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Design aspects of all atomic layer deposited TiO_2-Fe_2O_3 scaffold-absorber photoanodes for water splitting

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Supporting Information

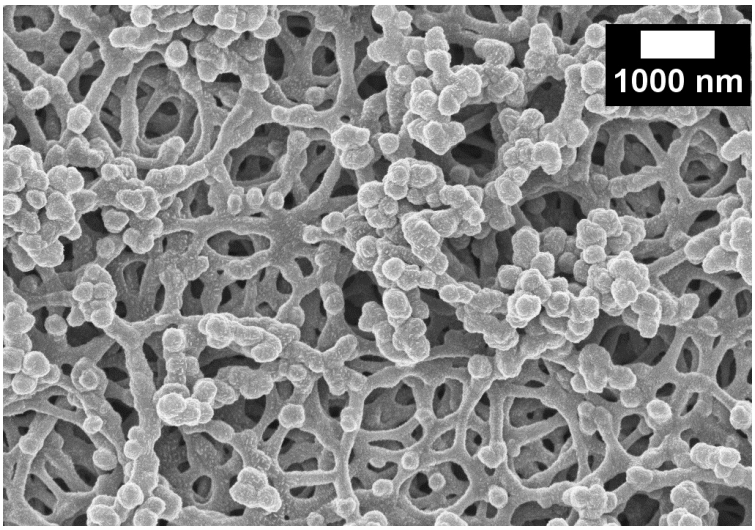
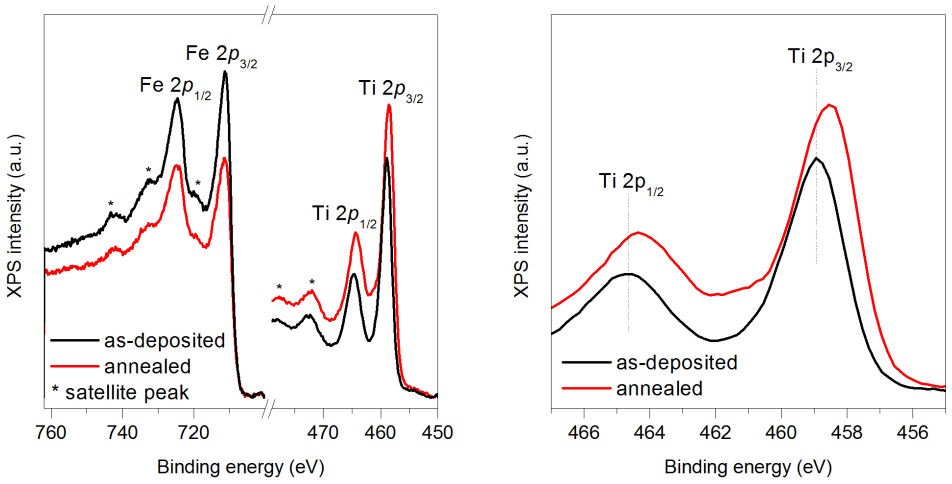


Figure S1: SEM image of a TiO_2 scaffold coated with 100 cycles of ALD-Fe_2O_3.



(a) (b)

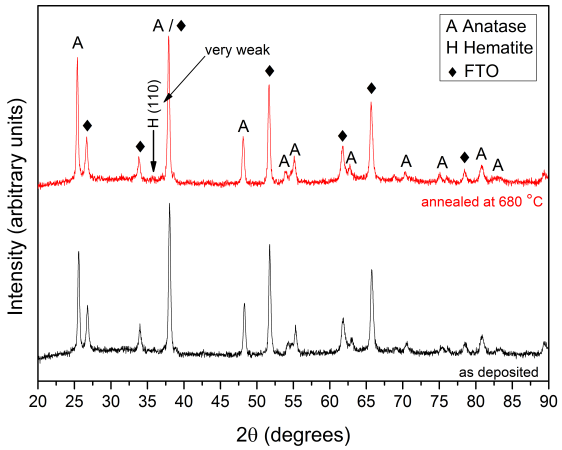
Figure S2: a) XPS spectra of Fe 2p and Ti 2p energy regions for TiO_2 scaffold sensitized with 100 cycles of ALD-Fe_2O_3 before and after annealing. The peak at 719.5 eV corresponds to $Fe^{3+}2p_{3/2}$ satellite. b) Zoomed-in view of the Ti 2p energy region to show the Ti peak shift to lower BE. Linear background was subtracted from the spectra.

Table S1: Concentrations and core level binding energies of all the detected elements for the TiO_2 scaffold coated with 100 cycles of Fe_2O_3. The BE scale was calibrated according to the C 1s C-C/H component at 285.0 eV.

