Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Photovoltaic Characteristics and Dye Regeneration Kinetics in D149-Sensitized ZnO with Varied Dye Loading and Film Thickness

Supporting Information

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SI1. Fitting of steady-state SECM approach curves with finite first order kinetics at the sample and diffusion controlled kinetics at the UME

Normalized heterogeneous rate constants κ have been extracted from experimental approach curves by fitting them to an analytical approximation of simulated data evaluated by Cornut and Lefrou.[1] The radius of the active part of the UME, r_T, the ratio RG of insulating sheath r_{glass} and r_T, and the point of closest approach d_0 have been determined from independent experiments. *RG* was determined by optical microscopy; r_T and d_0 were determined from approach curves to glass or D149/ZnO film in the dark and fitting them to theoretical curves proposed by Amphlett and Denuault.[2] The formula of Amphlett and Denuault given for *RG* = 10.2. Constants for other selected *RG* are also available.

$$I_T^{cond}(L) = 0.72627 + \frac{0.76651}{L} + 0.26015\exp\left(\frac{-1.41332}{L}\right) \quad \text{(SI-1)}$$

Normalized approach curves I_T vs. L have been calculated from each experimental approach curves $i_T(z)$ using $I_T = i_T/i_{T,\infty}$ and $L = d/r_T$. The analytical approximation of Cornut and Lefrou[1] was used for calculating a theoretical current I_T for each experimental, normalized distance L.

$$I_T(L,\kappa,RG) = I_T^{cond}\left(L+\frac{1}{\kappa},RG\right) + \frac{I_T^{ins}(L,RG)-1}{\left(1+2.47RG^{0.31}L\kappa\right)\left(1+L^{0.006RG+0.113}\kappa^{-0.0236RG+0.91}\right)} \quad \text{(SI-2)}$$

with

$$I_T^{cond}\left(L+\frac{1}{\kappa},RG\right) = \alpha(RG) + \frac{1}{2\beta(RG)\xi\left(L+\frac{1}{\kappa}\right)} + \left(1-\alpha(RG)-\frac{1}{2\beta(RG)}\right)\xi\left(L+\frac{1}{\kappa}\right) \quad \text{(SI-3)}$$

$$I_T^{ins}(L,RG) = \frac{\frac{2.08}{RG^{0.358}}\left(L - \frac{0.145}{RG}\right) + 1.585}{\frac{2.08}{RG^{0.358}}(L + 0.0023RG) + 1.57 + \frac{\ln RG}{L} + \frac{2}{\pi RG}\ln\left(1 + \frac{\pi RG}{2L}\right)} \quad \text{(SI-4)}$$

$$\alpha(RG) = \ln 2 + \ln 2\left(1 - \frac{2}{\pi}\arccos\left(\frac{1}{RG}\right)\right) - \ln 2\left(1 - \left(\frac{2}{\pi}\arccos\left(\frac{1}{RG}\right)\right)^2\right) \quad \text{(SI-5)}$$

$$\beta(RG) = 1 + 0.639\left(1 - \frac{2}{\pi}\arccos\left(\frac{1}{RG}\right)\right) - 0.186\left(1 - \left(\frac{2}{\pi}\arccos\left(\frac{1}{RG}\right)\right)^2\right) \quad \text{(SI-6)}$$

$$\xi\left(L + \frac{1}{\kappa}\right) = \frac{2}{\pi}\arctan\left(L + \frac{1}{\kappa}\right) \quad \text{(SI-7)}$$

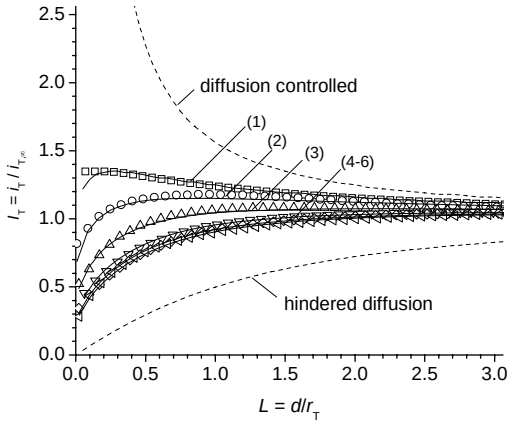
$$\kappa = \frac{k_{eff} r_T}{D} \quad \text{(SI-8)}$$

κ, $i_{T,\infty}$ and d_0 (within reasonable range) were varied in order to fit the experimental approach curves. Heterogeneous rate constant k_{eff} was calculated from κ.

