Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information for

Numerical Monte Carlo Simulations of Charge Transport across the Surface of Dye and Cocatalyst Modified Spherical Nanoparticles under Conditions of Pulsed or Continuous Illumination

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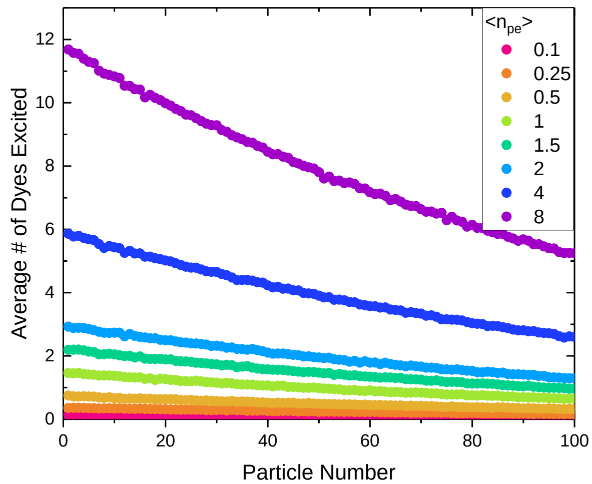

Figure S1. Simulated assignment of photoexcited dyes based on the Beer–Lambert law as a function of particle number/depth at the indicated excitation fluences and repeated a total of 50,000 times per condition.

Table S1. Values and expressions used for parameters in the Monte Carlo simulations.

Name	Value(s)	Unit
$\tau_{hop(Dye–Dye)}$	40, 80, 160, 400, 800, 1600, 4000, 8000, 16000, 40000, 80000, 160000, 400000, 800000	ns
$\tau_{hop(Cat–Cat)}$	$\tau_{hop–DyetoDye}$	ns
$\tau_{hop(Dye–Cat)}$	$\tau_{hop–DyetoDye}$ / 27	ns
$\tau_{hop(Cat–Dye)}$	$\tau_{hop–DyetoDye}$ x 10^{13}	ns
$\tau_{recomb(SC–Dye)}$ per particle	40, 80, 160, 400, 800, 1600, 4000, 8000, 16000, 40000, 80000, 160000, 400000, 800000	ns
$\tau_{recomb(SC–Cat)}$ per particle	$\tau_{recomb–SCtoDye}$	ns
time step, t_{step}	Minimum[3.75 x $\tau_{hop–DyetoDye}$, $\tau_{recomb–SCtoDye}$] / 350	ns
number of trials per data point	25	–
percent of incident light transmitted through the thin film	43.4	%
number of initially excited dyes per stack	10, 50, 100, 200, 400, 800, 2000, 4000, 8000, 16000	–
number of particles in the stack	100	–
number of molecular positions (points) per particle	252	–
percent surface coverage of molecules	100	%
maximum number of points adjacent to each molecule	6†	–
maximum redox state of electrocatalysts	1, 2, 4	–
number of electrocatalysts per stack	252	–
number of electrocatalysts per particle††	2	–
number of initial photoexcitation events per particle (n_{pe})††	1, 2, 4, 8, 20	–

† in 12/252 cases, tessellation resulted in points that were pentagonally packed with only 5 adjacent points

†† only used when absorption was homogeneous across the stack and did not follow the Beer–Lambert law

