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Regenerator Dependent Photoinduced Desorption of a Dicarboxylated Cyanine Dye from the Surface of Single-Crystal Rutile

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A photon-initiated desorption of a dicarboxylated thiocarbocyanine dye from a dye-sensitized semiconducting oxide crystal has been observed when hydroquinone is used as a regenerator. No desorption was found under the same conditions when KI was used as the regenerator. Intermittent illumination experiments suggest that the oxidation products of the hydroquinone regenerator compete for dye adsorption sites. By comparing the photocurrent decay at both the dye monomer sensitization maximum and the dimer sensitization maximum, a rearrangement of monomer into dimer was observed. A kinetic model for the photocurrent decay as a function of desorption time was derived, and the desorption rate constants were obtained by fitting the experimental data to the model.

Introduction

Dye-sensitized solar cells (DSSC) have attracted interest due to a need for novel and inexpensive devices for solar energy conversion.¹ To date the most efficient dyes in these solar cells are a series of very stable Ru based complexes that sensitize a TiO₂ electrode.^{2,3} However, there are ongoing efforts to discover inexpensive and stable organic dye sensitizers as substitutes for the ruthenium complexes because of the scarcity of the metal and the advantage of higher extinction coefficients of the organic dyes.^{4–7} These substitutes for Ru dyes should also have a strong electronic coupling to the semiconductor and be strongly bound to the semiconductor surface.

Dyes with the possibility of binding to the oxide surface with multiple covalent linkages are the most useful for dye sensitized solar cells. This is a result of the “chelate effect” where the dissociation of a single binding site will not result in desorption of the dye molecule because of the high probability that two site binding can be reestablished either at the original or an adjacent binding site. Binding sites are presumed to be five coordinate Ti sites on the TiO₂ surface. Desorption of a chelated dye will only occur in the relatively unlikely event of dissociation of the second binding group before reattachment of the first group. We have previously studied the adsorption of the ruthenium based N3 dye (cis-di(thiocyanato)- bis(2,2'-bipyridyl -4,4'-dicarboxylate) ruthenium(II)) to single crystal anatase (101), (001) and rutile (100), (001) surfaces with atomically flat terraces.^{8–10} The kinetics of N3 adsorption was also studied on the four surfaces. The initial adsorption of the dye, accounting for 40–

70% of the maximum coverage, was very fast, probably diffusion controlled, followed by a slow adsorption step lasting tens of minutes where the adsorption kinetics could be fit with a Langmuir kinetic model. Although with four possible carboxylate surface binding groups the exact adsorption mechanism of N3 to oxide surfaces is complex and so the good fits of the adsorption rates to a simple Langmuir model was probably fortuitous especially considering the possible existence of dye aggregates¹¹

In the case of the dicarboxylated cyanine dyes studied herein, the adsorption mechanism probably consists of two steps: a fast initial binding of one carboxylate group with a subsequent attachment of the second group on a nearby five-coordinate Ti surface site, but due to the spacing of the carboxylate groups, not an adjacent binding site. At low dye coverages of the semiconductor surface, there is little competition for binding sites on the surfaces, and most dye molecules will be able to attach by more than one carboxylate group. However at high dye coverages, it is likely that many dyes will be attached by only one group due to a lack of uncovered nearby binding sites. These “one legged dyes” should be susceptible to desorption. Since high dye coverages are needed to optimize the performance of dye sensitized solar cells, desorption of the sensitizing dyes after adsorption onto TiO₂ surfaces needs to be minimized.

The exact binding method of the carboxylate group to the five coordinate Ti sites on the TiO₂ surface is the subject of debate in the literature. Studies exploring specific dye binding sites include an IR investigation by Nazeeruddin et al.¹² on the N-series of ruthenium-based dyes on nanocrystalline anatase, indicating that the attachment is via the carboxylic acid groups anchored in a bridging coordination mode. An attachment to the surface using the bridging bidentate mode was also seen to be the most stable binding model in theoretical studies of sodium formate on the anatase (101) surface.¹³ A previous study,¹⁴ using high-

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resolution X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption spectroscopy (NEXAFS), to analyze carboxylic acid adsorption on single-crystal rutile (110) indicated that the carboxylate groups bind to the TiO_2 surface with 4 equiv oxygens (two for each carboxylate) in monodentate fashion to the five coordinate Ti sites on the surface. An additional study¹⁵ of isonicotinic acid on the surface of rutile (110) corroborated the bridge-binding motif and proposed a model of the dye binding that favored dimerization where the molecules 'lean' toward each other. In this study the exact binding mode of the carboxylate group to the TiO_2 surface is not important to the analysis of the results.

We have made studies of the attachment of dyes to TiO_2 surfaces that employ an atomically flat rutile (100) single-crystal surface sensitized by structurally more simple organic dye molecules¹⁶ since we believe the use of atomically flat single crystals will make the binding mechanism more easily understood. Herein we report studies of the desorption and rearrangement of a dicarboxylated cyanine dye covalently bound to an atomically flat single-crystal rutile (100) surface and the effect of the identity of the regenerator on the desorption process.

Experimental Section

Rutile crystals with a (100) orientation were purchased from Commercial Crystal Laboratories, LTD, and atomically flat terraces were obtained on these surfaces as described earlier.¹⁷ Atomic force microscopy (AFM; Digital Instruments Nanoscope IIIA controller and a multimode SPM) was used to verify that the polished surfaces were flat and showed characteristic terraces. Silicon AFM tips from MikroMasch were used with a 40 N/m force constant and resonant frequency around 170 kHz.