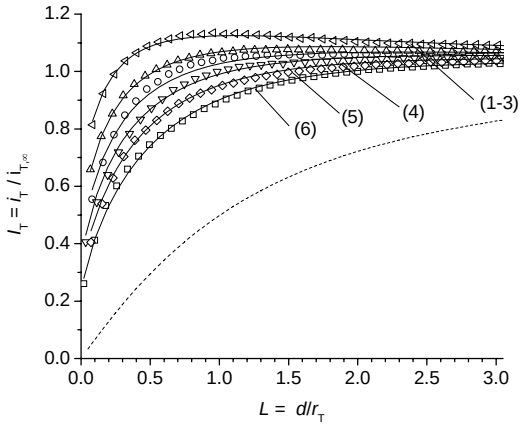
SI2. SECM approach curves on D149/ZnO samples of $^{2.3}S2_{2.6}$ - $^{0.4}S6_{2.9}$

a) SECM approach curves with varying $[I_3^-]$*

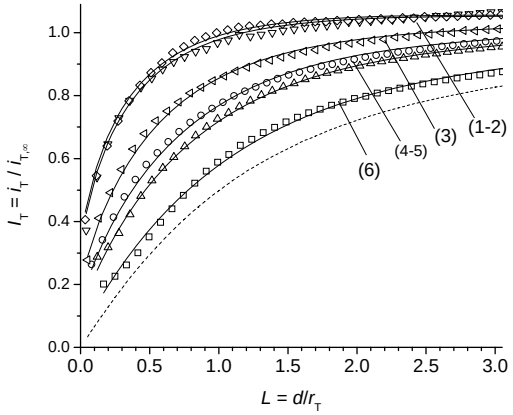
$^{2.3}S2_{2.6}$



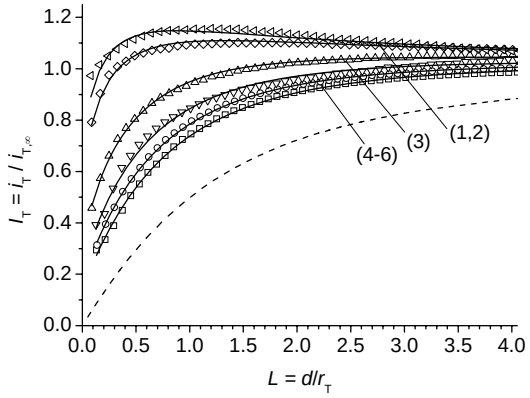
$^{3.3}S3_{3.0}$



$^{1.8}S4_{4.6}$



$^{1.8}S5_{2.1}$



$^{0.4}S6_{2.9}$

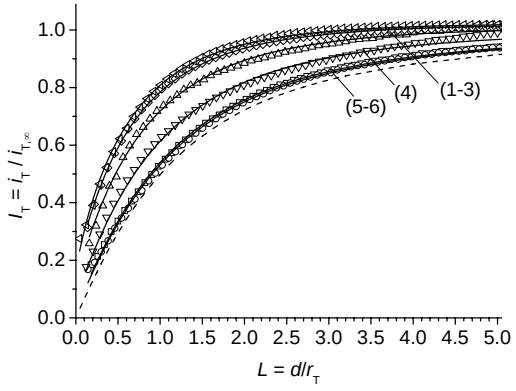
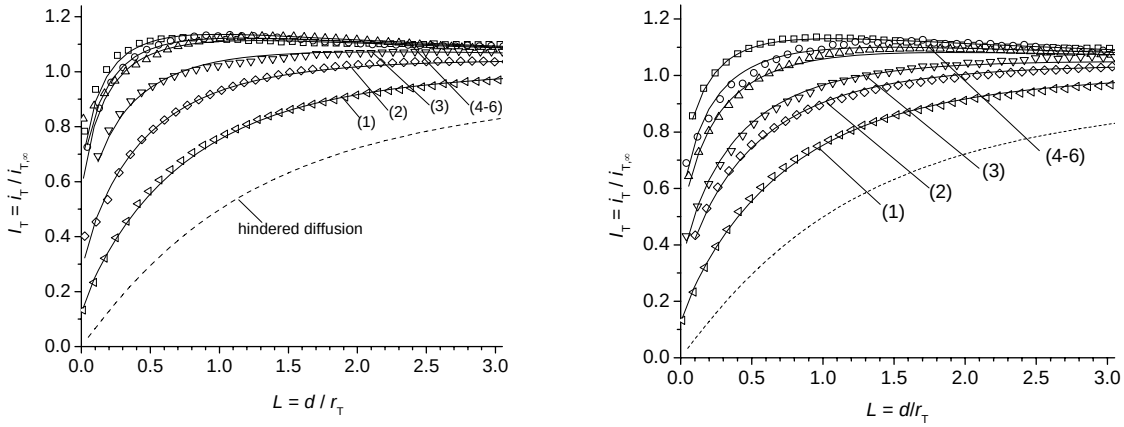