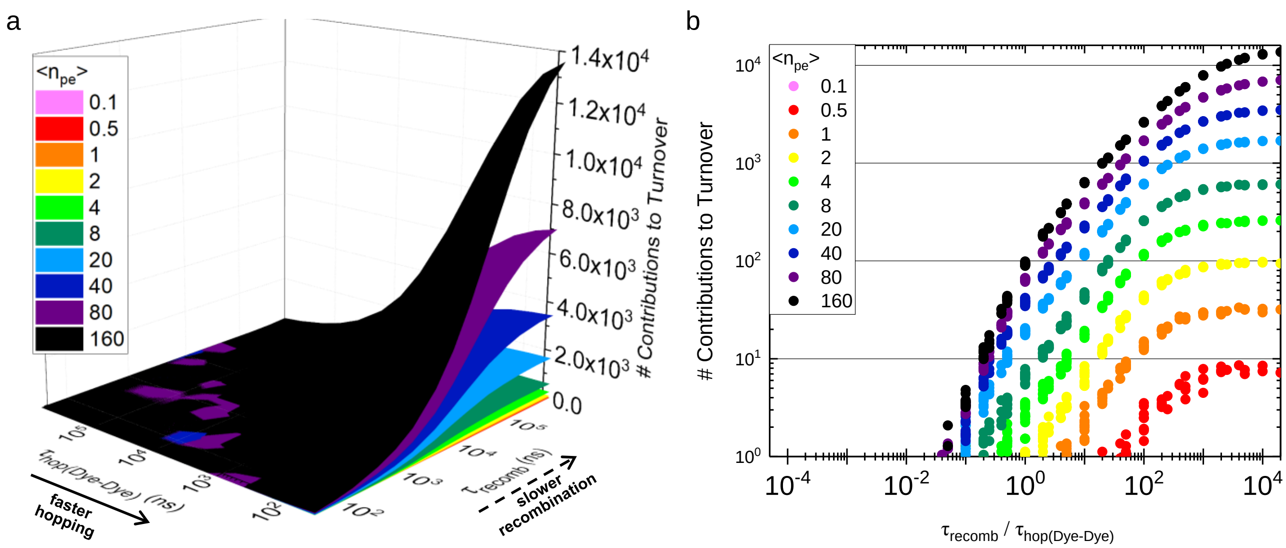

Figure S2. (a) Sheet plot representing the number of photoexcited dyes that ultimately *contribute to double oxidation/reduction of an electrocatalyst and turnover* when electrocatalysts are present at 1% surface coverage at the indicated initial pulsed-light excitation fluences. (b) Representation of the data in panel a as a function of the ratio of the recombination time constant to the hopping time constant using base-10 logarithmic scaling of the y-axis values so that lower fluence data can be seen more clearly.

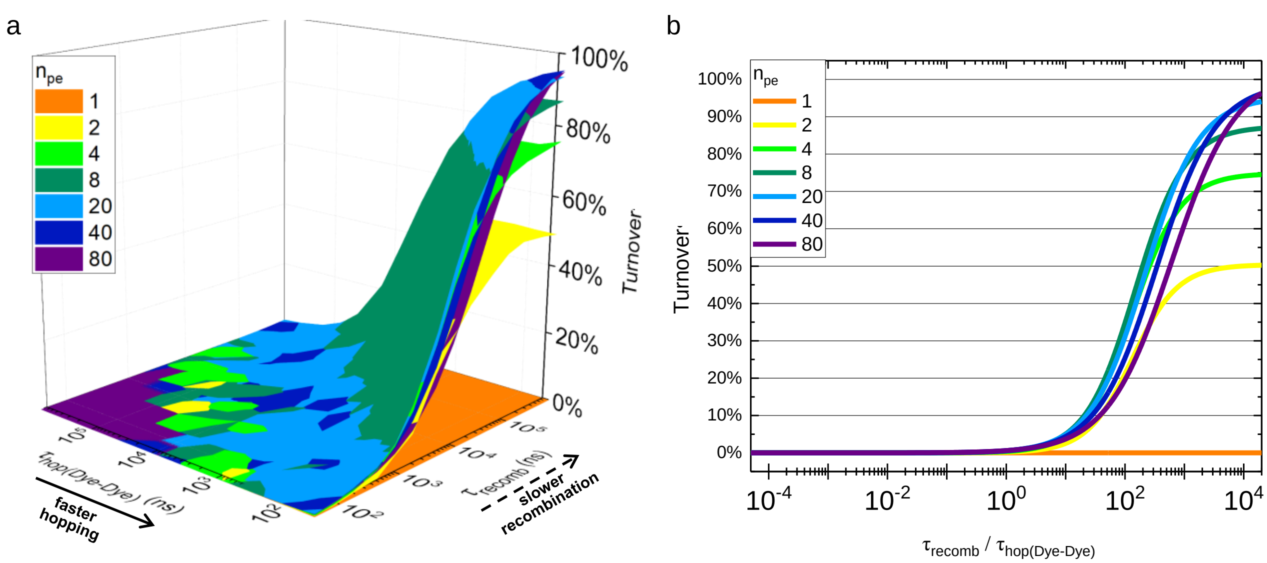

Figure S3. (a) Sheet plot representing the percentage of photoexcited dyes that ultimately contribute to double oxidation/reduction of an electrocatalyst and turnover when *electrocatalysts are present at exactly 2 per particle* at the indicated initial pulsed-light excitation *fluences as a uniform distribution over the stack*. (b) Non-linear least squares sigmoidal best-fits of the data in panel a as a function of the ratio of the recombination time constant to the hopping time constant.

