Origin of non-linear recombination in dye-sensitized solar cells – Supporting Information

Gonzalez-Vazquez, J.P.\textsuperscript{a}, Gerko Oskam\textsuperscript{b}, Juan A. Anta\textsuperscript{a}

\textsuperscript{a} Área de Química Física, Universidad Pablo de Olavide, Sevilla, Spain.
\textsuperscript{b} Departamento de Física Aplicada, CINVESTAV-IPN, Mérida, Yucatán, México.

Frequently-asked questions about Random Walk Numerical Simulation.

\textit{a) How many particles were used in the simulations?}

The number of particles used in the simulations depend on the range of open-circuit voltages to be studied. It can range from just a few electrons to hundreds. This input parameter is also dependent on the dimension of the simulation box as for the same electron density the number of particles is a linear function of the size of the simulation box.

\textit{b) What is the strategy to determine the Fermi-level?}

The strategy first consist in adjusting the appropriate electron density from the following equation:

\[ n_t = N_t \exp \left( \frac{E_F-E_e}{k_BT_0} \right) \]

The Fermi-level can also be extracted from a fitting of the population histogram to a Fermi-Dirac distribution as described in Refs. 53 and 54.

\textit{c) Is the implementation of the recombination process postponed until a well-defined Fermi-level is established in the system?}

The determination of magnitudes related to recombination processes (electron diffusion length and lifetime) is not postponed until an stationary situation is reached but the time evolution of both magnitudes is monitored. In this way, it is found that constant values are reached after a certain time. As demonstrated in Ref 23, It is found that these constant values correspond to real values measured in experiments.

\textit{d) Approximately how many runs are needed to achieve small enough statistical errors?}

The more samples are run the better statistics is reached. In general, there is a point where no more changes in the values of magnitudes is observed. The number is not fixed, it depends on the specific system to be reproduced. It can range between just 10-20 to almost 1000. This is explained because the statistics is more specifically given by the total number of moves or jumps. Thus, as there are more jumps in simulations with many particles, a good statistics is obtained in this case with not so many runs.

\textit{e) Has periodic boundary condition been used in the simulations?}

Yes, in the three directions of space.
Figure S1. Electron diffusion length calculated by steady-state RWNS calculations using the hybrid model for different values of the recombination prefactors (Eqs. (7) and (8)). The simulations correspond to systems defined by $\lambda = 0.6$ eV, $T_0 = 700$ K and $T = 300$ K. Two values of the conduction-band position are considered: $E_c - E_{\text{redox}} = 0.95$ eV (solid lines) and $E_c - E_{\text{redox}} = 0.70$ eV (dashed lines). Results are obtained from the Marcus-Gerischer formula (Eqs. (7) and (8)) and a density of electronic states in the semiconductor given by Eq. (6).
Figure S2. Electron diffusion length calculated by steady-state RWNS calculations using the hybrid model. The simulations correspond to a system defined by $\lambda = 2$ eV, $T_0 = 700$ K, $T = 300$ K and $E_c - E_{\text{redox}} = 0.95$ eV (red) and 0.70 eV (black). Results are obtained from the Marcus-Gerischer formula (Eqs. (7) and (8)) and density of electronic states in the semiconductor (Eq. (6), trap energy distribution).

![Figure S2](image1)

Figure S3. Electron diffusion length calculated by steady-state RWNS calculations using Model 1 for different values of the recombination prefactor (Eq. (7)). The simulations correspond to a system defined by $\lambda = 0.25$ eV, $T_0 = 700$ K, $T = 300$ K. Two values of the conduction-band position are considered: $E_c - E_{\text{redox}} = 0.95$ eV (solid lines) and $E_c - E_{\text{redox}} = 0.70$ eV (dashed lines). Results are obtained from the Marcus-Gerischer formula (Eqs. (7)) and density of electronic states in the semiconductor (Eq. (6), trap energy distribution).

![Figure S3](image2)

Figure S4. Electron diffusion length calculated by steady-state RWNS calculations using Model 2 for different values of the recombination prefactor (Eq. (8)). The simulations correspond to systems defined by $\lambda = 2.0$ eV, $T_0 = 700$ K, $T = 300$ K. Two values of the conduction-band position are considered: $E_c - E_{\text{redox}} = 0.95$ eV (solid lines) and $E_c - E_{\text{redox}} = 0.70$ eV (dashed lines). Results are obtained from the Marcus-Gerischer formula (Eqs. (8)) and density of electronic states in the semiconductor (Eq. (6), trap energy distribution).

![Figure S4](image3)
states in the semiconductor (Eq. (6), trap energy distribution).