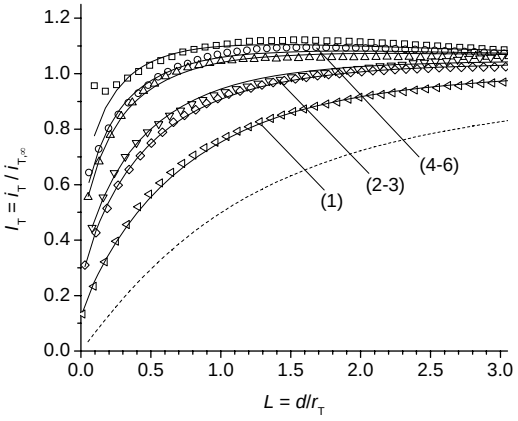
Figure SI-1. Normalized SECM approach curves obtained with Pt UME (r_T = 12.5 µm) on D149/ZnO films of $^{2.3}S2_{2.6}$ $^{3.3}S3_{3.0}$. $^{1.8}S4_{4.6}$, $^{1.8}S5_{2.1}$ and $^{0.4}S6_{2.9}$ containing different $[I_3^-]$*: (1) 0.057 mM, (2) 0.124 mM, (3) 0.248 mM, (4) 0.687 mM, (5) 1.24 mM and (6) 2.01 mM with E_T = -0.7 V and $J_{h\nu} = 9.1 \times 10^{-9}$ mol cm^{-2} s^{-1}. The summary of κ obtained from the best fits of experimental data (open symbols) to theoretical model (solid lines) were, respectively, $^{2.3}S2_{2.6}$: (1) 1.18, (2) 0.75, (3) 0.44, (4) 0.28, (5) 0.24, (6) 0.22; $^{3.3}S3_{3.0}$: (1) 0.66, (2) 0.50, (3) 0.41, (4) 0.25, (5) 0.19, (6) 0.12, $^{1.8}S4_{4.6}$: (1) 0.40, (2) 0.28, (3) 0.18, (4) 0.09, (5) 0.06, (6) 0.02; $^{1.8}S5_{2.1}$: (1) 0.74, (2) 0.60, (3) 0.42, (4) 0.28, (5) 0.11, (6) 0.08; $^{0.4}S6_{2.9}$ (1) 0.0195, (2) 0.0151, (3) 0.0089, (4) 0.0067, (5) 9.03×10^{-4}, (6) 6.39×10^{-4}. The top and bottom dashed curves in (a) represent responses limited by diffusion-controlled feedback and hindered diffusion, respectively.

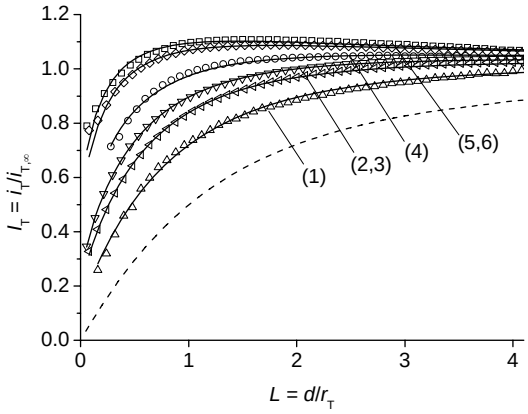
b) SECM approach curves with varying $[I_3^-]$*

