Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

for

Impact of improvements in mesoporous titania layers on ultrafast electron transfer dynamics in perovskite and dye-sensitized solar cells

Katarzyna Pydzińska-Białek,[a] Adam Glinka,[a] Viktoriia Drushliak,[a] Grzegorz Nowaczyk,[b] Patryk Florczak [b] and Marcin Ziółek [a] *

[a] *Faculty of Physics, Adam Mickiewicz University, Uniwersytetu Poznańskiego 2, 61-614 Poznań, Poland*

[b] *NanoBioMedical Centre, Adam Mickiewicz University, Wszechnicy Piastowskiej 3, 61-614 Poznań, Poland*

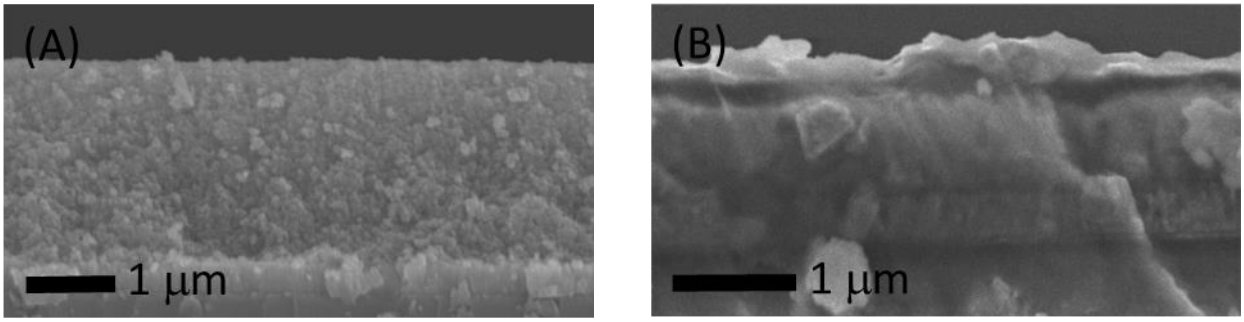

Figure S1. SEM cross sections of **SP30** titania layer (A) and PSC made using **SC18dil** layer (B).

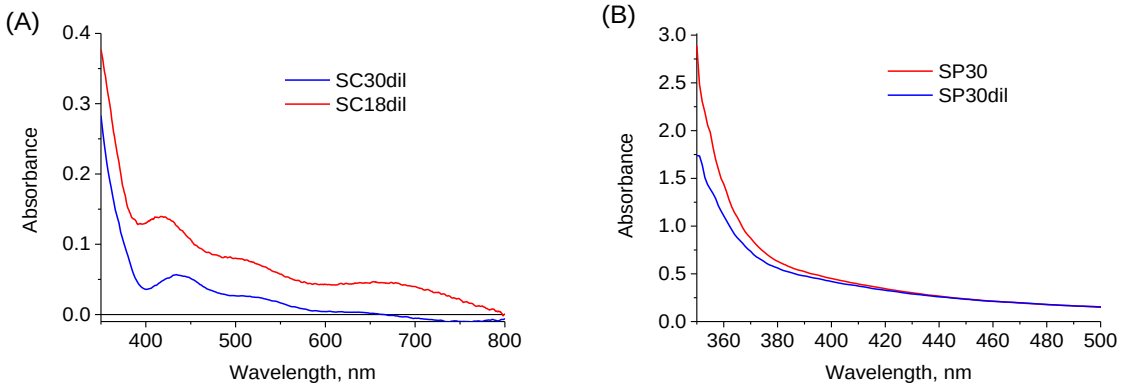

Figure S2. Stationary absorption of the electrodes with titania layers: **SC30dil** and **SC18dil** (A), **SP30dil** and **SP30** (B).

