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Electronic Supplementary Information

Onset potential behavior in α-Fe_2O_3 photoanodes: The influence of surface and diffusion Sn doping on the surface states

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Table S1. The absolute and relative intensities for (104) and (110) reflections of pristine and Sn-doped Fe_2O_3 photoanodes fabricated by different annealing temperatures and methods

Samples/ Lattice Parameters	Fe_2O_3					
	[104]			[110]		
	2θ (°)	Abs. Int.	I/I_o (%)	2θ (°)	Abs. Int.	I/I_o (%)
LT500	33.177	13518	19.1	35.653	10778	15.2
LT550-Sn10	33.168	5870	9.8	35.631	5108	8.5
STP800	33.191	9491	21.9	35.629	10983	25.3
STP800-Sn1	33.182	10972	23.5	35.622	12611	27.0
D800	33.180	11074	25.6	35.619	10169	23.7
D800-Sn1	33.163	13797	20.0	35.614	10091	14.6
D800-Sn10	33.148	14124	24.8	35.611	4307	20.4
D825	33.167	12855	21.3	35.610	10577	6.5

Table S2. Average lattice parameters of Fe_2O_3 and SnO_2 in pristine and Sn-doped Fe_2O_3 photoanodes fabricated by different annealing temperatures and methods (Parameters were obtained after structural refinrement of XRD patterns)

Samples/ Lattice Parameters	Fe_2O_3				SnO_2			
	a=b (Å)	*c* (Å)	*c/a* ratio	*Vol.* (Å^3)	*a=b* (Å)	*c* (Å)	*c/a* ratio	*Vol.* (Å^3)
Standard	5.039	13.770	2.733	302.2	4.755	3.199	0.673	72.34
LT500	5.044	13.715	2.719	302.5	4.762	3.207	0.673	72.73
LT550-Sn10	5.044	13.677	2.712	301.3	4.765	3.211	0.674	72.89
STP800	5.049	13.628	2.704	300.9	4.767	3.200	0.671	72.76
STP800-Sn1	5.051	13.627	2.698	301.0	4.768	3.200	0.671	72.77
D800	5.039	13.730	2.724	301.9	4.768	3.200	0.671	72.77
D800-Sn1	5.041	13.735	2.725	302.2	4.765	3.212	0.674	72.93
D800-Sn10	5.041	13.742	2.726	302.4	4.769	3.212	0.674	73.04
D825	5.051	13.641	2.700	301.4	4.765	3.211	0.673	73.02

Table S3. Structural parameters calculated from Fe K-edge EXAFS fits for untreated and Sn-treated α-Fe_2O_3 photoanodes fabricated at low annealing temperature of 550 °C

	R_1 (Å)[a]	R_2 (Å)[b]	σ^2 (Å^2)[c]	R-factor[d]
LT550	1.93	2.10	0.0037(13)	0.0181
LT550-Sn10	1.97	2.14	0.0040(14)	0.0044
Ref α-Fe_2O_3	1.96	2.13	0.0086(16)	0.0074

[a,b]Fe-O bond distance (uncertainty <0.01), [c]Debye-Waller factor, [d]a sum-of-squares, measure of the fractional misfit

The number in parenthesis for *c* denotes an uncertainty of the calculated parameter at the last digit place.