$^{2.3}S2_{2.6}$ $^{3.3}S3_{3.0}$



$^{1.8}S4_{4.6}$ $^{1.8}S5_{2.1}$





$^{0.4}S6_{2.9}$

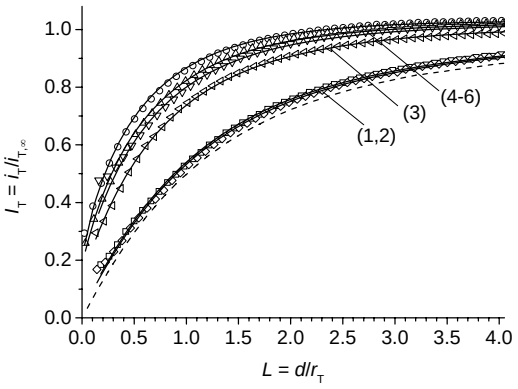


Figure SI-2. Normalized SECM approach curves obtained with Pt UME (r_T = 12.5 µm) on D149/ZnO films of $^{2.3}S2_{2.6}$, $^{3.3}S3_{3.0}$, $^{1.8}S4_{4.6}$, $^{1.8}S5_{2.1}$ and $^{0.4}S6_{2.9}$ with $[I_3^-]$* = 0.124 mM with different $J_{h\nu}$ (10^{-9} mol cm^2 s^{-1}): (1) 0.982, (2) 1.70, (3) 4.50, (4) 9.10, (5) 15.1 and (6) 25.5, E_T = -0.7 V. The summary of κ obtained from the best fits of experimental data (open symbols) to the theoretical model (solid lines) were, respectively, $^{2.3}S2_{2.6}$: (1) 0.18, (2) 0.25, (3) 0.43, (4) 0.61, (5) 0.65, (6) 0.70; $^{3.3}S3_{3.0}$: (1) 0.09, (2) 0.22, (3) 0.30, (4) 0.48, (5) 0.56, (6) 0.68, $^{1.8}S4_{4.6}$: (1) 0.089, (2) 0.15, (3) 0.22, (4) 0.30, (5) 0.38, (6) 0.45; $^{1.8}S5_{2.1}$: (1) 0.07, (2) 0.16, (3) 0.34, (4) 0.50, (5) 0.64. (6) 0.72; $^{0.4}S6_{2.9}$: (1) 0.0006, (2) 0.0008, (3) 0.009, (4) 0.013, (5) 0.014, (6) 0.018. Dashed lines represent response controlled by hindered diffusion.

Table SI-1: Apparent heterogeneous first-order rate constants k_{eff} derived from normalized pseudo first order rate constants κ for the reduction of photoexcited D149 by I^- for D149-

sensitized ZnO photoelectrochemical electrodes of l and [D^o]. (a) For varying [I_3^-]* at a fixed $J_{h\nu}$ = 9.1 × 10^{-9} mol cm^{-2} s^{-1} and (b) for varying $J_{h\nu}$ at fixed [I_3^-]* = 0.124 mM. Other parameters D (I_3^-) = 1.37 × 10^{-5} cm^2 s^{-1}, r_T = 12.5 μm, RG = 10, $k_{eff} = \kappa D/r_T$.

(a) For varying [I_3^-]*

[I_3^-]* / mM	k_{eff} / 10^{-3} cm s^{-1}					
	$^{1.3}S1_{1.2}$	$^{2.3}S2_{2.6}$	$^{3.3}S3_{3.0}$	$^{1.8}S4_{4.6}$	$^{1.8}S5_{2.1}$	$^{0.4}S6_{2.9}$
0.057	23.02	12.93	7.23	4.33	8.11	0.214
0.124	10.3	8.22	5.48	3.11	6.58	0.165
0.248	5.48	4.82	4.46	1.97	4.60	0.097
0.687	3.07	3.12	2.73	1.02	3.02	0.073
1.24	2.41	2.63	2.07	0.621	1.25	0.0099
2.01	2.26	2.41	1.32	0.212	0.93	0.007

(b) For varying LED intensity

$J_{h\nu}$ / 10^{-9} mol cm^2 s^{-1}	k_{eff} / 10^{-3} cm s^{-1}					
	$^{1.3}S1_{1.2}$	$^{2.3}S2_{2.6}$	$^{3.3}S3_{3.0}$	$^{1.8}S4_{4.6}$	$^{1.8}S5_{2.1}$	$^{0.4}S6_{2.9}$
25.5	9.96	7.67	7.45	4.93	7.85	0.198
15.1	9.10	7.12	6.14	4.16	6.98	0.157
9.10	8.10	6.74	5.22	3.31	5.44	0.138
4.50	4.77	4.71	3.30	2.39	3.71	0.093
1.70	2.78	2.74	2.41	1.64	1.70	0.0091
0.982	1.57	1.99	1.03	0.97	0.82	0.0071

SI 3. Complete derivation of SECM model for dye regeneration

The following reaction mechanism for dye regeneration is widely accepted: We assumed similar molecular mechanism of dye regeneration in D149-sensitzed ZnO and N179/TiO_2. Therefore, using D149-sensitzed ZnO electrode the model developed for steady state SECM experiments in the feedback mode.

$$D/ZnO + h\nu \xrightarrow{\phi_{h\nu}} D^*/ZnO \quad \text{(SI-9)}$$

$$D^*/ZnO \xrightarrow{k_{inj}} D^+/ZnO + e^-_{CB}(ZnO) \quad \text{(SI-10)}$$

$$D^+/ZnO + I^- \xrightarrow{k_1} [D^{\cdots}I]^-/ZnO \quad \text{(SI-11)}$$

$$[D^{\cdots}I]/ZnO + I^- \xrightarrow{k_2} D/ZnO + I_2^{-\bullet} \quad \text{(SI-12)}$$

$$2\, I_2^{-\bullet} \xrightarrow{k_3} I_3^- + I^- \quad \text{(SI-13)}$$

Steady state for $[D^*]$

$$\frac{\partial[D^*]}{\partial t} = 0 = \phi_{h\nu} J_{h\nu}[D] - k_{inj}[D^*] \quad \text{(SI-14)}$$

$$\frac{[D]}{[D^*]} = \frac{k_{inj}}{\phi_{h\nu} J_{h\nu}} \quad \text{(SI-15)}$$