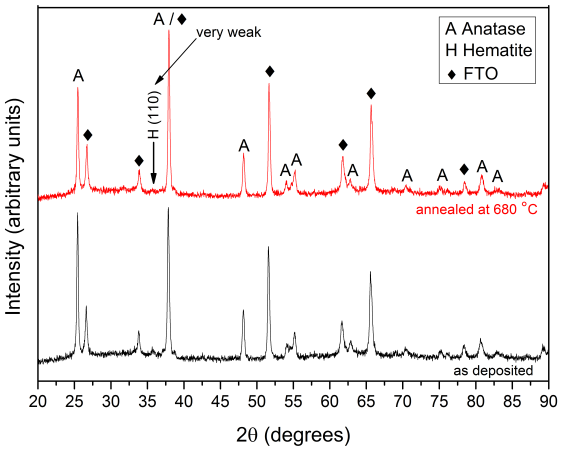
Sample	Concentration, at. % (XPS peak position, eV)									
	Fe $2p_{3/2}$	Ti $2p_{3/2}$	O 1s	C 1s	N 1s	Ca $2p_{3/2}$	Na 1s	Mg 1s	Si 2s	Al 2p
as-deposited	9.70	11.23	62.05	12.30	0.25	0.40	0.47	0.10	1.48	2.03
	(710.62)	(458.84)	(530.07)	(285)	(399.66)	(347.8)	(347.8)	(1303.72)	(152.96)	(73.63)
annealed	6.25	12.66	65.08	10.05	0.27	0.32	2.53	0.07	1.36	1.40
	(710.53)	(458.43)	(529.78)	(285)	(400.18)	(347.23)	(347.23)	(1304.45)	(153.11)	(73.66)

Table S2: Lifetimes with error limits obtained from the global 3 exponential fitting

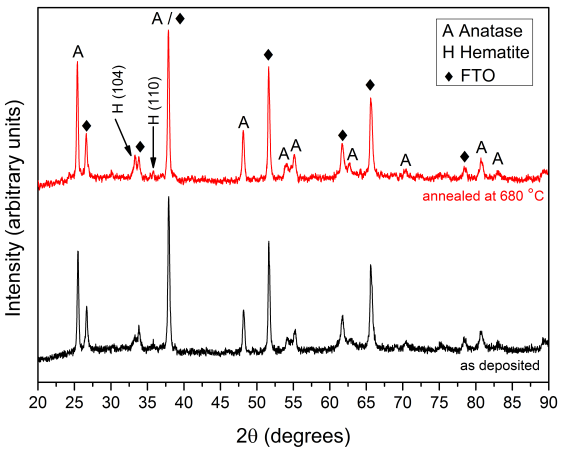
Sample	τ_1 (ps)	τ_2 (ps)	τ_3 (ps)
TiO_2|FTO	0.50 ± 0.07	90 ± 20	4000 ± 1100
Fe_2O_3|FTO	0.29 ± 0.01	17 ± 6	320 ± 90
Fe_2O_3|TiO_2|FTO	0.26 ± 0.04	4.7 ± 0.9	320 ± 80



(a) 100 cycles



(b) 200 cycles



(c) 400 cycles

Figure S3: XRD diffractograms before and after annealing.

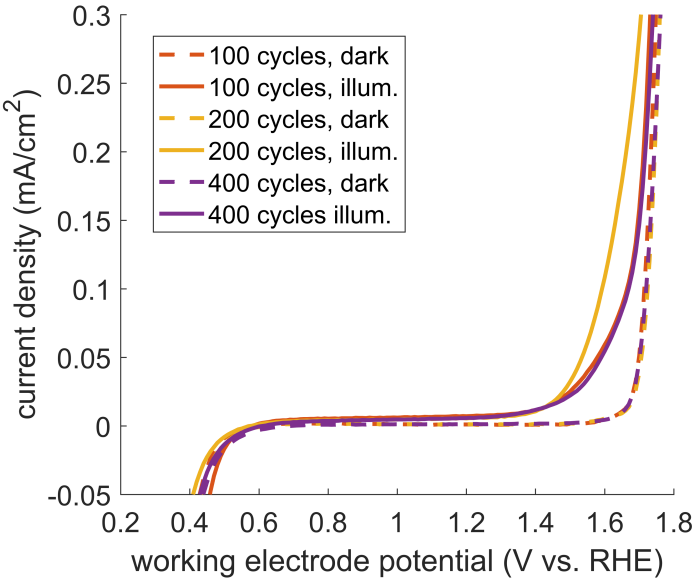
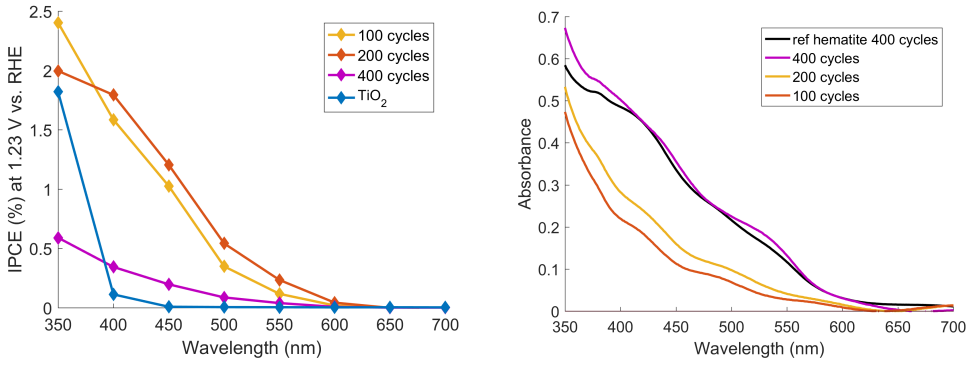