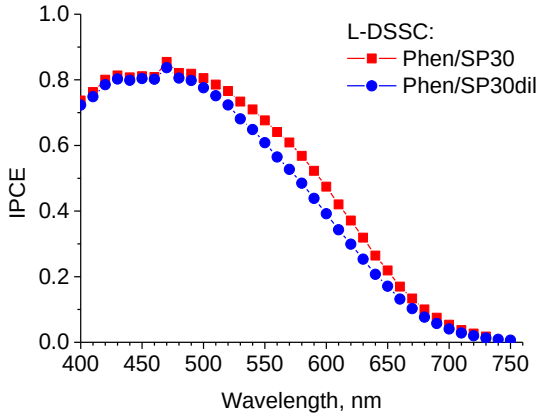

Figure S3. IPCE spectra of L-DSSC with **SP30dil** and **SP30** layers.

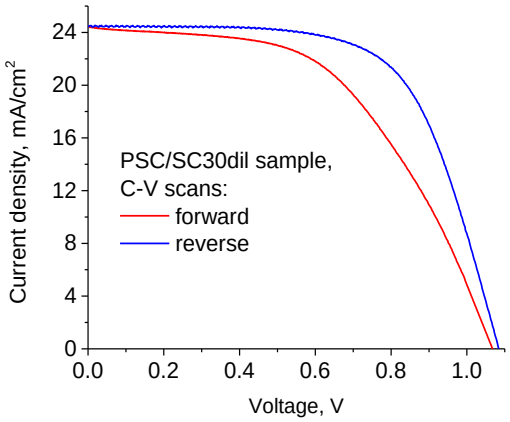

Figure S4. Example of current-voltage curves of PSC made using **SC30dil** layer measured at forward and backward directions (scanning rate 50mV/s). Hysteresis index *HI* obtained from the graph ($HI = \frac{J_{rev}\left(\frac{V_{oc}}{2}\right) - J_{for}\left(\frac{V_{oc}}{2}\right)}{J_{rev}\left(\frac{V_{oc}}{2}\right)}$) is equal to 0.05.

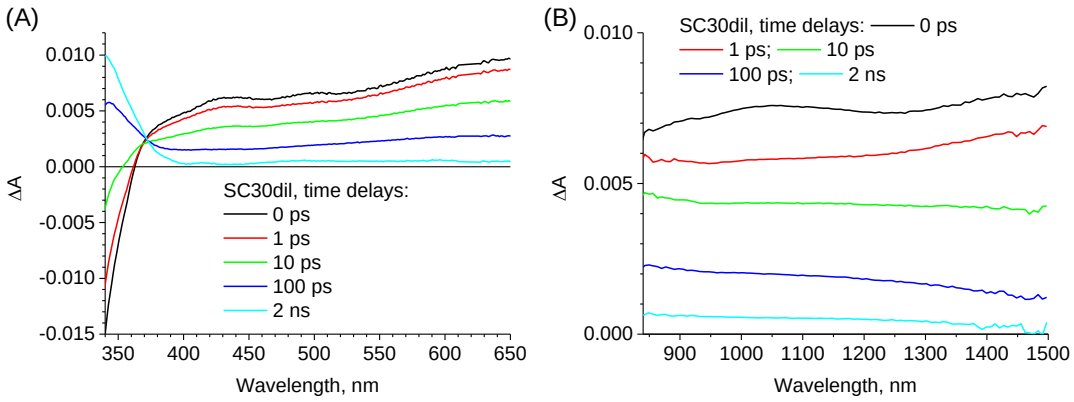

Figure S5. Transient absorption spectra at selected time delays between pump and probe pulses for electrode with SC30dil layer: in UV- VIS range excited at 310 nm with 4 mJ/cm^2 (A) and in NIR range excited at 355 nm with 4 mJ/cm^2 (B).