Steady state for $[D^{\cdots}I]$

$$\frac{\partial[D\cdots I]}{\partial t} = 0 = k_1[D^+][I^-]_S - k_2[D\cdots I][I^-]_S = k_1[D^+] - k_2\left[D\cdots I\right] \quad \text{(SI-16)}$$

$$\frac{[D\cdots I]}{[D^+]} = \frac{k_1}{k_2} \quad \text{(SI-17)}$$

Diffusion limited tip current (n = 2) for reduction of one I_3^-

$$i_{\mathrm{T,lim}} = 8FD[\mathrm{I_3^-}]^* r_{\mathrm{T}} I_{\mathrm{T}}(L) \tag{SI-18}$$

Steady state for $[\mathrm{D^+}]$

$$\frac{\partial[\mathrm{D^+}]}{\partial t} = 0 = k_{\mathrm{inj}}[\mathrm{D^*}] - k_1[\mathrm{D^*}][\mathrm{I^-}]_{\mathrm{S}} \tag{SI-19}$$

$$\frac{[\mathrm{D^+}]}{[\mathrm{D^*}]} = \frac{k_{\mathrm{inj}}}{k_1[\mathrm{I^-}]_{\mathrm{S}}} \tag{SI-20}$$

Combining (SI-17) with (SI-20)

$$\frac{[\mathrm{D\cdots I}]}{[\mathrm{D^*}]} = \frac{k_{\mathrm{inj}}}{k_2[\mathrm{I^-}]_{\mathrm{S}}}$$

Mass balance for the total dye content

$$\begin{aligned}[\mathrm{D^0}] &= [\mathrm{D}] + [\mathrm{D^+}] + [\mathrm{D^*}] + [\mathrm{D\cdots I}] \\ &= [\mathrm{D^*}]\left(\frac{[\mathrm{D}]}{[\mathrm{D^*}]} + \frac{[\mathrm{D^+}]}{[\mathrm{D^*}]} + \frac{[\mathrm{D\cdots I}]}{[\mathrm{D^*}]} + 1\right)\end{aligned} \tag{SI-21}$$

Steady state expression for ratio of $[\mathrm{D^0}]$

$$[\mathrm{D^0}] = [\mathrm{D^*}]\left(\frac{k_{\mathrm{inj}}}{\phi_{h\nu} J_{h\nu}} + \frac{k_{\mathrm{inj}}}{k_1[\mathrm{I^-}]_{\mathrm{S}}} + \frac{k_{\mathrm{inj}}}{k_2[\mathrm{I^-}]_{\mathrm{S}}} + 1\right) \tag{SI-22}$$

$$[\mathrm{D^*}] = \frac{[\mathrm{D^0}]}{\frac{k_{\mathrm{inj}}}{\phi_{h\nu} J_{h\nu}} + \frac{k_{\mathrm{inj}}}{k_1[\mathrm{I^-}]_{\mathrm{S}}} + \frac{k_{\mathrm{inj}}}{k_2[\mathrm{I^-}]_{\mathrm{S}}} + 1} \tag{SI-23}$$

The kinetic current i_{k} is expressed from the iodide concentration $[\mathrm{I^-}]_{\mathrm{s}}$ at the surface of the dye-sensitized electrode, the volume concentration of the oxidized dye $[\mathrm{D^+}]$. The current is generated over the thickness of the porous film l_{porous} and the area of the electrode A. The experimentally accessible dye loading Γ_{D} (total dye content per geometric area $\Gamma_{\mathrm{D}} = [\mathrm{D}]\, l_{\mathrm{porous}}$).

$$i_K = nFA\left(k_1 l_{porous}[D^+][I^-]_S\right) = nFA\left(k_1 \Gamma_{D^+}[I^-]_S\right) \quad \text{(SI-24)}$$

Substitution of the bracketed term using the Bodenstein principle for the steady state experiment (SI-19) and introducing the dye loading yields $k_{inj}\Gamma_{D^*} = k_1\Gamma_{D+}[I^-]_S$ (n = 1)

$$i_K = FAk_{inj}\Gamma_{D^*} \quad \text{(SI-25)}$$

Substitute the expression for Γ_{D^*} from mass balance analogous to eq. SI-23.

