Electronic Supplementary Information (ESI)

The Effect of Recombination under Short-circuit Conditions on the Determination of Charge Transport Properties in Nanostructured Photoelectrodes

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Sample preparation

A thin compact layer of TiO_2 is deposited onto a transparent conducting oxide covered glass (TCO; F-doped SnO_2; 8 ohms/square) by spraying 0.2 M titanium diisopropoxide bis(acetylacetonate) in isopropanol followed by heating the deposited layer at 450 C for 30 min. The TiO_2 nanocrystals paste (Dyesol 18NR-T) was deposited by the doctor-blade technique on the TiO_2 compact layer and then sintered sequentially at 325C for 5 min, 375C for 5 min, 450C for 15 min, and 500C for 15 min. The average TiO_2 NP film thickness was 12 μm as measured by a surface profiler. After annealing the TiO_2 films again at 500 C in air for 30 min and then cooling them to 80–100 C, they were immersed in a solution of acetonitrile/tert-butyl alcohol (1:1, v/v) containing 0.3 mM Z907 dye for 15 h. The semitransparent counter electrodes were prepared by spreading two drops of 5 mM H_2PtCl_6 solution in 2-propanol onto the TCO substrates (F-doped SnO_2; 15 ohms/square) and subsequently firing them at 400C for 20 min. The TiO_2 electrode and Pt-covered counter electrode were then sandwiched together using a 25-μm thick themoplastic (Surlyn, Dupont grade 1702). The electrolyte used in the DSSCs contained 0.6 M 1-butyl-3- methylimidazolium iodide, 0.1 M LiI, 0.05 M I_2, 0.5 M 4-tert-butylpyridine, and 0.1 M guanidinium thiocyanate in acetonitle/valeronitrile (85:15, v/v%).