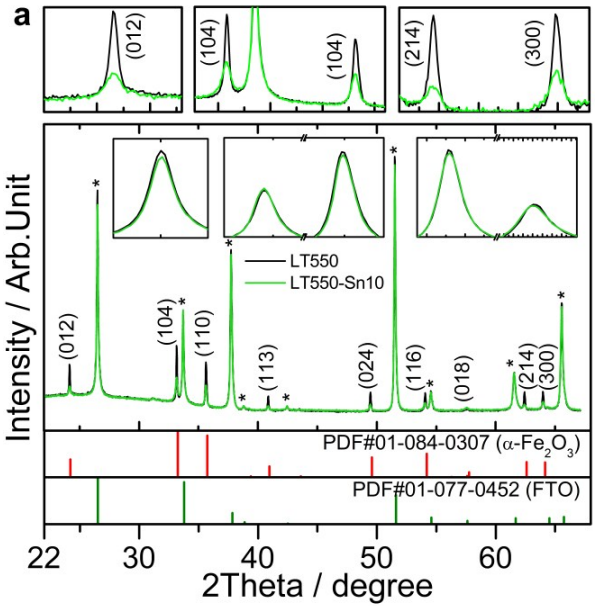

Figure S1a. XRD patterns of pristine and 10 mM Sn-doped α-Fe_2O_3 photoanodes fabricated at low annealing temperature (Note: Plots at the top and insets of graph show the magnified views of major peaks for hematite and substrate, respectively).

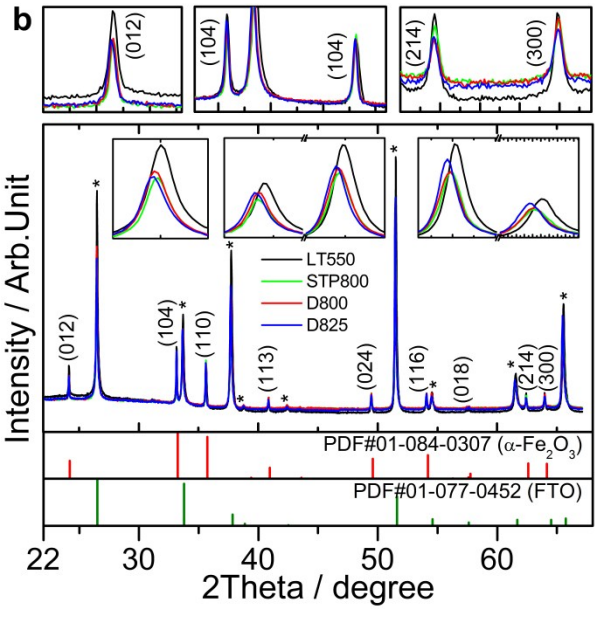

Figure S1b. XRD patterns of α-Fe_2O_3 photoanodes fabricated under different temperature conditions: LT550, STP800, D800, and D825. (Note: Plots at the top and insets of graph show the magnified views of major peaks for hematite and substrate, respectively).

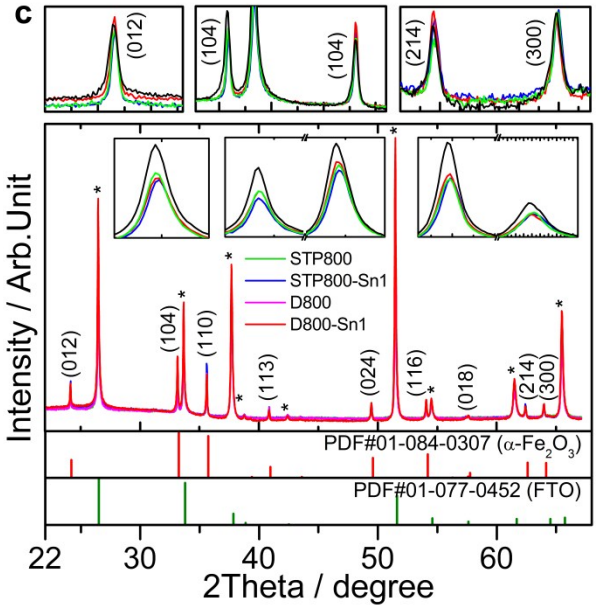

Figure S1c. XRD patterns of pristine and 1mM Sn-doped α-Fe_2O_3 photoanodes fabricated at high annealing temperature by two-step and one-step method. (Note: Plots at the top and insets of graph show the magnified views of major peaks for hematite and substrate, respectively).

