Supporting Information

Extending charge separation lifetime and distance in dye-sensitized SnO_2-TiO_2 µm-thin films.

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1. Experimental procedures.

Thin-film preparation. Semitransparent mesoporous nanocrystalline SnO_2-TiO_2 films were prepared as follows. A colloidal SnO_2 paste was prepared using a procedure reported in the literature.[1] In short, 1 mL acetic acid was added dropwise to 30 mL of 15% wt SnO_2 colloidal dispersion in water (Alfa Aesar). The solution was stirred overnight before undergoing hydrothermal treatment for 60 h at 240 °C in a hydrothermal synthesis reactor. The resulting solution was cooled down to room temperature and sonicated before adding 2.5 wt % of both polyethylene oxide (mol wt 100,000) and polyethylene glycol (mol wt 12,000), the solution was stirred for 12 h to obtain a homogeneous paste. A first SnO_2 layer was deposited on FTO-coated glass (Pilkington, TEC-15) substrates using the doctor-blading method. The films were heated to 250 °C for 15 min prior to TiO_2 deposition.

TiO_2 layers were screen printed on top of the SnO_2 layers using a commercial TiO_2 nanoparticle paste (Dyesol 18NR-T). The screen print mesh design is depicted in Fig. S2. After paste deposition, the samples were progressively heated to 450 °C in air flow for 30 minutes.

SEM. Scanning electron microscopy images were obtained using an Ultra 55 FEG SEM instrument. **Fig. S1** shows SEM images of SnO_2 and TiO_2 nanoparticles on patterned thin films.

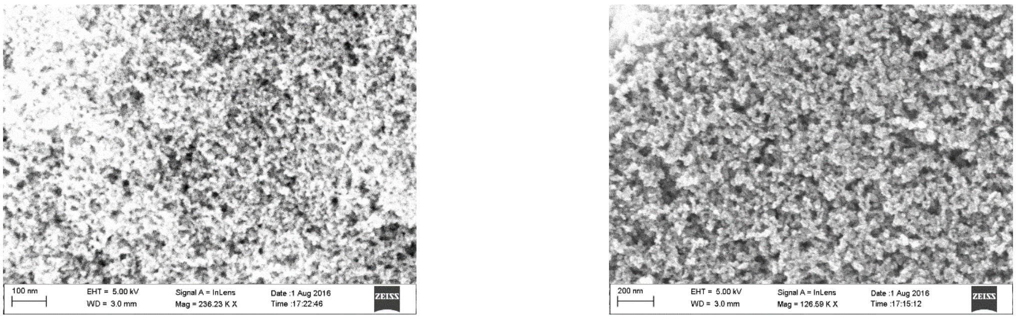

Fig. S1 SEM images of SnO_2 nanoparticles (left) and TiO_2 nanoparticles (right) in a patterned film.

Dye sensitization. Solutions of 0.3 mM D35 in ethanol and 0.3 mM CoPPIX in DMSO were used for film sensitization. Type- I films (homogeneously sensitized), where obtained by dipping the film into the dye bath. Type -II films where obtain by injection of the dye solution through the polydimethylsiloxane (PDMS) microfluidic chip which was manually placed on the patterned substrates. A peristaltic pump was used help the flow of the liquid through the channels. The chip was designed to have 5 parallel channels matching the dimensions of the screen print mesh pattern, Fig. S2. The PDMS chip was fabricated by casting a mixture of platinum based curing agent (H_2PtCl_6) and PDMS base solution (1:10) onto a silicon wafer master. After curing the mixture in an oven at 90 C for 1 hour, a thick PDMS sheet (~3mm) can be peeled off.

For the proof-of-principle experiments, the films were first sensitized with the dye D35 as in Type-II samples. After, a new PDMS microfluidic chip was placed on top of the film ensuring that the channels were positioned at the dye-free areas. Then, the CoPPIX solution was injected through the channels with a syringe and left over night before removing the chip and rinsing with ethanol.