Sample Measurements

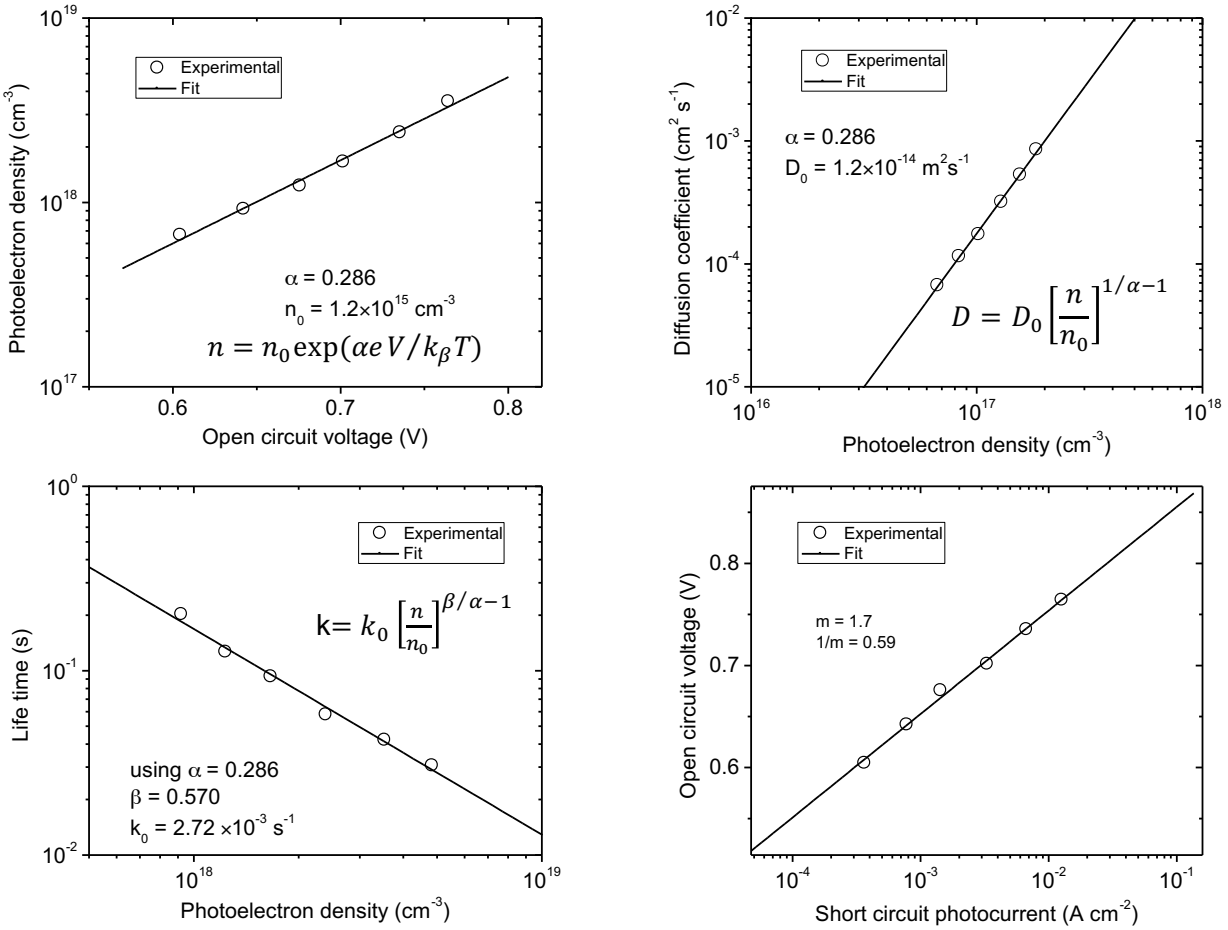

Figure S1Parameters extraction from IMPS and IMVS measurements. Fitting equation in agreement with the total electron density model are included.

Transport and recombination were measured by intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS).[1,2] The DSSCs were probed with a modulated beam of 660 nm light (probe) superimposed on a relatively large background (bias) illumination also at 660 nm light. The probe and bias light entered the cells with the TCO substrates from the TCO-TiO_2 side. The modulation frequencies were varied between 1 mHz and 10 kHz. Neutral density filters were used to vary the illumination intensity.

The electron diffusion coefficients D for the TiO_2 films were determined from the expression $D = d^2/(2.35\tau)$, where d is the film thickness and τ is the electron transport time as obtained from IMPS measurements. The steady-state photoinjected electron density n in the TiO_2 films was estimated from the relation $n = T_\alpha J_{SC}\tau/(qd(1-P))$,5 where T_α is the thermodynamic factor,[3,4] J_{SC} is the short-circuit photocurrent density established by the bias light, P is the film porosity, q is the absolute value of the electron charge, τ is the corresponding electron transport time or the life time depending whether the electron density at short circuit or open circuit is calculated. The thermodynamic factor[3,4] is a measure of the parameter $\alpha^{-1} = T_0/T$, where T_0 is the characteristic temperature, which is related to the steepness of the trap distribution or the average trap depth of

the trap distribution. The current density versus voltage curve was calculated with aid of a solar simulator and potentiostat. The input parameters for the model were obtained as showed on **Figure S1**.

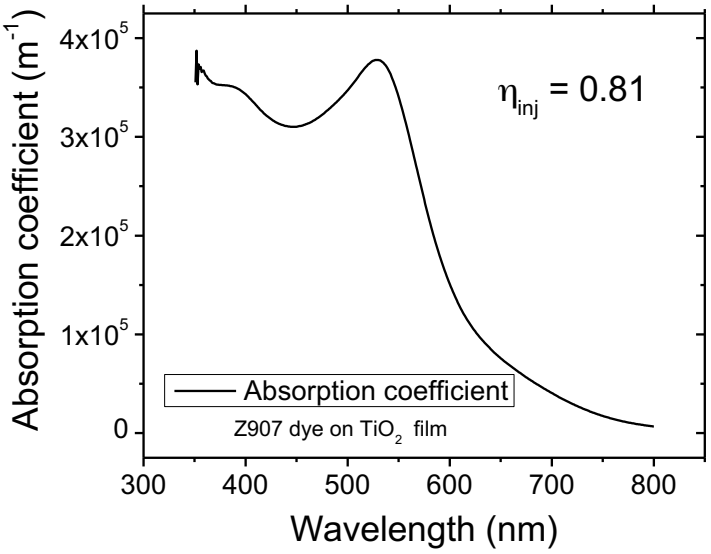

Figure S2 Absorption spectra of the sensitized TiO_2 film

The absorption spectra of the sensitized TiO_2 film was used to calculated the photo-generated charge, defined as the addition between the collected current and the recombination current. Charge injection efficiency η_{inj}, assumed to be constant, was used as a fitting parameter in order to fit the experimental short-circuit current density (**Figure S4**). Finally, the input parameters for the total electron density model are summarized on **Table S1**.

Table S1 Simulation parameters extracted from different measurements

Parameter	Value	Method
α	0.286	IMPS/IMVS
β	0.570	IMVS
n_0 (m^{-3})	$1.2x10^{21}$	IMVS
D_0 ($m^2\ s^{-1}$)	$1.2x10^{-14}$	IMPS
k_0 (s^{-1})	$2.72x10^{-3}$	V_{OC}
n_{inj}	0.810	J_{SC}
d (m)	$12x10^{-6}$	----

Continuity equation solution for 660 nm illumination.