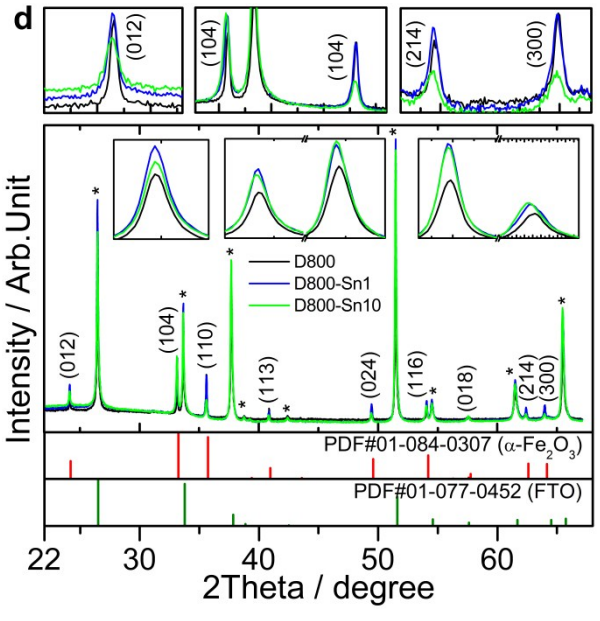

Figure S1d. XRD patterns of pristine and Sn-doped α-Fe_2O_3 photoanodes fabricated by one-step annealing at high temperature, with Sn concentrations of 1 and 10 mM. (Note: Plots at the top and insets of graph show the magnified views of major peaks for hematite and substrate, respectively).

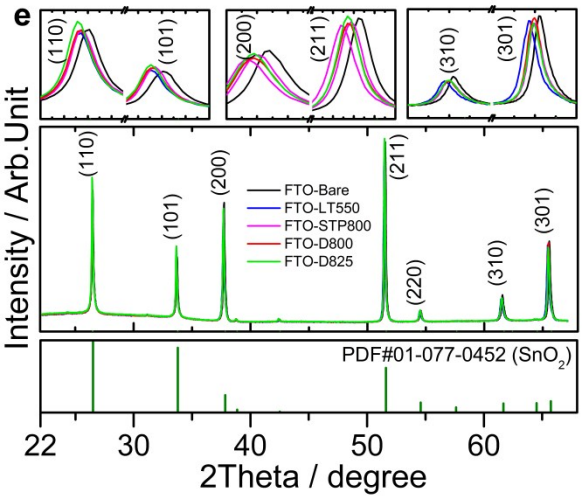

Figure S1e. XRD patterns of bare and annealed FTO electrodes fabricated by different annealing conditions. Enlarged portion of six major diffraction peaks of corresponding FTO electrodes are shown on top. (Note: Plots at the top of the graph shows the magnified views of major peaks for FTO substrate, respectively).

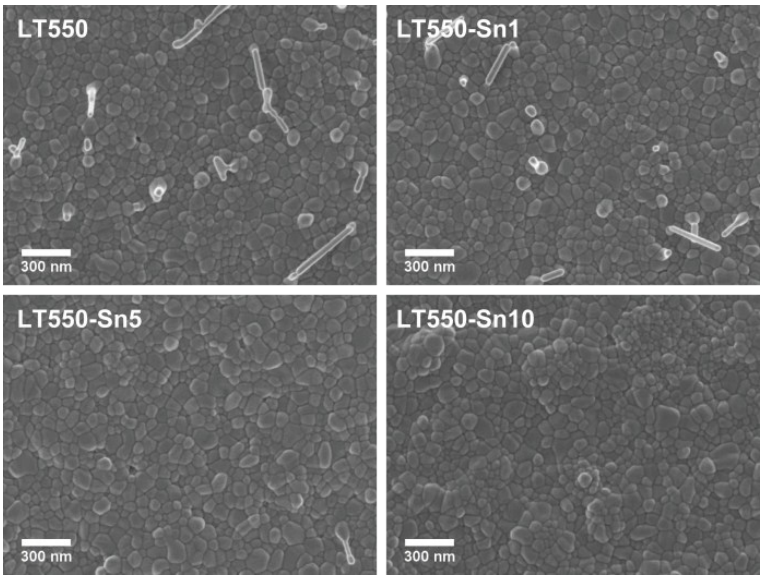

Figure S2a. Surface morphologies of pristine (untreated) and Sn-doped α-Fe_2O_3 photoanodes fabricated by LT-annealing at 550 °C: LT550, LT550-Sn1, LT550-Sn5 and LT550-Sn10.