Mixed first and second order function:

The change of the population of the excited carriers (n) over time (t) in the semiconductor can be described by:

$$-\frac{dn}{dt} = k_1 n + k_2 n^2$$

The first order decay with the rate constant k_1 is related to the trap-assisted recombination (Shockley-Read-Hall recombination). The second order process described by the rate constant k_2 is due to free carrier recombination (band-to-band radiative recombination). Solution of the above equation can be given by the following analytical function, which is the mixed first and second order decay function:

$$n(t) = \frac{n_0 k_1}{k_1 \exp(k_1 t) + n_0 k_2 (\exp(k_1 t) - 1)},$$

where n_0 is initial number of excited carriers.

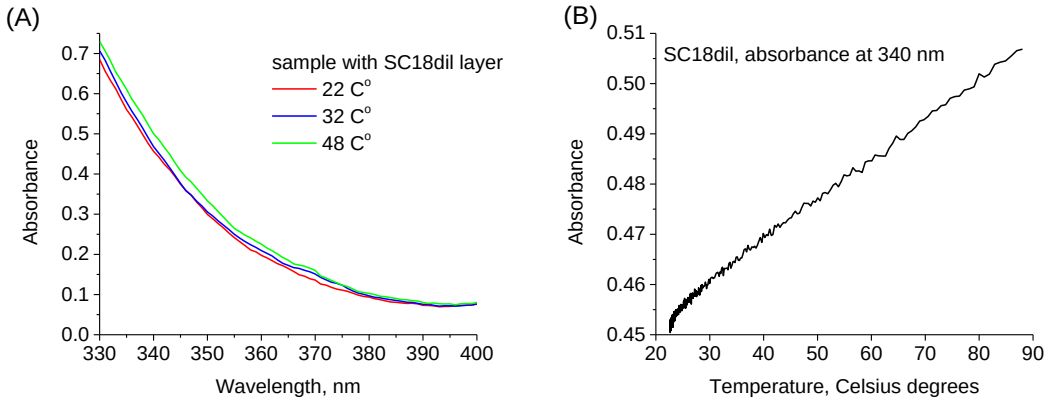

Figure S6. Temperature dependence of the stationary absorption of the electrodes with titania.

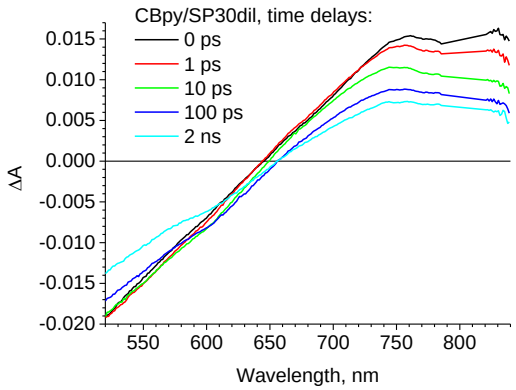

Figure S7. Transient absorption spectra at selected time delays between pump and probe pulses for **CBpy/SP30dil** liquid DSSC sample. The excitation wavelength was 500 nm with 100 μJ/cm^2 fluence.

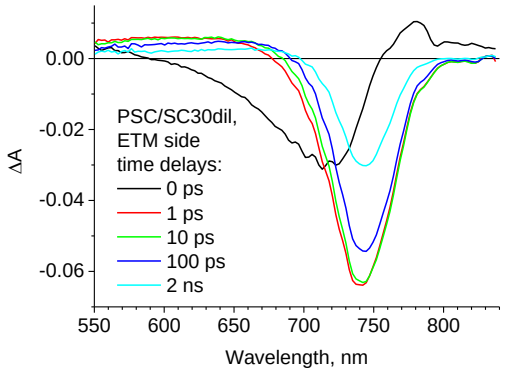

Figure S8. Transient absorption spectra at selected time delays between pump and probe pulses for **PSC/SC30dil** sample pumped from ETM side. The excitation wavelength was 500 nm with 30 μJ/cm^2 fluence.