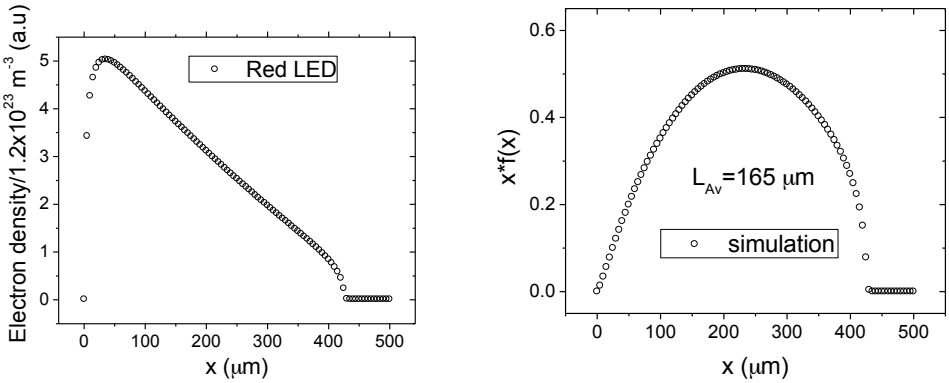

Figure S3 Electron density profile and the probability that a carrier is at position x multiplied per position as a function of charge density for Red LED illumination source

The parameters on **Table S1** were used to solve the continuity equation for the total electron density on the TiO_2 electrode, **Equation 1** on the main manuscript, under real working conditions with a 660 nm LED of illumination. Method 3 was used to calculate the average diffusion length L_{Av}=165 μm with the aid of **Equations 5** and **Equation 6** in the main text. SLIT simulations were performed with aid of **Table S1** to obtain the electron transport time and calculate the diffusion coefficients.[5]

Figure S4 compare the experimental versus the simulated electron transport time versus short-circuit photocurrent, open circuit voltage versus short-circuit photocurrent and the current density versus voltage curves.

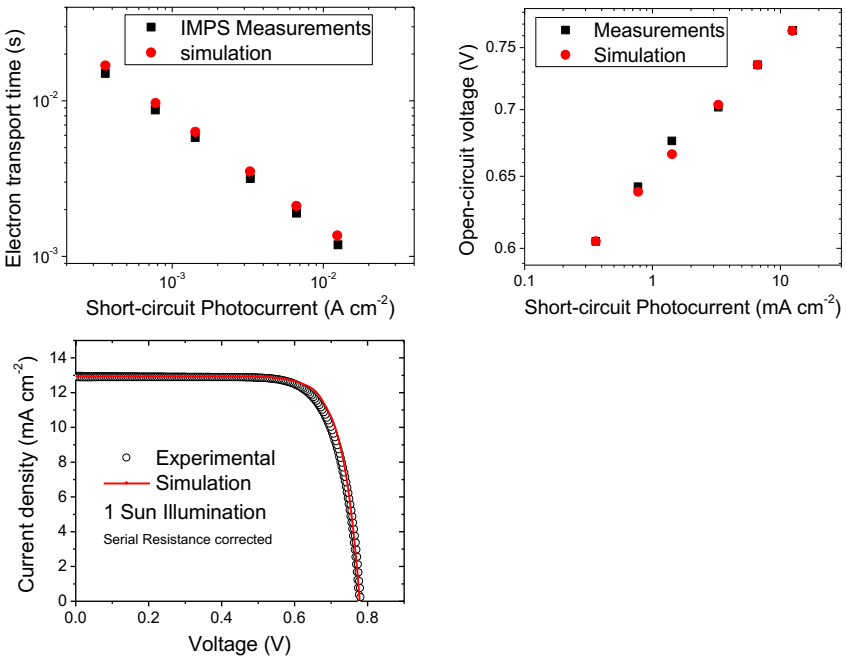

Figure S4 Comparison between experimental and simulated steady state and time dependent properties of a DSSC.