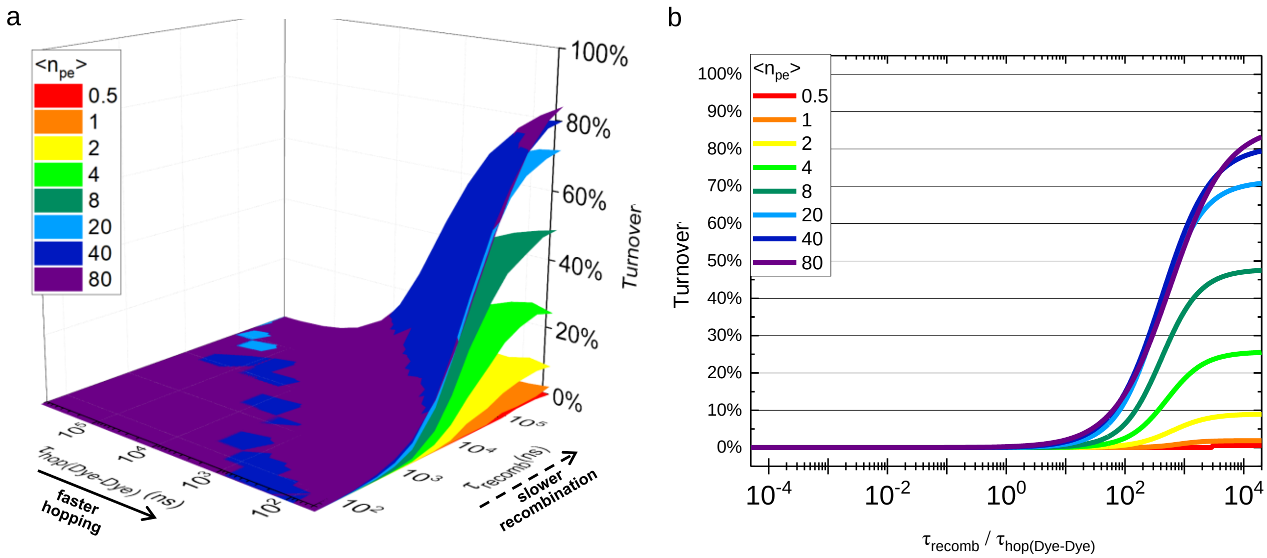

Figure S4. (a) Sheet plots representing the percentage of photoexcited dyes that ultimately *contribute to quadruple oxidation/reduction of an electrocatalyst and turnover* when electrocatalysts are present at 1% surface coverage at the indicated initial pulsed-light excitation fluences. (b) Non-linear least squares sigmoidal best-fits of the data in panel a as a function of the ratio of the recombination time constant to the hopping time constant.

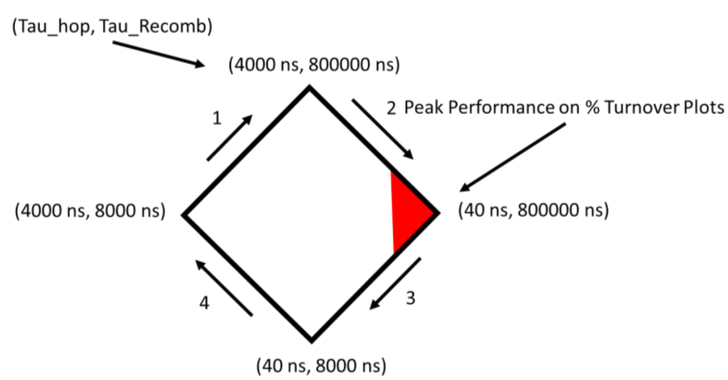

Figure S5. Schematic detailing the process used to create a panoramic plot by tracing the perimeter of the parameter space covered by the sheet plot as 1, 2, 3, and 4, to allow for facile two-dimensional viewing for a wide range of parameters.

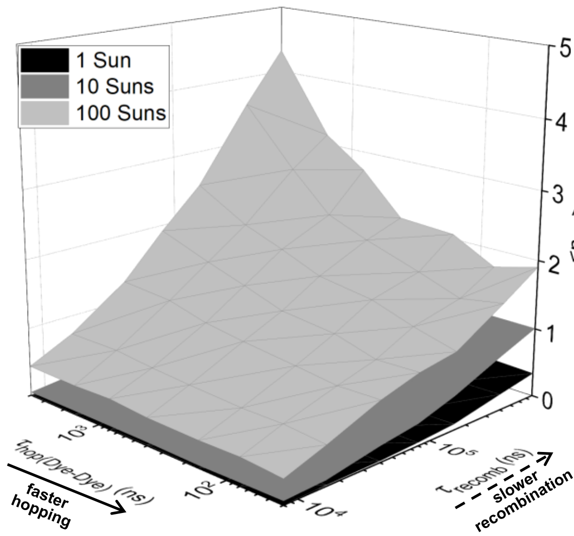

Figure S6. (a) Sheet plots – oriented like all other sheet plots – *representing the steady-state number of oxidized/reduced species when electrocatalysts require double oxidation/reduction for turnover* and are present at 1% surface coverage at the indicated continuous illumination solar-simulated fluences.

