Effect of TiO₂ photoanodes morphology and dye structure on dye-regeneration kinetics investigated by scanning electrochemical microscopy

Supporting Material

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SM-1 Experimental details

Table S1 lists the details of the TiO_2 photoanodes sensitized with the all-organic indoline dyes D358 and DN216.

Table S1. TiO₂-sensitized photoanodes with variable porous layer thickness, compact blocking layer, passivation by TiO₂-NPs, and average dye loading $\Gamma_{\rm D}$.

Sample name	lporous / µm	BL / µm	TiO ₂ NPs	Γ _D / (10 ⁻⁸ mol cm-2)
A-DN216	3	0.682	No	1.22
D- DN216	3	0.716	Yes	1.12
B-DN216	4	0.661	No	1.81
E-DN216	4	0.769	Yes	1.34
C-DN216	6	0.584	No	2.31
F- DN216	6	0.863	Yes	2.27
A-D358	3	0.682	No	1.07
D-D358	3	0.716	Yes	1.21
B-D358	4	0.661	No	1.45
E-D358	4	0.769	Yes	1.63
C-D358	6	0.584	No	2.36
F-D358	6	0.863	Yes	2.30

SM-2 Approach curves to photoanodes

The experimental approach curves were fitted with the theory of Cornut and Lefrou 1 for a first order, finite and irreversible kinetic mediator regeneration with the model in Eq. (S1).

$$I_{\rm T}(L,\kappa,RG) = I_{\rm T}^{\rm cond}\left(L + \frac{1}{\kappa},RG\right) + \frac{l_{\rm T}^{\rm ins}(L,RG) - 1}{(1 + 2.47\,RG^{0.31}L\,\kappa)(1 + L^{0.006\,RG + 0.113}\kappa^{-0.0236\,RG + 0.91})}$$
(S1)

 $I_{\rm T} = i_{\rm T}/i_{{\rm T},\infty}$ is the dimensionless microelectrode current obtained from the microelectrode current $i_{\rm T}$ normalised for the current at infinite distance from the sample $i_{{\rm T},\infty}$. The dimensionless distance $L = d/r_{\rm T}$ is obtained by normalizing the microelectrode-sample distance d by the microelectrode radius $r_{\rm T}$. The dimensionless geometric RG factor is the ratio between the radius of the insulating glass sheath of the microelectrode and the radius of the active area ($RG = r_{\rm glass}/r_{\rm T}$). In Eq. (S1), $I_{\rm T}^{\rm cond}$ [Eq. (S2)] and $I_{\rm T}^{\rm ins}$ [Eq. (S3)] are the normalised current at the microelectrode for hindered diffusion ($\kappa = 0$) and for diffusion-controlled mediator recycling ($\kappa = \infty$), respectively.

$$I_{\rm T}^{\rm cond}\left(L+\frac{1}{\kappa},RG\right) = \alpha(RG) + \frac{1}{2\beta(RG)\xi\left(L+\frac{1}{\kappa}\right)} + \left(1-\alpha(RG)-\frac{1}{2\beta(RG)}\right)\xi\left(L+\frac{1}{\kappa}\right)$$
(S2)

$$I_{\rm T}^{\rm ins}(L,RG) = \frac{\frac{2.08}{RG^{0.358}} \left(L - \frac{0.145}{RG}\right) + 1.585}{\frac{2.08}{RG^{0.358}} \left(L + 0.0023\,RG\right) + 1.57 + \frac{\ln RG}{L} + \frac{2}{\pi RG} \ln\left(1 + \frac{\pi RG}{2L}\right)}$$
(S3)

 α and β in Eq. (S-2) are respectively calculated with Eqs. (S4) and (S5).

$$\alpha(RG) = ln2 + ln2\left(1 - \frac{2}{\pi}\arccos\left(\frac{1}{RG}\right)\right) - ln2\left(1 - \left(\frac{2}{\pi}\arccos\left(\frac{1}{RG}\right)\right)^2\right)$$
(S4)

$$\beta(RG) = 1 + 0.639 \left(1 + \frac{2}{\pi} \arccos\left(\frac{1}{RG}\right) \right) - 0.186 \left(1 - \left(\frac{2}{\pi} \arccos\left(\frac{1}{RG}\right) \right)^2 \right)$$
(S5)

For each approach curve, a normalized heterogeneous rate constant κ was obtained from the fit having $r_{\rm T}$, *RG* and the smallest distance of approach d_0 as fixed parameters. They were obtained from an independent approach curve to glass and fitting to Eq. (S3). Using the bulk diffusion coefficient *D* and $r_{\rm T}$, the effective heterogeneous rate constant $k_{\rm eff}$ [cm s⁻¹] was obtained from Eq. (2) of the main manuscript. The numerical values of $k_{\rm eff}$ are reported in **SM-4**.