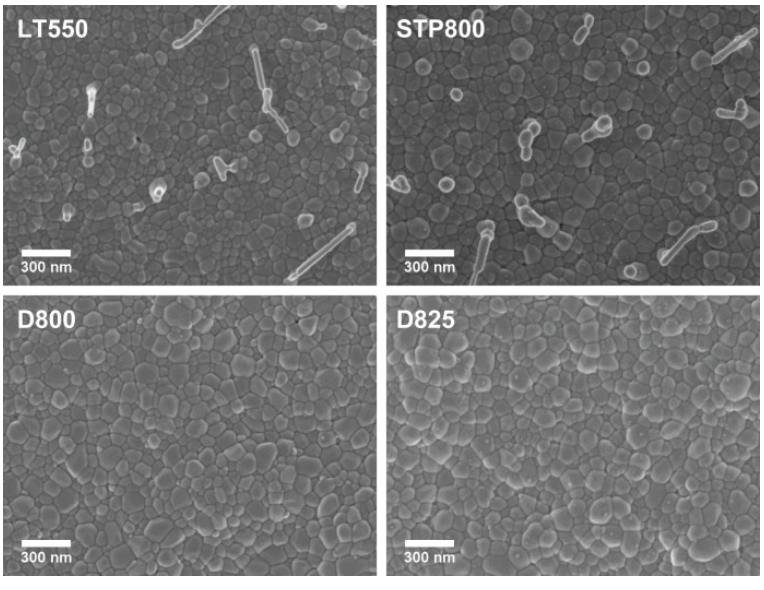

Figure S2b. Surface morphologies of pristine (untreated) α-Fe_2O_3 photoanodes fabricated with different annealing conditions: LT550, STP800, D800 and D825.

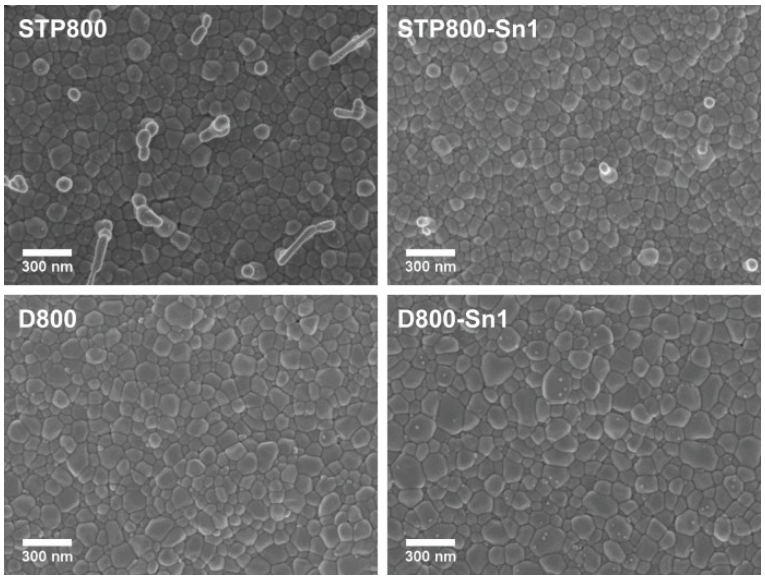

Figure S2c. Surface morphologies of pristine (untreated) and 1 mM Sn-doped α-Fe_2O_3 photoanodes fabricated at high temperature by two-step and one-step annealing methods: STP800, STP800-Sn1, D800, and D800-Sn1.