$$i_K = FAk_{inj}\frac{\Gamma_{D^o}}{\frac{k_{inj}}{\phi_{h\nu}J_{h\nu}} + \frac{k_{inj}}{k_1[I^-]_S} + \frac{k_{inj}}{k_2[I^-]_S} + 1} \quad \text{(SI-26)}$$

$$i_K = FA\Gamma_{D^o}\frac{\phi_{h\nu}J_{h\nu}k_1k_2[I^-]_S k_{inj}}{k_1k_2[I^-]_S k_{inj} + k_{inj}\phi_{h\nu}J_{h\nu}k_2 + k_{inj}\phi_{h\nu}J_{h\nu}k_1 + k_1k_2\phi_{h\nu}J_{h\nu}[I^-]_S} \quad \text{(SI-27)}$$

$$\frac{1}{i_K} = \frac{1}{FA\Gamma_{D^o}\phi_{h\nu}J_{h\nu}} + \frac{1}{FA\Gamma_{D^o}k_1[I^-]_S} + \frac{1}{FA\Gamma_{D^o}k_2[I^-]_S} + \frac{1}{FA\Gamma_{D^o}k_{inj}} \quad \text{(SI-28)}$$

Simplifying the expression for light absorption, electron injection and dye regeneration by summarizing the steps using $\left(k_{h\nu,\text{eff}}\right)^{-1} = \left(k_{\text{inj}}\right)^{-1} + \left(\phi_{h\nu}J_{h\nu}\right)^{-1} \approx \left(\phi_{h\nu}J_{h\nu}\right)^{-1}$ and $\left(k_{ox}^{'}\right)^{-1} = \left(k_1\right)^{-1} + \left(k_2\right)^{-1}$

$$\frac{1}{i_K} = \frac{1}{FA\Gamma_{D^o}k_{h\nu,\text{eff}}} + \frac{1}{FA\Gamma_{D^o}k_{ox}^{'}[I^-]_S} \quad \text{(SI-29)}$$

The limiting substrate current would be reached if the iodide concentration is 3 time the triiodide concentration, i.e. all iodide formed at the tip is available to the sample without any dilution, $[I^-]_S = 3[I_3^-]$*

$$\frac{1}{i_{\mathrm{K,lim}}} = \frac{1}{FA\Gamma_{\mathrm{D^o}} k_{h\nu,\mathrm{eff}}} + \frac{1}{3FA\Gamma_{\mathrm{D^o}} k_{\mathrm{ox}}^{'}[\mathrm{I_3^-}]^*} \tag{SI-30}$$

Normalizing the limiting substrate by $i_{\mathrm{T},\infty}$ yields $I_{\mathrm{K,lim}}$

$$I_{\mathrm{K,lim}} = \frac{i_{\mathrm{K,lim}}}{i_{\mathrm{T},\infty}} = \frac{i_{\mathrm{K,lim}}}{4nFD[\mathrm{I_3^-}]^* r_{\mathrm{T}}},\ n = 2 \text{ at the tip for } \mathrm{I_3^-},\ A \approx \pi r_{\mathrm{T}}^2 \tag{SI-31}$$

$$\frac{1}{I_{\mathrm{S}}} = \frac{i_{\mathrm{T},\infty}}{i_{\mathrm{K,lim}}} + \frac{1}{I_{\mathrm{T,cond}}} + \frac{1}{I_{\mathrm{el,lim}}},\ \frac{1}{I_{\mathrm{el,lim}}} \approx 0 \tag{SI-32}$$

$$\begin{aligned} \frac{1}{I_{\mathrm{S}}} &= \frac{1}{I_{\mathrm{T,cond}}} + \frac{8FD[\mathrm{I_3^-}]^* r_{\mathrm{T}}}{F\pi r_{\mathrm{T}}^2 \Gamma_{\mathrm{D^o}} \phi_{h\nu} J_{h\nu}} + \frac{8FD[\mathrm{I_3^-}]^* r_{\mathrm{T}}}{3F\pi r_{\mathrm{T}}^2 \Gamma_{\mathrm{D^o}} k_{\mathrm{ox}}^{'}[\mathrm{I_3^-}]^*} \\ &= \frac{1}{I_{\mathrm{T,cond}}} + \frac{8D[\mathrm{I_3^-}]^*}{\pi r_{\mathrm{T}} \Gamma_{\mathrm{D^o}} \phi_{h\nu} J_{h\nu}} + \frac{8D}{3\pi r_{\mathrm{T}} \Gamma_{\mathrm{D^o}} k_{\mathrm{ox}}^{'}} \end{aligned} \tag{SI-33}$$