Comparison between 660nm and Uniform illumination to obtain the real diffusion length

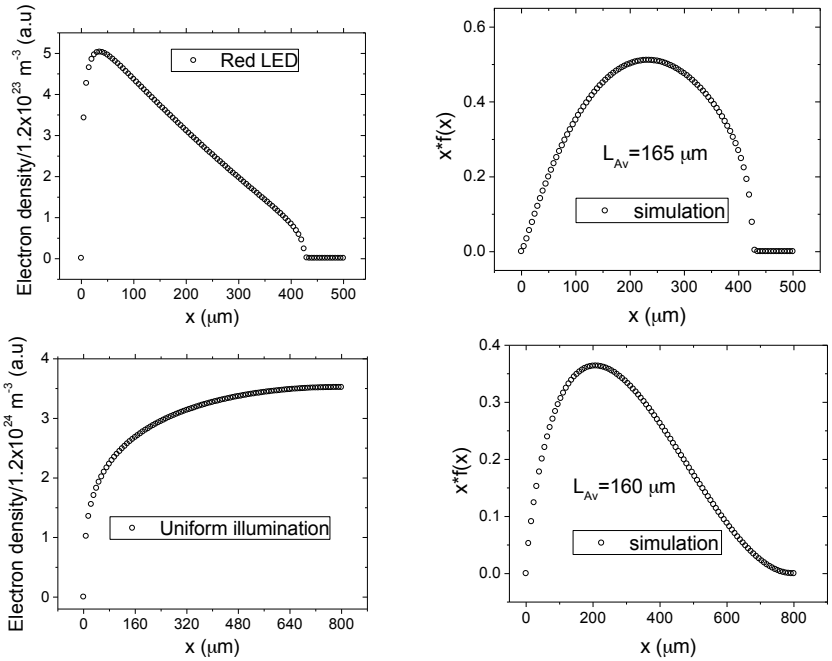

Figure S5 Electron density profile and the probability that a carrier is at position x multiplied per position as a function of charge density for Red LED and Uniform illumination sources.

The parameters on **Table S1** were used to solve the continuity equation for the total electron density on the TiO_2 film, **Equation 1** on the main manuscript, under real working conditions with a 660 nm LED and uniform illumination light. Method 3 was used to calculate the average diffusion length μm with the aid of Equations 5 and 6 in the main text. In the case for Red illumination (660 nm) the optical length is λ=14.3 μm, as consequence when x trend to infinity the density profile goes to zero as noticed on **Figure S5**. By another side, for uniform illumination (Generation independent of position x) the optical length is infinity and as consequence the density profile never goes to zero.

Finally, as can be notice on **Figure S5** there is not significant difference on the real diffusion length when is illuminated with red LED or with uniform light source.

Analytical solution for the continuity equation at steady state

The continuity equation, Equation 1 on the main text, is reduced to

$$D_0 \frac{\partial^2 n(x)}{\partial x^2} + G(x) - k_0 n(x) = 0$$

For α=β=1 and at steady state, with solution:

$$n(x) = (n_0 - n_b)e^{-x/L_0} + n_b$$

where n_b is dependent of the illumination profile:

a) For exponential decay Generation

$$G(x) = I_0 e^{-\alpha_{abs} x}; \quad n_G = \frac{I_0 {L_0}^2}{D_0[1 - (\alpha_{abs} L_0)^2]}$$

b) For uniform Generation

$$G(x) = I_0; \quad n_G = \frac{I_0 {L_0}^2}{D_0}$$

where:

- L_0 is the constant diffusion length, $L_0=(D_0/k_0)^{1/2}$
- k_0 is the recombination rate in dark (V=0)
- D_0 diffusion coefficient at V=0
- I_0 incident photon flux (100 mW cm^{-2})
- α_{abs} is the absorption coefficient at 660 nm (α_{abs} = 7x10^4 m^{-1})

Numerical solution (Method 3) was compared with the analytical solution under the following conditions: 1) uniform illumination and 2) when α = β = 1.
As can be notice on **Figure S6** and **Figure S7** analytical and numerical solution converge to similar value on the diffusion length.

Parameter	Value	Method
α	1	IMPS/IMVS
β	1	IMVS
n_0 (m^{-3})	$1.2x10^{21}$	IMVS
D_0 (m^2 s^{-1})	$1.2x10^{-14}$	IMPS
k_0 (s^{-1})	$2.72x10^{-7}$	V_{OC}
n_{inj}	0.81	J_{SC}
d (m)	$12x10^{-6}$	----

$L_0=(D_0/k_0)^{1/2}$ =209 μm

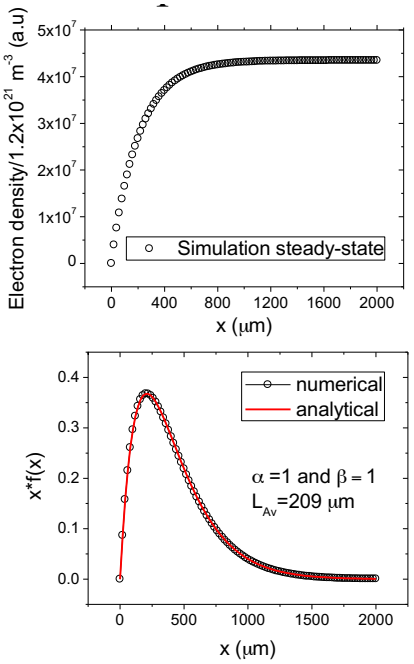

Figure S6 Numerical and Analytical solutions comparison with uniform generation profile with a constant diffusion length of 209 μm