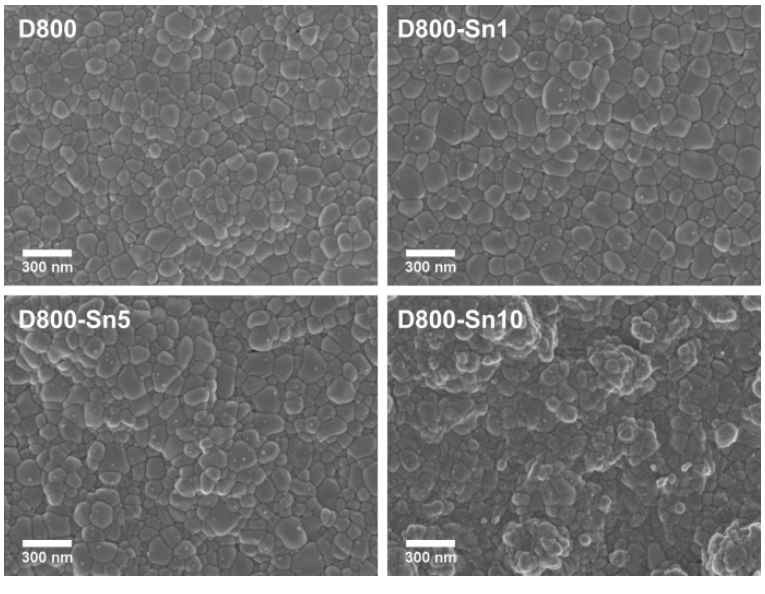

Figure S2d. Surface morphologies of pristine (untreated) and Sn-doped α-Fe_2O_3 photoanodes fabricated by one-step HT-annealing at 800 °C: D800, D800-Sn1, D800-Sn5, and D800-Sn10.