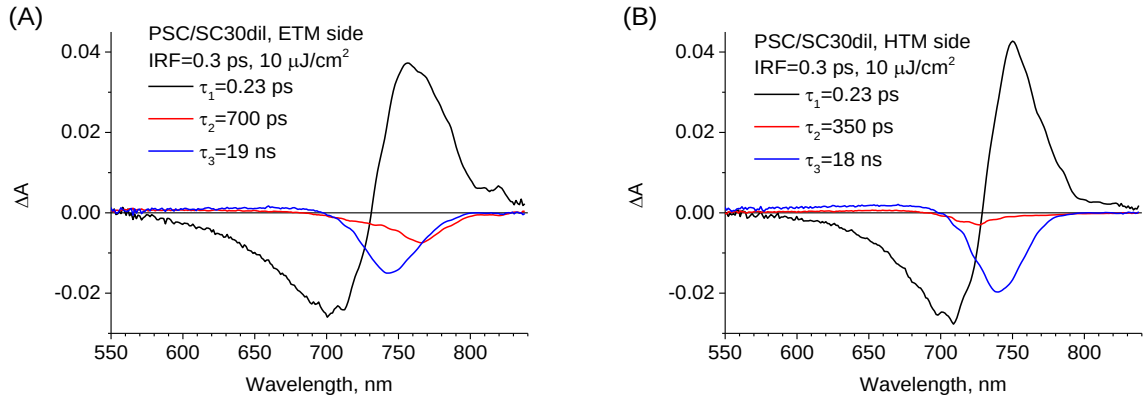

Figure S9. The results of global analysis of transient absorption data using three-exponential function for PSC samples. The graphs present pre-exponential factor spectra associated to the indicated time constants. The pump fluence was 10 μJ/cm^2 and IRF was 0.3 ps.

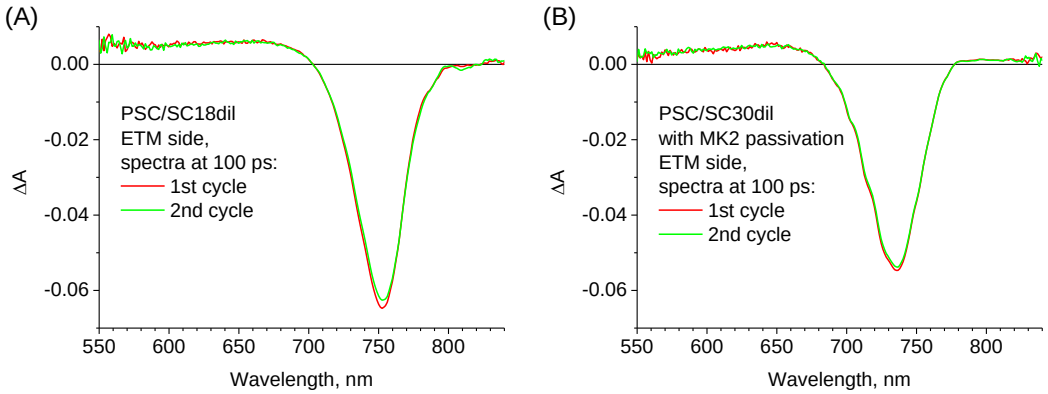

Figure S10. Transient absorption spectra for PSC with **SC18dil** layer (A) and with **SC30dil** layer passivated with MK2 dyes (B), both measured at 100 ps for different consecutive cycles at ETM side. The pump fluence was 30 μJ/cm^2.

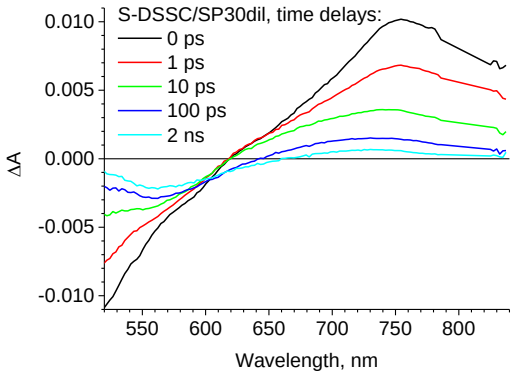

Figure S11. Transient absorption spectra at selected time delays between pump and probe pulses for S- DSSC cell with **SP30dil** layer pumped from HTM side.
The excitation wavelength was 500 nm at 100 μJ/cm^2 fluence.