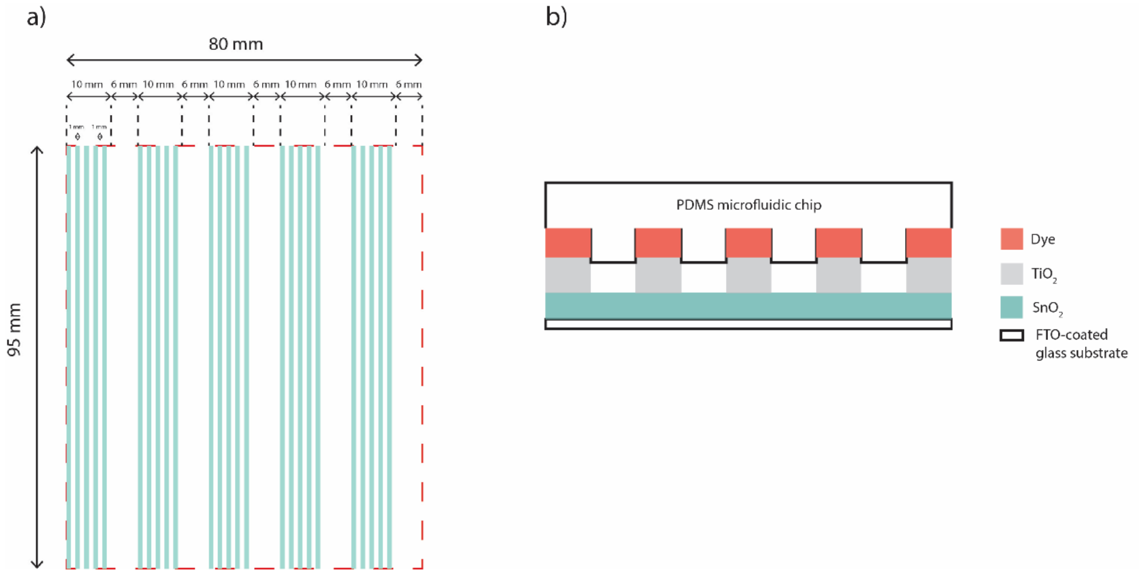

Fig. S2 a) Screen print mesh design. b) Side view of patterned SnO_2-TiO_2 thin films with the PDMS microfluidic chip on top, the dye flows through the microchannels positioned on top of the SnO_2-TiO_2 areas.

Fabrication of the silicon master. A 4” silicon wafer was treated with 50 W oxygen plasma (Batchtop, Plasma-Therm) for one minute. The surface was silanized by spin coating 1:4 mixture of Hexamethyldisilazane and Poly(ethylene glycol) methacrylate at 4000 rpm for 30 seconds to improve the adhesion of the photoresist to the substrate. SU8 3035 (MicroChem, USA) was spin coated on the substrate at 300 rpm for 20 sec at 100 rpm/sec acceleration and 1200 rpm for 30 seconds at 300 rpm/sec acceleration. The soft baking was done at 65 ^{o}C and 95 ^{o}C for 10 and 30 minutes respectively and cooled down to room temperature in 1 hour. The resist was exposed through a Cr mask, designed by Advanced Design System, containing microfluic patterns with 5, 41 mm long parallel channels with a pitch of 2 mm and width of 900 um, connected to a feeding channels at both ends. The post exposure bake was done at 65 ^{o}C and 95 ^{o}C for 1 and 10 minutes respectively. The SU-8 was developed in mr-Dev 600 developer (micro resist technology GmbH) for 5 minutes and further developed in a fresh developer solution for another minute, then rinsed with IPA and dried with nitrogen blow. To remove the possible resist residuals and the HDMS on the bare surface, the master was undergone another O_2 plasma treatment at 50 W for a minute. The mold was hard baked at 180 °C for 10 minutes with heating and cooling ramps of 10 minutes. To facilitate the release of the PDMS, the master was silanized for at least 2 hours through vapor phase deposition of 6 uL FTDS (Perfluorodecyltrichlorosilane. Sigma-Aldrich) in a 20L desiccator.

2. Complementary transient absorption data

Fig. S3 displays single-wavelength transient kinetics corresponding to the lowest excitation energies used for the back-electron transfer kinetics measurements.