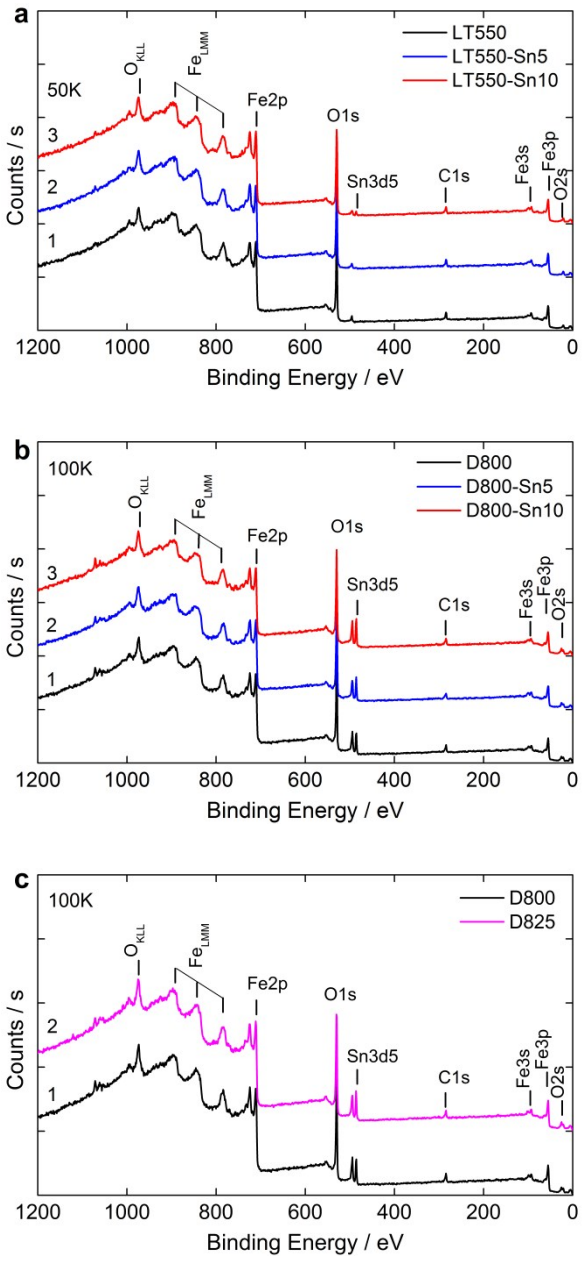

Figure S3. Survey XPS spectra of pristine (untreated) and Sn-doped α-Fe_2O_3 photoanodes fabricated by (a) LT-annealing (550°C for 4h) and (b) one-step HT-annealing (800 °C for 13.5 min) with Sn^{4+} concentrations of (1) 0 mM, (2) 5 mM, and (3) 10 mM; (c) Survey XPS spectra of un-treated α-Fe_2O_3 photoanodes fabricated by one-step HT-annealing at (1) 800 °C and (2) 825 °C for 13.5 min.

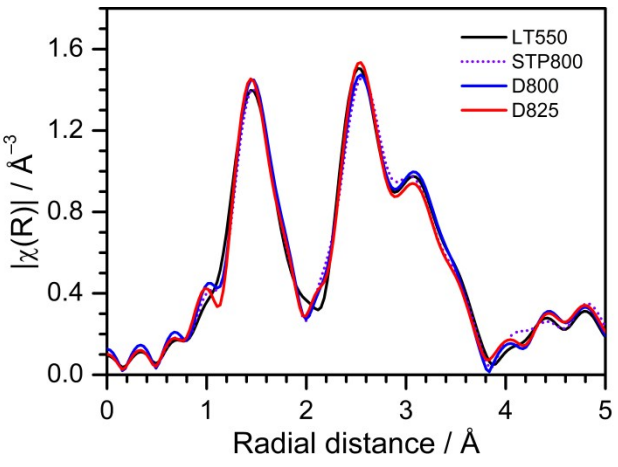

Figure S4. k^2-weighted Fourier transforms of EXAFS functions for Fe K-edges of α-Fe_2O_3 photoanodes fabricated by different annealing temperatures (550, 800 and 825 °C) and different methods (STP800 and D800/D825).