Comparison to uncomplicated first order process at the sample[3]

$$\begin{aligned} &\frac{1}{I_{\mathrm{S}}} = \frac{1}{I_{\mathrm{T,cond}}} + \frac{4}{\pi}\frac{1}{\kappa},\quad \kappa = k_{\mathrm{eff}}\frac{r_{\mathrm{T}}}{D} \\ &\frac{1}{I_{\mathrm{S}}} = \frac{1}{I_{\mathrm{T,cond}}} + \frac{4D}{\pi r_{\mathrm{T}}}\frac{1}{k_{\mathrm{eff}}} \end{aligned} \tag{SI-34}$$

$$\frac{1}{I_{\mathrm{S}}} = \frac{1}{I_{\mathrm{T,cond}}} + \frac{4D}{\pi r_{\mathrm{T}}}\left[\frac{2[\mathrm{I_3^-}]^*}{\Gamma_{\mathrm{D^o}} \phi_{h\nu} J_{h\nu}} + \frac{2}{3\Gamma_{\mathrm{D^o}} k_{\mathrm{ox}}^{'}}\right] \tag{SI-35}$$

$$\frac{1}{k_{\mathrm{eff}}} = \frac{2[\mathrm{I_3^-}]^*}{\Gamma_{\mathrm{D^o}} \phi_{h\nu} J_{h\nu}} + \frac{2}{3\Gamma_{\mathrm{D^o}} k_{ox}^{'}} \tag{SI-36}$$

$$k_{\mathrm{eff}} = \frac{3\Gamma_{\mathrm{D^o}} \phi_{h\nu} J_{h\nu} k_{ox}^{'}}{6k_{\mathrm{ox}}^{'}[\mathrm{I_3^-}]^* + 2\phi_{h\nu} J_{h\nu}} \tag{SI-37}$$

SI 4. Dye regeneration kinetic model of reaction order 3/2 with respect [I$^-$], Ref [4]

a) b)

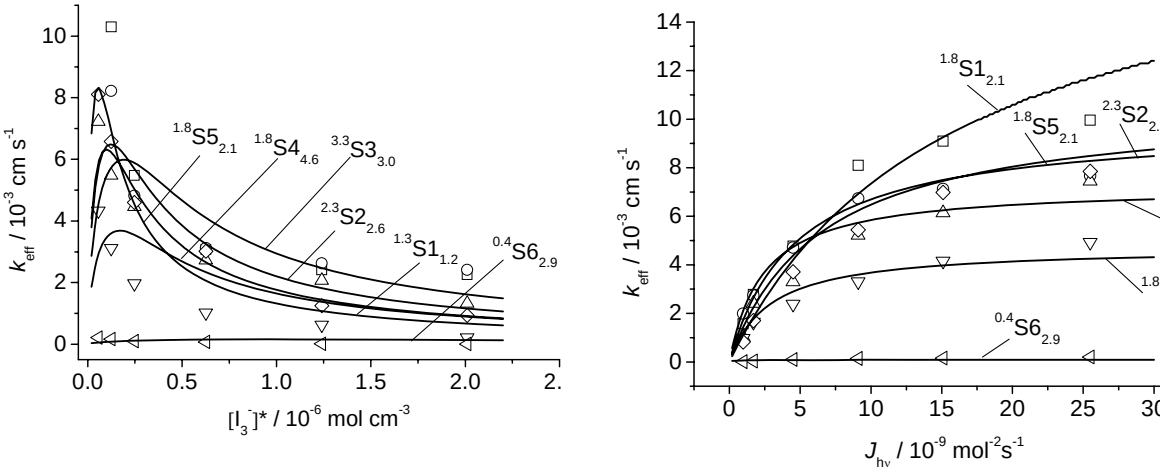


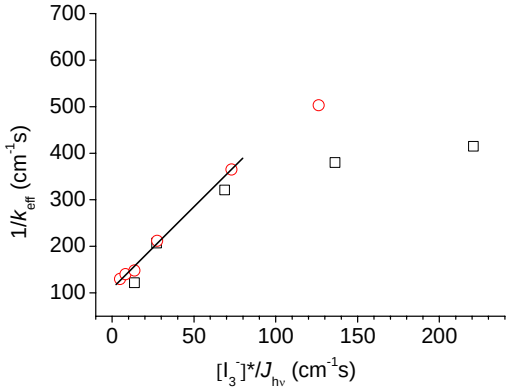
Figure SI-3. Plot of (a) k_{eff} *vs.* $[I_3^-]^*$ and (b) k_{eff} *vs.* $J_{h\nu}$ for six different D149-sensitized ZnO photoelectrodes with systematically varied thickness and dye loading. Symbols correspond to experimental k_{eff} and lines are theoretical fittings of the model described in Ref [4] [eq. 18]. The best fit of experimental and theoretical response of k_{eff} yielded a single value $\varphi_{h\nu}$ of 2.29×10^7 cm^2 mol^{-1} and varying k_{ox} by fitting the data for all electrodes in one set shown. The corresponding k_{ox} values are given in Table

Table SI-2: The k_{ox} obtained using the D149 regeneration reaction rate law of order 3/2.

