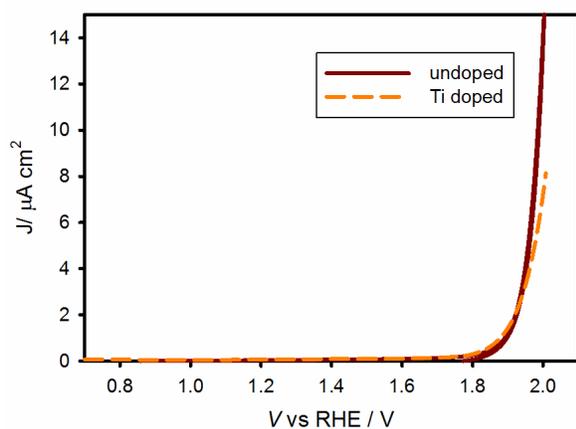
**Figure 5S.** Equivalent circuits used to fit the experimental IS data. The equivalent circuit elements include a space charge capacitance of the bulk hematite,  $C_{\text{bulk}}$ , surface state capacitance,  $C_{\text{ss}}$ , a resistance which represents the trapping of holes in the surface states,  $R_{\text{trap}}$ , and a charge transfer resistance from the surface states to solution,  $R_{\text{ct,ss}}$ .  $R_s$  represents total series resistances resulting from external circuit, solution etc.



**Figure 6S.** Impedance spectroscopy parameters calculated from fitting the experimental data to the equivalent circuits for 300 cycles thick electrodes, under water oxidation and 1 sun illumination with undoped hematite (red circles) of doped of 3.22 (orange triangles) 6.25 (yellow cubes) and 11.11 (green diamonds) c% Ti.



**Figure 7S.** Mott-Schottky plots of 300 cycles thick electrodes, in dark and under water oxidation for undoped hematite (red circles) and doped of 3.22 (yellow cubes) 6.25 (orange triangles) and 11.11 (green diamonds) c% Ti.



**Figure 8S.** Dark  $J$ - $V$  of doped (dashed orange) and undoped (solid red) electrodes produced the  $J$ - $V$ s shown in Figure 4a under illumination.