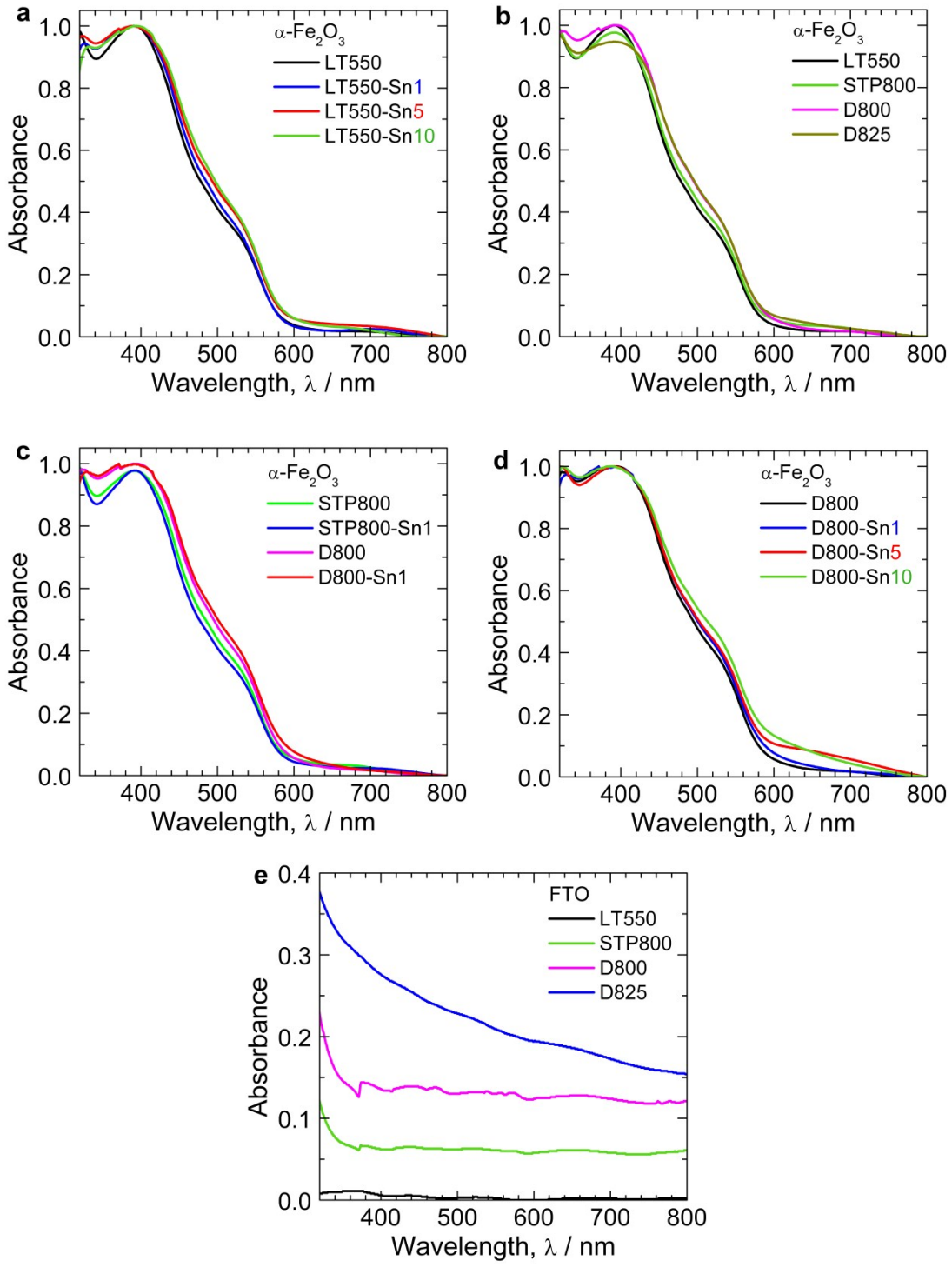

Figure S5. Normalized UV-Vis absorbance spectra of (a) pristine and Sn-doped α-Fe_2O_3 prepared by LT-annealing; (b) pristine α-Fe_2O_3 fabricated by different annealing methods; (c) pristine and 1 mM Sn-doped α-Fe_2O_3 fabricated by two-step and one-step HT-annealing, and (d) pristine and Sn-doped α-Fe_2O_3 photoanodes fabricated by one-step HT-annealing. (e) The absolute absorbance behavior of FTO substrates fabricated by different annealing methods.

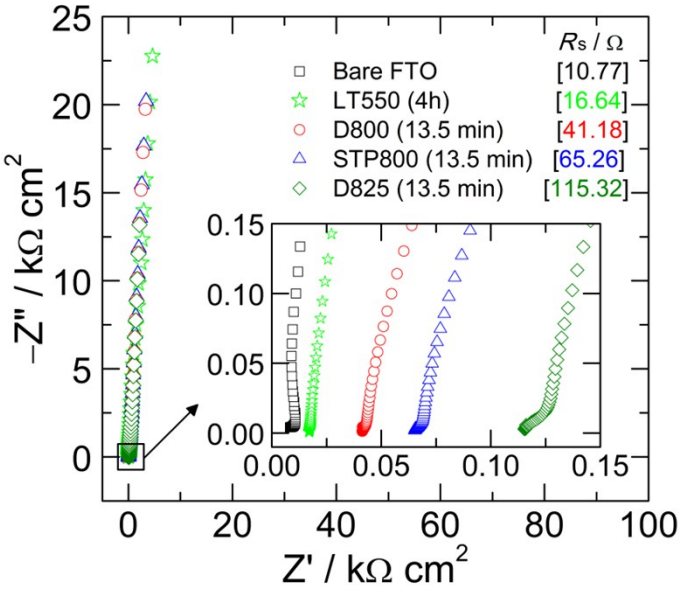

Figure S6. Nyquist plots of FTO electrodes fabricated with different annealing conditions, recorded at a bias of 1.23 V_{RHE} under 1 sun illumination in 1 M NaOH.