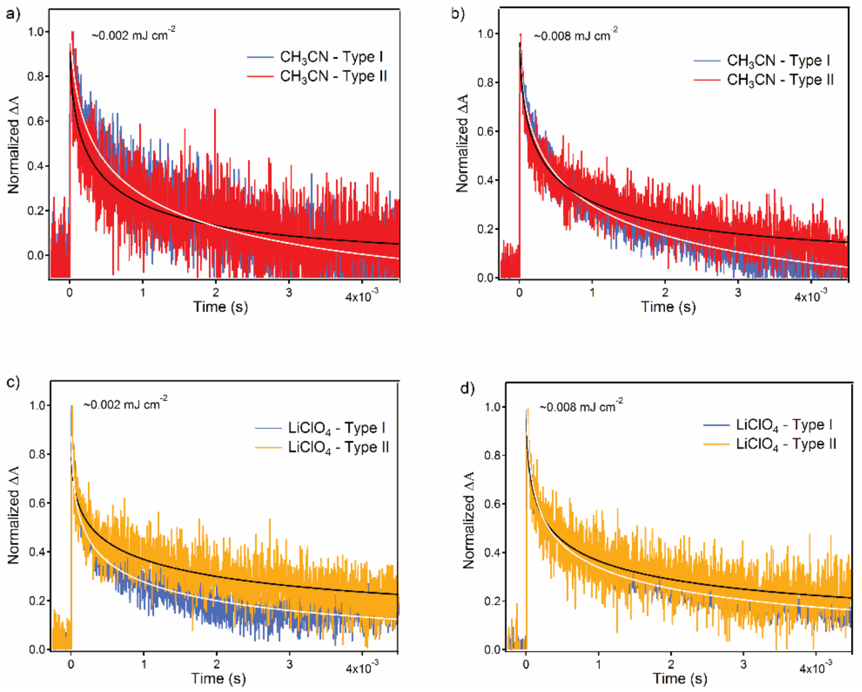

Fig. S3 Single wavelength transient absorption kinetics of patterned SnO_2-TiO_2 thin films and their corresponding KWW global fit curves. ΔA recorded at 750 nm after pulsed 525 nm laser excitation. a) In CH_3CN. b) In 0.1 M $LiClO_4/CH_3CN$.

A comparison of the back-electron transfer kinetics in dye-sensitized patterned and non-patterned SnO_2-TiO_2 thin films is displayed in **Fig. S4**. All the curves represent measurements at the highest irradiation intensity (~0.4mJ cm^{-2}). Each trace correspond to a different sample.

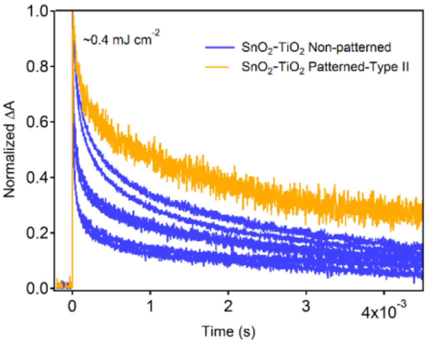

Fig. S4 Single wavelength transient absorption traces of D35 sensitized SnO_2-TiO_2 thin films. ΔA recorded at 750 nm after pulsed 525 nm and 510 nm laser excitation for patterned and non-patterned films respectively. All samples measured in 0.1M $LiClO_4$/CH_3CN

Individual fitting parameters of patterned SnO_2-TiO_2 traces.

Table S1. Charge recombination rate constats (k_{cr}) and β parameters obtained from KWW fittings of individual transient absorption traces of patterned SnO_2-TiO_2 thin films.