Figure S1 shows the experimental approach curves recorded over D358/TiO₂ and Figure S2 recorded over DN216/TiO₂ photoanodes of 3 μ m, 4 μ m, and 6 μ m, with and without TiO₂-NPs passivation, irradiated with eight different photon fluxes J_{hv} .



Figure S1. Approach curves of D358/TiO₂ photoanodes with l_{porous} thickness A = 3 µm, B = 4 µm, C = 6 µm, and D, E and F respectively like A, B and C with TiO₂-NPs passivation. The experimental approach curves (•) are recorded for 0.1 mM [Co(bpy)₃]³⁺ bulk concentration under variable photon fluxes J_{hv} in 10⁻⁷ mol cm⁻² s⁻¹ as dark (0.0 mol cm⁻² s⁻¹), (1) 0.05, (2) 1.2, (3) 0.19, (4) 0.24, (5) 0.32, (6) 0.51, (7) 0.64, (8) 1.93.



Figure S2. Approach curves of DN216/TiO₂ photoanodes with l_{porous} thickness A = 3 µm, B = 4 µm, C = 6 µm, and D, E and F respectively like A, B and C with TiO₂-NPs passivation. The experimental approach curves (•) are recorded for 0.1 mM [Co(bpy)₃]³⁺ bulk concentration under variable photon fluxes J_{hv} in 10⁻⁷ mol cm⁻² s⁻¹ as dark (0.0 mol cm⁻² s⁻¹), (1) 0.05, (2) 1.2, (3) 0.19, (4) 0.24, (5) 0.32, (6) 0.51, (7) 0.64, (8) 1.93.

SM-3 Determination of the mediator diffusion coefficient in the bulk solution

The diffusion coefficient *D* of 0.1 mM [Co(bpy)₃](PF₆)₃ in 0.1 M TBAPF₆ in acetonitrile was calculated from diffusion-controlled steady-state currents at the microelectrode at a potential of E_T = -0.15 V of a cyclic voltammogramm (Figure S3) at a gold microelectrode of r_T = 28.85 µm. This potential is also used to record the approach curves. Around this potential, the steady-state current i_T is reached and defined by the Eq. (S6)

$$i_{\rm T} = 4 \ n \ F \ D \ c^* \ r_{\rm T},\tag{S6}$$

where n = 1 is the number of electrons transferred per molecule, F = 96485 As mol⁻¹ is the Faraday constant, $D [\text{cm}^2 \text{ s}^{-1}]$ is the diffusion coefficient, $c^* = 1 \ 10^{-7}$ mol cm⁻³ is the bulk concentration of $[\text{Co}(\text{bpy})_3]^{3+}$, $r_T = 0.002885$ cm is the radius of the microelectrode. The D calculated for the $[\text{Co}(\text{bpy})_3]^{3+}$ in the bulk as 8.3×10^{-6} cm² s⁻¹ is in line with literature data [2,3] The error margin of this value is about 10%.



Figure S3. Cyclic voltammetry of a Au microelectrode ($r_T = 28.85$) in a potential range of 0.02 to -0.18 V vs. Pt qua-reference electrode, v = 20 mV s⁻¹, in 0.1 mM [Co(bpy)₃](PF₆)³⁺ + 0.1 M TBAPF₆ in acetonitrile.

SM-4 Details of the fitting of SECM approach curves

From the κ values extracted from each approach curve a effective pseudo-first order rate constant $k_{eff} = \kappa D/r_T$ was calculated using the values of $r_T = 24.85 \,\mu\text{m}$ and the diffusion coefficient *D* calculates in **SM-3**. The k_{eff} values are reported in Table S2 for D358/TiO₂ photoanodes with and without passivation, and in Table S3 DN216/TiO₂ photoanodes with and without passivation.