Table S1. Parameters of the different mesoporous titania layers:

Abbre-viation	**Deposition method**	**Particle size [nm]**	**Preparation**	**Resulted layer thickness [nm]**
SC18dil	**S**pin-**C**oating	**18**	Dyenamo DN-GPS-18TS paste **dil**uted 1:6 in ethanol	300-350
SC30dil	**S**pin-**C**oating	**30**	GreatCell Solar 30NR-D paste **dil**uted 1:6 in ethanol	150-200
SP30	**S**creen-**P**rinting	**30**	Dyenamo DN-GPS-30TS paste without any dilution	2500-3000
SP30dil	**S**creen-**P**rinting	**30**	Dyenamo DN-GPS-30TS paste **dil**uted 2:1 in (cellulose + ethanol + alpha-terpineol)	1300-1500

Table S2. Averaged photovoltaic parameters and their errors (standard deviation) of the different cells:

Sample	V_{OC} **[V]**	J_{SC} **[mA/cm^2]**	***FF***	***PCE*** **[%]**
L-DSSC/Phen/SP30	0.85 ± 0.01	7.79 ± 0.25	0.66 ± 0.03	4.32 ± 0.02
L-DSSC/Phen/SP30dil	0.88 ± 0.01	7.43 ± 0.10	0.69 ± 0.01	4.43 ± 0.02
PSC/SC30dil	1.08 ± 0.01	22.5 ± 2.1	0.63 ± 0.04	15.2 ± 2.3
S-DSSC/SC30dil	0.72 ± 0.01	0.95 ± 0.04	0.57 ± 0.01	0.39 ± 0.02
S-DSSC/SP30dil	0.45 ± 0.13	3.52 ± 0.32	0.35 ± 0.07	0.57 ± 0.23
S-DSSC/SP30	0.44 ± 0.03	2.67 ± 0.88	0.35 ± 0.03	0.41 ± 0.12

Table S3. Effects of spattered gold thickness and smaller or bigger active surface on the photovoltaic parameters of the cells:

Sample	Thickness [nm]	Surface [cm^2]	V_{OC} [V]	J_{SC} [mA/cm^2]	*FF*	*PCE* [%]	*Total APCE*
PSC/SC30dil	50-100	0.05	1.09	24.5	0.64	17.1	1.17
PSC/SC30dil	25-50	0.05	1.07	24.4	0.68	17.8	1.17
PSC/SC30dil	50-100	0.125	0.98	15.5	0.56	8.5	0.74
PSC/SC30dil	25-50	0.125	1.02	16.8	0.66	11.3	0.81
S-DSSC/SP30dil	50-100	0.05	0.32	3.83	0.28	0.34	0.59
S-DSSC/SP30dil	25-50	0.05	0.58	3.20	0.42	0.79	0.49

Effect of gold sputtering method

As reported, sputtering method may introduce additional series resistance between spiro-OMeTAD and Au or cause partial damage to the organic HTM, which results in lowering *FF* and, for very high resistance, even the photocurrent. To confirm this possibility we prepared the test PSCs with gold electrodes of larger surface (resulting in the active surface increase from 0.05 cm^2 to 0.125 cm^2) and also we checked the effect of thinner gold layer (25-50 nm instead of 50-100 nm). As can be seen in Table S2, indeed the larger active surface decreases *FF*, while the shorter deposition increases *FF*.

Table S4. Average decrease of the amplitude for consecutive scans during transient absorption measurements of S-DSSC:

Sample and excitation side	Difference in the amplitude
SC30dil HTM side	-1%
SP30dil ETM side	+1.5%
SP30dil HTM side	-5%
SP30 ETM side	**-12.5%**
SP30 HTM side	-2.5%