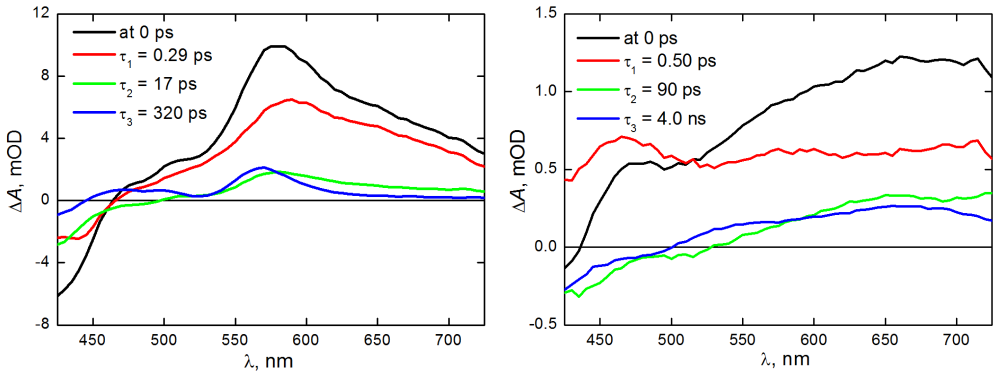
Figure S4: IV-curves of the samples in as-deposited condition.



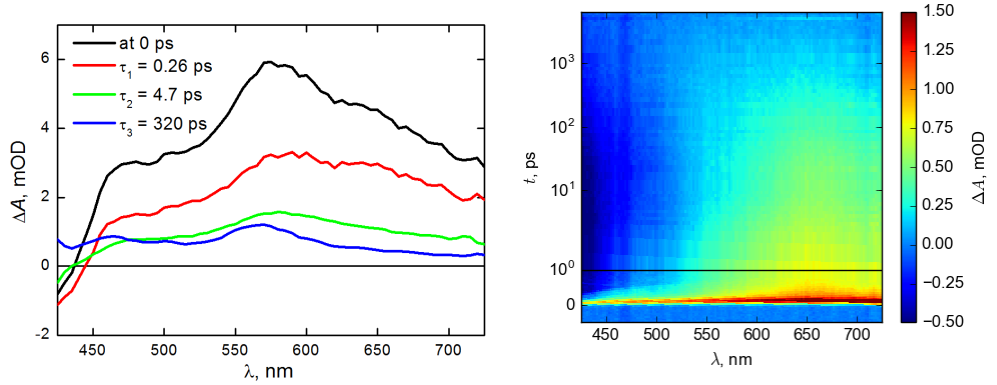
(a) IPCE

(b) Absorbance

Figure S5: (a) IPCE of the porous structures and (b) UV-Vis absorption of annealed planar thin films where 100, 200 or 400 cycles of ALD-Fe_2O_3 were deposited on a 30 nm ALD-TiO_2|FTO|glass substrate.



(a) Fe_2O_3|FTO (b) TiO_2|FTO



(c) Fe_2O_3|TiO_2|FTO (d) TiO_2 excited at 355 nm

Figure S6: a,b,c) Decay component spectra obtained from global three exponential fitting of the measured transient absorption spectra. The decays were fit with $f(t) = a+b\cdot\exp(-t/\tau_1)+c\cdot\exp(-t/\tau_2)+d\cdot\exp(-t/\tau_3)$. The individual lines represent the amplitudes of the specific exponential components at different wavelengths. d) Transient absorption spectrum for TiO_2.