mM [Co(bpy) ₃] ³⁺ with bulk diffusion coefficient $D = 8.34 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$							
Sample and dye	J_{hv} / 10 ⁻⁷ mol cm ⁻² s ⁻¹	К	<i>k</i> _{eff} / 10 ⁻³ cm s ⁻¹	Sample and dye	J_{hv} / 10 ⁻⁷ mol cm ⁻² s ⁻¹	К	<i>k</i> _{eff} / 10 ⁻³ cm s ⁻¹
	0	0.055	0.18		0	0.040	0.13
	0.054	0.060	0.20		0.064	0.320	1.07
	0.116	0.070	0.23		0.130	0.400	1.34
	0.180	0.085	0.29		0.195	0.450	1.51
A-D358	0.245	0.100	0.34	D-D358	0.259	0.500	1.68
	0.310	0.120	0.40		0.324	0.520	1.75
	0.506	0.150	0.50		0.519	0.620	2.08
	0.631	0.160	0.54		0.649	0.650	2.18
	1.928	0.180	0.60		1.947	0.880	2.95
	0	0.050	0.17	E-D358	0	0.060	0.20
	0.055	0.090	0.30		0.042	0.080	0.27
	0.112	0.105	0.35		0.104	0.110	0.37
	0.177	0.120	0.40		0.171	0.120	0.40
B-D358	0.240	0.150	0.50		0.233	0.155	0.52
	0.307	0.185	0.62		0.304	0.210	0.70
	0.502	0.185	0.62		0.497	0.230	0.77
	0.628	0.230	0.77		0.622	0.270	0.91
	1.924	0.245	0.82		1.920	0.420	1.41
	0	0.070	0.23		0	0.075	0.25
C-D358	0.038	0.085	0.29	F-D358	0.042	0.100	0.34
	0.103	0.105	0.35		0.104	0.080	0.27
	0.167	0.130	0.44		0.171	0.090	0.30
	0.231	0.130	0.44		0.233	0.075	0.25
	0.297	0.145	0.49		0.304	0.095	0.32
	0.493	0.170	0.57		0.497	0.105	0.35
	0.621	0.220	0.74		0.622	0.110	0.37
	1.916	0.200	0.67		1.920	0.170	0.57

Table S2. Fitted κ and calculated k_{eff} per J_{hv} for the D358/TiO₂ of thickness A = 3 μ m, B = 4 μ m, C = 6 μ m and with TiO₂-NPs (D = 3 μ m, E = 4 μ m, F = 6 μ m), investigated with 0.1 mM [Co(bpy)₃]³⁺ with bulk diffusion coefficient $D = 8.34 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$

Sample	J_{hv} /		k _{eff} /	Sample	J _{hv} /		k _{eff} /
and dye	10 ⁻⁷ mol cm ⁻² s ⁻¹	K	10 ⁻³ cm s ⁻¹	and dye	10 ⁻⁷ mol cm ⁻² s ⁻¹	К	10 ⁻³ cm s ⁻¹
A-DN216	0	0.040	0.13		0	0.050	0.17
	0.064	0.230	0.77		0.045	0.070	0.23
	0.129	0.365	1.23		0.107	0.070	0.23
	0.194	0.440	1.48		0.175	0.090	0.30
	0.236	0.110	0.37	D-DN216	0.238	0.090	0.30
	0.303	0.110	0.37		0.306	0.120	0.40
	0.499	0.140	0.47		0.499	0.130	0.44
	0.627	0.160	0.54		0.626	0.150	0.50
	1.920	0.230	0.77		1.921	0.270	0.91
	0	0.065	0.22	E-DN216	0	0.060	0.20
	0.064	0.280	0.94		0.065	0.620	2.08
	0.108	0.130	0.44		0.130	0.780	2.62
	0.171	0.120	0.40		0.194	0.143	0.48
B-DN216	0.237	0.130	0.44		0.259	0.230	0.77
	0.304	0.130	0.44		0.324	0.360	1.21
	0.498	0.140	0.47		0.519	0.450	1.51
	0.628	0.160	0.54		0.649	0.850	2.85
	1.880	0.175	0.59				
	0	0.080	0.27	F-DN216	0	0.110	0.37
C-DN216	0.053	0.080	0.27		0.065	0.450	1.51
	0.116	0.080	0.27		0.130	0.590	1.98
	0.185	0.070	0.23		0.194	0.650	2.18
	0.244	0.110	0.37		0.259	0.665	2.23
	0.315	0.150	0.50		0.324	0.730	2.45
	0.510	0.220	0.74		0.519	0.750	2.52
	0.635	0.250	0.84		0.649	0.750	2.52
	1.929	0.280	0.94		1.944	0.800	2.69

Table S3. Fitted κ and calculated k_{eff} per J_{hv} for the DN216/TiO₂ of thickness A = 3 μ m, B = 4 μ m, C = 6 μ m and with TiO₂-NPs (D = 3 μ m, E = 4 μ m, F = 6 μ m), investigated with 0.1 mM [Co(bpy)₃]³⁺ with bulk diffusion coefficient $D = 8.34 \times 10^{-6}$ cm² s⁻¹

SM-5 Fitting of the dependence of *k*_{eff} on passivation and dye nature

The k_{eff} data for the samples with and without passivation and sensitized with the D358 or the DN216 dye molecules are fitted for different light intensitis J_{hv} to equation (3) of the main manuscript. The results are shown in Figure S4.