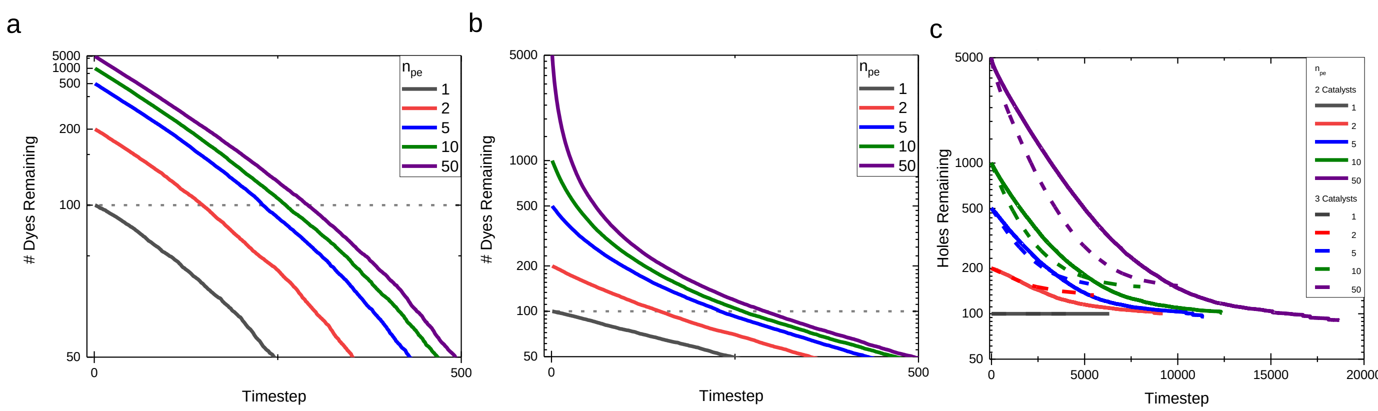

Figure S7. (a,b) Number of oxidized/reduced dyes remaining over time on the 100 particle stack after the indicated initial uniform pulsed-light excitation fluences, in the absence of electrocatalysts. (c) Number of oxidized/reduced species remaining over time on the 100 particle stack after the indicated initial uniform pulsed-light excitation fluences at the indicated uniform number of electrocatalysts per particle, in the absence of recombination. The y-axis in panel a is reciprocally scaled so that linear behavior indicates equal-concentration 2nd-order kinetic processes, while the y-axes in panels b and c are logarithmically scaled so that linear behavior indicates 1st-order kinetic processes. Kinetic parameters from best-fits of these data are shown in Table S2.

Table S2. Best-fit rate constants from the linear regions of the data in Figure S7.

	Recombination, *# excitations remaining > 100* (Figure S7a)	**Recombination, *# excitations remaining < 100* (Figure S7b)**	**Turnover, *initial* (2 electrocatalysts per particle) (Figure S7c)**	**Turnover, *initial* (3 electrocatalysts per particle) (Figure S7c)**
kinetics	**equal-concentration 2nd-order**	**1st-order**	**1st-order**	**1st-order**
$\boldsymbol{n_{pe} = 1}$	–	1.23 x 10^{-3} timestep^{-1}	0 timestep^{-1}	0 timestep^{-1}
$\boldsymbol{n_{pe} = 2}$	3.32 x 10^{-5} timestep^{-1}	1.43 x 10^{-3} timestep^{-1}	5.46 x 10^{-5} timestep^{-1}	5.92 x 10^{-5} timestep^{-1}
$\boldsymbol{n_{pe} = 5}$	3.15 x 10^{-5} timestep^{-1}	1.34 x 10^{-3} timestep^{-1}	1.52 x 10^{-4} timestep^{-1}	1.86 x 10^{-4} timestep^{-1}
$\boldsymbol{n_{pe} = 10}$	3.17 x 10^{-5} timestep^{-1}	1.38 x 10^{-3} timestep^{-1}	2.01 x 10^{-4} timestep^{-1}	2.80 x 10^{-4} timestep^{-1}
$\boldsymbol{n_{pe} = 50}$	3.11 x 10^{-5} timestep^{-1}	1.47 x 10^{-3} timestep^{-1}	2.44 x 10^{-4} timestep^{-1}	3.55 x 10^{-4} timestep^{-1}
mean	(319 ± 9) x 10^{-7} timestep^{-1}	(137 ± 9) x 10^{-5} timestep^{-1}	–	–