Parameter	Value	Method
α	1	IMPS/IMVS
β	1	IMVS
n_0 (m^{-3})	$1.2x10^{21}$	IMVS
D_0 (m^2 s^{-1})	$1.2x10^{-14}$	IMPS
k_0 (s^{-1})	$2.72x10^{-3}$	V_{OC}
n_{inj}	0.81	J_{SC}
d (m)	$12x10^{-6}$	----

$L_0=(D_0/k_0)^{1/2}$ =2.09 μm

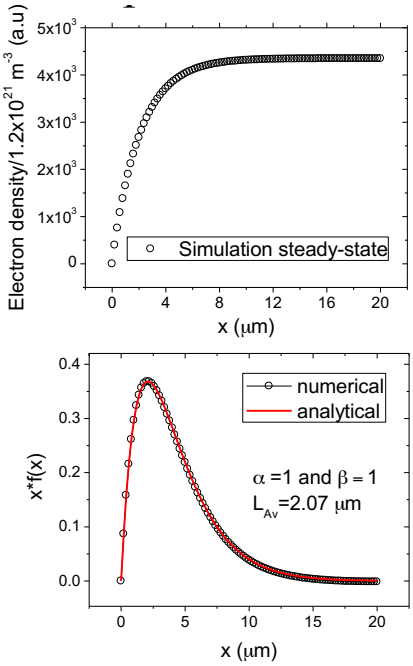

Figure S7 Numerical and Analytical solutions comparison with uniform generation profile with a constant diffusion length of 209 μm

Geometric constant used to calculate *D* from SLIT simulations

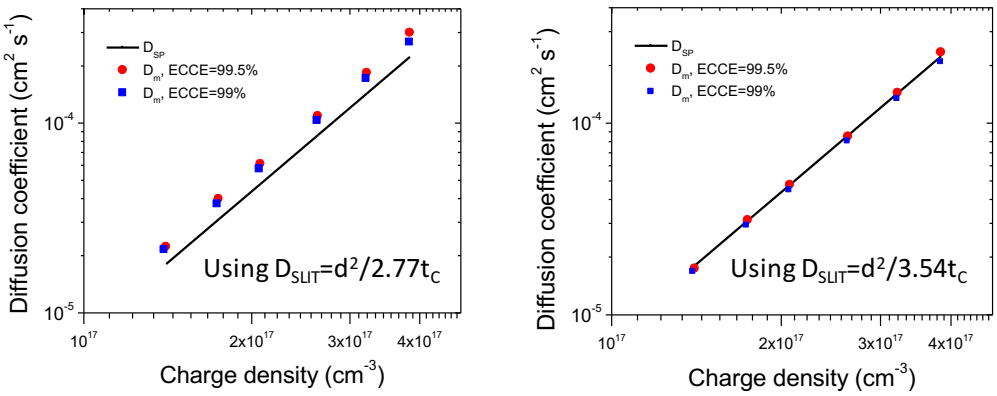

Figure S8 Geometrical constant to calculate the Diffusion coefficient from SLIT simulations

SLIT simulations were performed with aid of **Table S1** to obtain the electron transport time and calculate the diffusion coefficient[5] in order to compare the three methods stablished on the main text. As can be seen in **Figure S8**, if the factor 3.45 is used in the equation to calculate D_{SLIT} instead of 2.77, the three methods give similar diffusion coefficients.

1) G. Schlichthörl, S. Y. Huang, J. Sprague, and A. J. Frank. *J. Phys. Chem. B,* 1997, **101**, 8141-8155.
2) J. van de Lagemaat and A. J. Frank. *J. Phys. Chem. B,* 2001, **105**, 11194-11205.
3) J. van de Lagemaat, N. Kopidakis, N. R. Neale and A. J. Frank. *Phys. Rev. B,* 2005, **71,** 035304.
4) J. Bisquert. *J. Phys. Chem. B,* 2004, **108**, 2323-2332.
5) J. A. Anta, J. Idígoras, E. Guillén, J. Villanueva-Cab, H. J. Mandujano-Ramírez, G. Oskam, L. Pellejàc and E. Palomares. *Phys. Chem. Chem. Phys*., 2012, **14**, 10285-10299.