		Type I films		**Type II films**		
Solvent	**Excitation energy [mJcm^{-2}]**	**B***	**k_{cr}(I)* [s^{-1}]**	**B***	**k_{cr} (II)* [s^{-1}]**	**k_{cr}(II)/k_{cr}(I)**
CH_3CN	0.002	0.27±0.07	7.79x10^3±5.50x10^3	0.37±0.04	4.08x10^3±2.89x103	**0.5**
CH_3CN	0.008	0.34±0.07	1.13x10^4±1.31x10^4	0.46±0.06	3.65x10^3±3.15x10^3	**0.3**
CH_3CN	0.02	0.28±0.04	7.03x10^3±7.96x10^3	0.45±0.02	7.40x10^3±2.40x10^3	**1.1**
CH_3CN	0.4	0.28±0.01	7.20x10^3±4.80x10^3	0.32±0.1	1.11x10^4±7.06x10^3	**1.5**
0.1M $LiClO_4$	0.002	0.19±0.07	3.76x10^2±4.19x10^2	0.28±0.09	4.3x10^3±4.89x10^3	**11.4**
0.1M $LiClO_4$	0.008	0.14±0.07	1.82x10^4±3.14 x10^4	0.22±0.02	3.86 x10^3±2.31x10^3	**0.2**
0.1M $LiClO_4$	0.02	0.28±0.04	5.97 x10^2±4.56 x10^2	0.25±0.05	3.16 x10^3±1.72x10^3	**5.3**
0.1M $LiClO_4$	0.4	0.17±0.00	4.18 x10^1±2.69 x10^1	0.20±0.02	1.53 x10^4±1.06x10^4	**364.8**

*The indicated uncertainties represent the standard deviation obtained from averaging individual fits of triplicate samples.

3. Absorption spectra of the co-sensitized patterned thin film with the photosensitizer D35 and the electron acceptor CoPPIX.

The following absorption spectra confirm anchoring of the photosensitizer and the electron acceptor onto the patterned thin film used for the proof-of-principle experiment. From the spectrum in panel b, it is confirmed that the SnO_2 areas are dye-free and contain the CoPPIX only. The spectrum in panel a shows that the D35-SnO_2-TiO_2 areas present a small contribution from the CoPPIX as it can be seen from the peak centered at 425 nm. This small contamination is due to some infiltration of the CoPPIX solution into the D35 areas. We believe that the reason for this is that the DMSO used to dissolve the CoPPIX can slightly affect adhesion of the PDMS to the substrate. However, by calculating the ratio of D35/CoPPIX we obtained a value of 17:1 (**Equation S1)** and thus concluded that there is a considerable excess of dye compared to CoPPIX by a ratio of 17:1. Therefore, the accuracy of the proof-of-principle experiment is not affected by this, which is also confirmed by the control experiments presented in Fig 6 in the paper.

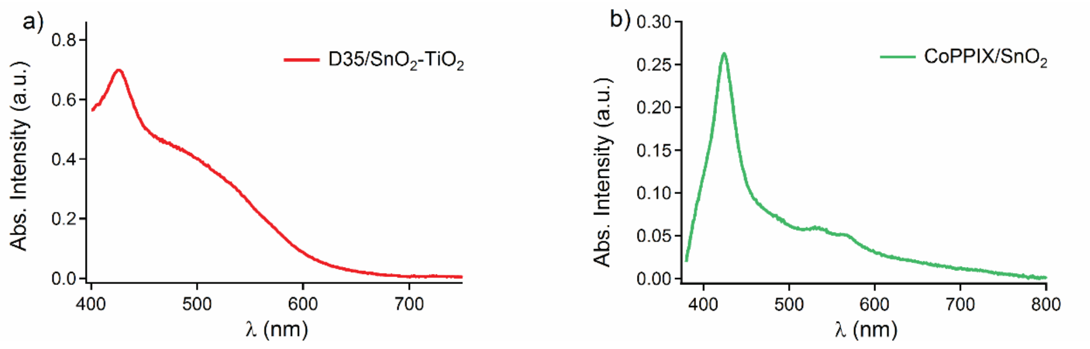

Fig. S5 Absorption spectra of the Type-II co-sensitized thin film probed at a) the D35-SnO_2-TiO_2 area and b) at the CoPPIX/SnO_2 area.