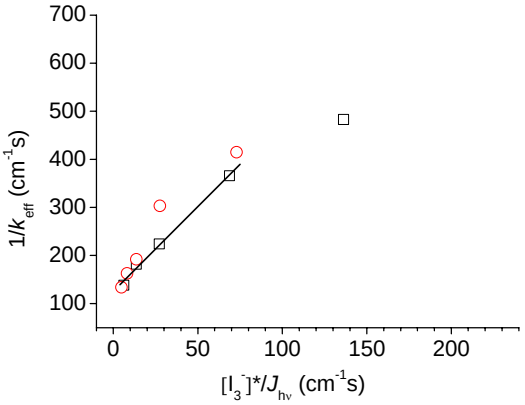
Sample	$^{1.3}S1_{1.2}$	$^{2.3}S2_{2.6}$	$^{3.3}S3_{3.0}$	$^{1.8}S4_{4.6}$	$^{1.8}S5_{2.1}$	$^{0.4}S6_{2.9}$
k_{ox} / ($cm^{9/2}$ $mol^{-3/2}$ s^{-1})	1.59×10^9	4.65×10^8	2.40×10^8	2.87×10^8	6.45×10^8	2.23×10^7

SI 5: The k'_{ox} values obtained for D149/ZnO from the linear fit SECM kinetic model (eq. 12) in the manuscript.

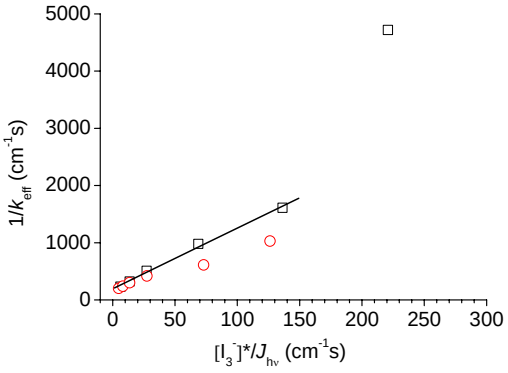
$^{2.3}S2_{2.6}$



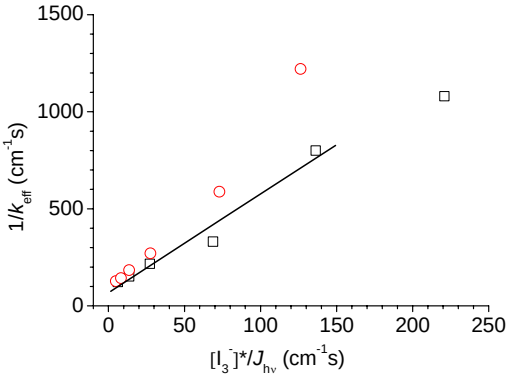
$^{3.3}S3_{3.0}$



$^{1.8}S4_{4.6}$



$^{1.8}S5_{2.1}$



$^{0.4}S6_{2.9}$

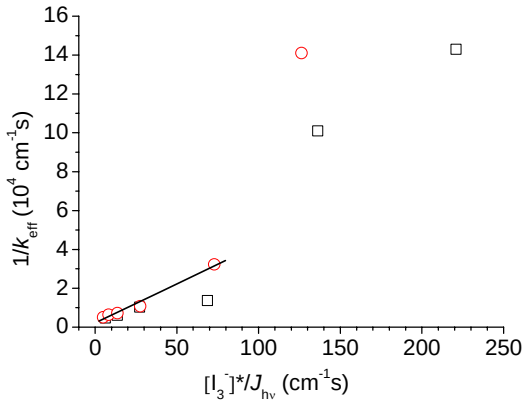


Figure SI 4. Plot of $1/k_{eff}$ *vs.* $[I_3^-]^*/J_{h\nu}$ for sample $^{2.3}S2_{2.6}$ - $^{0.4}S6_{2.9}$ showing a linear fit of the data at lower $[I_3^-]^*/J_{h\nu}$ ratio.

Table SI-3: The k'_{ox} obtained from the linear fit in Figure SI 4 for kinetic model eq. (12) in manuscript

Sample	$^{2.3}S2_{2.6}$	$^{3.3}S3_{3.0}$	$^{1.8}S4_{4.6}$	$^{1.8}S5_{2.1}$	$^{0.4}S6_{2.9}$
k'_{ox} / (mol^{-1} cm^3 s^{-1})	2.64×10^5	1.61×10^5	1.89×10^5	5.42×10^5	7.56×10^4

References

1. R. Cornut and C. Lefrou, *J. Electroanal. Chem.*, 2008, **621**, 178-184.
2. J. L. Amphlett and G. Denuault, *J. Phys. Chem. B*, 1998, **102**, 9946-9951.
3. C. Wei, A. J. Bard and M. V. Mirkin, *J. Phys. Chem.*, 1995, **99**, 16033-16042.
4. Y. Shen, K. Nonomura, D. Schlettwein, C. Zhao and G. Wittstock, *Chem. Eur. J.*, 2006, **12**, 5832-5839.