Figure S4. Non-linear fit of k_{eff} as function of J_{hv} for the calculation of k_{ox} and ϕ_{hv} of (a) D358/TiO₂ and (b) DN216/TiO₂ of (\Box) 3 µm, (\bigcirc) 4 µm and (\triangle) 6 µm fitted with dotted lines, and photoanodes with TiO₂ –NPs (\blacksquare) 3 µm, (\bigcirc) 4 µm and (\triangle) 6 µm fitted with solid lines. Two DN216-sensitized samples show diversified behavior for low and high photon fluxes, A (3 µm, \blacksquare low and \Box high photon fluxes) and E (4 µm with TiO₂ –NPs, \bigcirc low and \bigcirc high photon fluxes).

The fit yields a value of k_{ox} for each dye/TiO₂ photoanode, with or without passiation, and of different thicknesses. Two samples, the DN216/TiO₂ of 3 µm and the passivated of 4 µm, show a very scattered behaiour in terms of k_{eff} for higher J_{hv} values. Therefore, for the fitting only the k_{eff} values at small J_{hv} values.

All the k_{ox} values are plotted in Figure 3 of the main manuscript. The k_{ox} and ϕ_{hv} values calculated from the non –linear fit are reported in Table S4 for the D358-sensitized samples and in Table S5 for the DN216-sensitized samples. An scattered behaviour is detected for the sample D_DN216/TiO₂ on which was measured a very small k_{ox} , probably due to uncompleted sensitization.

Table S4. Table of ϕ_{hv} and k_{ox} values of D358/TiO₂ photoanodes bare (A = 3 µm, B = 4 µm, C = 6 µm) and with TiO₂-NPs (D = 3 µm, E = 4 µm, F = 6 µm), tested with 0.1 mM [Co(bpy)₃]³⁺ under variable J_{hv} .

Sample	$TiO_2/\mu m$	Passivation	$\phi_{\rm hv/}$ 10 ⁴ cm s ⁻¹	$k_{\rm ox}/$ 10 ⁵ mol ⁻¹ cm ³ s ⁻¹
A-D358	3	no	25.3	0.66
D-D358	3	yes	238.6	2.07
B-D358	4	no	39.5	0.49
E-D358	4	yes	28.4	0.84
C-D358	6	no	37.6	0.25
F-D358	6	yes	8.5	0.30

Table S5. Table of ϕ_{hv} and k_{ox} values of DN216/TiO₂ photoanodes bare (A = 3 µm, B = 4 µm, C = 6 µm) and with TiO₂-NPs (D = 3 µm, E = 4 µm, F = 6 µm), tested with 0.1 mM [Co(bpy)₃]³⁺ under variable J_{hv} .

•				
Sample	$TiO_2/\mu m$	Passivation	$\phi_{\rm hv}/$ 10 ⁴ cm s ⁻¹	$k_{\rm ox}/$ 10 ⁵ mol ⁻¹ cm ³ s ⁻¹
A-DN216	3	no	244.7	1.63
D-DN216	3	yes	25.9	(0.63)
B-DN216	4	no	19.9	0.62
E-DN216	4	yes	687.0	1.99
C-DN216	6	no	17.6	0.37
F-DN216	6	yes	170.9	1.23

SM-6 Transient photocurrent

Figure S5 shows the transient photocurrents at the photoanodes $D358/TiO_2$ and $DN216/TiO_2$. The electrolyte was composed of 0.1 mM [Co(bpy)₃](PF₆)₃ in acetonitrile with 0.1 M TBAPF₆ as supporting electrolyte.



Figure S5. Transient photocurrents recorded at the (a) D358/ 4 μ m TiO₂ photoanodes, (b) like (a) but passivated, (c) DN216/ 4 μ m TiO₂ photoanodes, (d) like (c) but passivated. Ligh intensity in 10⁻⁸ mol cm⁻² s⁻¹ of (L1) 0.76, (L2) 1.51, (L3) 2.26, (L4) 3.01, (L5) 3.77, (L6) 6.02 and (L7) 7.52.

Reference

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