The approximate relative amount of D35 and CoPPIX at the SnO_2-TiO_2 areas of the film was calculated by assuming that the molar absorptivity of the molecules at the film are the same as in solution. By neglecting the contribution from CoPPIX to the absorbance at 500 nm, the ratio [D35]:[CoPPIX] on the film was estimated as follows:

$$\frac{[D35]}{[CoPPIX]} = \frac{\left\{\frac{Abs_{459nm}^{Ref}}{Abs_{500nm}^{Ref}} Abs_{500}^{sample}\right\} / \varepsilon_{D35,max}}{\left\{Abs_{425}^{sample} - \frac{Abs_{425nm}^{Ref}}{Abs_{500nm}^{Ref}} Abs_{500}^{sample}\right\} / \varepsilon_{CoPPIX,max}} \qquad (S1)$$

Where Abs_{459nm}^{Ref}, Abs_{500nm}^{Ref}, Abs_{425nm}^{Ref} are the absorbance values for a Type-II film sensitized with D35 only. Abs_{425}^{sample} and Abs_{500}^{sample} are the absorbance values of the “contaminated” sample and

$\varepsilon_{D35,max}$ and $\varepsilon_{CoPPIX,max}$ are the molar extinction coefficients for D35 and CoPPIX at their λ_{max} in solution and have values of 31000 and 303000 $M^{-1}cm^{-1}$ respectively.

4. Electrochemical reduction of CoPPIX

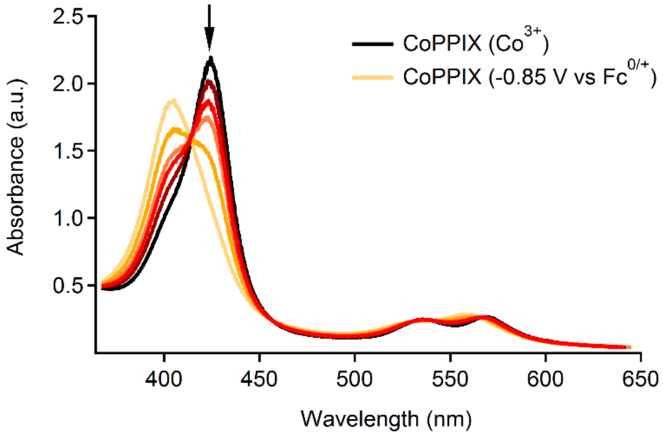

Fig. S6 Absorption changes of a CoPPIX in Ar-purged $TBAPF_6$/DMSO during electrochemical reduction at the potential indicated in the legend.

5. Difference absorption spectrum of the dye D35.

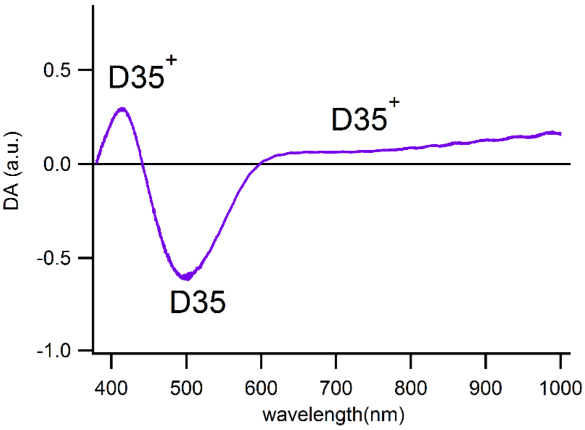

Fig. S7 Difference absorption spectrum of D35/TiO_2 obtained by electrochemical oxidation in 0.1 M $LiClO_4$/CH_3CN.

6. Estimation of density of injected electrons.

We estimated the number of injected electrons per nanoparticle in patterned SnO_2-TiO_2 thin films using **Equation S2**. Here, λ_{ex} is the excitation wavelength, F_{ex} is the energy fluence per laser pulse, A is the absorbance of the dye at λ_{ex}, r is the average particle radius, d is the thickness of the mesoporous film, and φ its porosity.[2] We assumed a porosity of 65% for both SnO_2 and TiO_2, and we used an average nanoparticle diameter of 15 nm. Variations in the values of these parameters results in moderate deviations of the $\langle x \rangle$ values, however this does not affect our conclusions.

$$\langle x \rangle = \frac{\lambda_{\mathrm{ex}} \cdot F_{ex} \cdot (10^{-A}) \cdot 4\pi \cdot \mathrm{r}^3}{3h \cdot c \cdot d \cdot \varphi} \tag{S2}$$

SI References

1. L. Alibabaei, B. D. Sherman, M. R. Norris, M. K. Brennaman and T. J. Meyer, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 5899-5902.
2. K. Kalyanasundaram, *Dye-sensitized Solar Cells*, EPFL Press, 2010.