The rutile (100) crystal was mounted as an electrode using Dexter Epoxy Patch with a Ga/In eutectic applied to the back of the crystal for an ohmic contact. After the epoxy set, the back and edges of the electrode were sealed with silicone rubber (RTV) and allowed to dry for a few hours. Prior to photoelectrochemical experiments, the crystal was polished with a soft polishing cloth using 20 nm colloidal silica and cleaned with 0.2 M NaOH, followed by a MilliQ 18 M Ω water rinse. The electrodes were then cleaned with photooxidation by illuminating at 0.6 V vs Ag/AgCl in 10 mM NaClO_4 for 5 min using an Oriel 150 W Xe lamp followed by a rinse with ACS grade ethanol. To allow more UV illumination to reach the sample surface, a quartz electrochemical cell was used.

A dicarboxylated thiacyanine dye G15, with a structure shown in Figure 1, was dissolved in ethanol to make a series of different solutions with varying concentrations from which dyes were adsorbed to the cleaned crystal surface. The apparatus for photocurrent spectra measurements was the same as reported previously.¹⁰ The photocurrent as a function of time was collected at several fixed wavelengths (574 nm or 530 nm) using the same apparatus. A three-electrode configuration with a platinum counter electrode and a Ag/AgCl reference electrode was used in the electrochemical cell. Fisher optima grade acetonitrile containing Fluka, electrochemical grade, 10 mM tetrabutylammonium perchlorate was used as a supporting electrolyte with 4.5 mM hydroquinone or 2 mM KI added as supersensitizer or regenerator.

Results

The molecular structure of G15, its solution absorption spectrum, and photocurrent action spectrum adsorbed onto a rutile (100) surface are shown in Figure 1. The solution absorption peaks at 562 nm with a shoulder on the blue side of the main

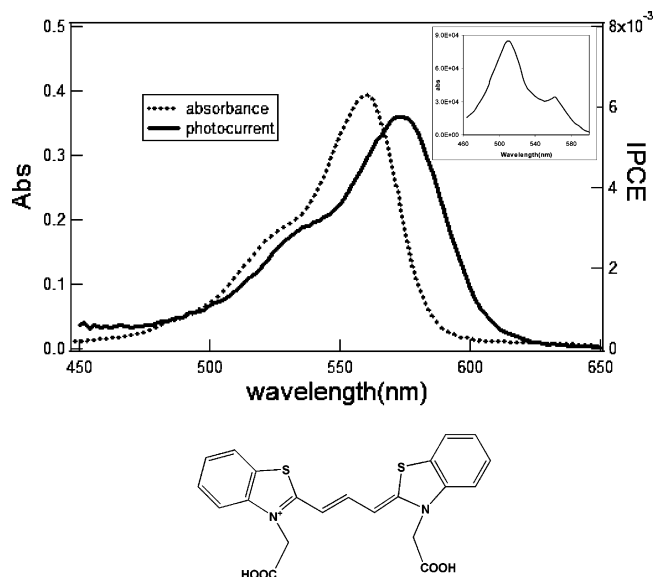


Figure 1. Molecular structure, solution absorption (dashed line), and action spectrum adsorbed on rutile (100) surface of the G15 dye from an ethanol solution. The inset shows the dimeric spectrum taken from ref 14.

peak. When adsorbed onto a single-crystal rutile (100) surface, the photocurrent action spectrum shows a monomer peak red-shifted about 12 nm together with a broadened blue-shifted dimer/aggregate peak at 549 nm. At its maximum at 530 nm, its extinction coefficient is $5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, whereas the extinction coefficient of the monomer at its maximum is reported to be $1.5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$. Given the role of dimers in this work, the spectrum of a pure dimeric carbocyanine dye in solution¹⁸ is provided in Figure 1.

Figure 2a shows photocurrent spectra from which the isotherm of Figure 2b for G15 adsorbed onto a rutile (100) surface was obtained. Hydroquinone was used as the regenerator in these measurements. The incident photon-to-current conversion efficiency (IPCE), which we assume is linearly proportional to the dye coverage, increases in Figure 2a with the increase of G15 dye solution concentration and plateaus at higher concentrations. Figure 2b shows the fraction of monomer and dimer present on the surface, which were obtained from fitting the photocurrent action spectra in Figure 2a to the observed and calculated monomer and dimer spectra of carbocyanine dyes.¹⁸ This fitting is rather simplistic in approach since it assumes that the spectrum of the surface dimer is the same as the solution dimer absorption spectrum, but it does give a first order approximation of the contribution of the aggregate to the action spectrum. The photocurrent action spectrum is therefore heterogeneous in nature, containing significant fractions of dimer species with absorption spectra that are controlled by the relative orientations of the component monomer dyes on the surface, which in turn is determined by the geometric arrangement of the underlying binding sites for the carboxylate functions on the TiO_2 lattice. Although monomer is the predominant adsorbed species, there is a significant amount of dimer present, making it possible to examine the desorption of both the monomer and dimer of the adsorbed G15 dye.

When KI was used as a reducing agent to regenerate the oxidized G15 dye molecules, the sensitized photocurrent is very stable with time suggesting that there is very little desorption of the dye, as shown in Figure 3 as a dotted line. However when

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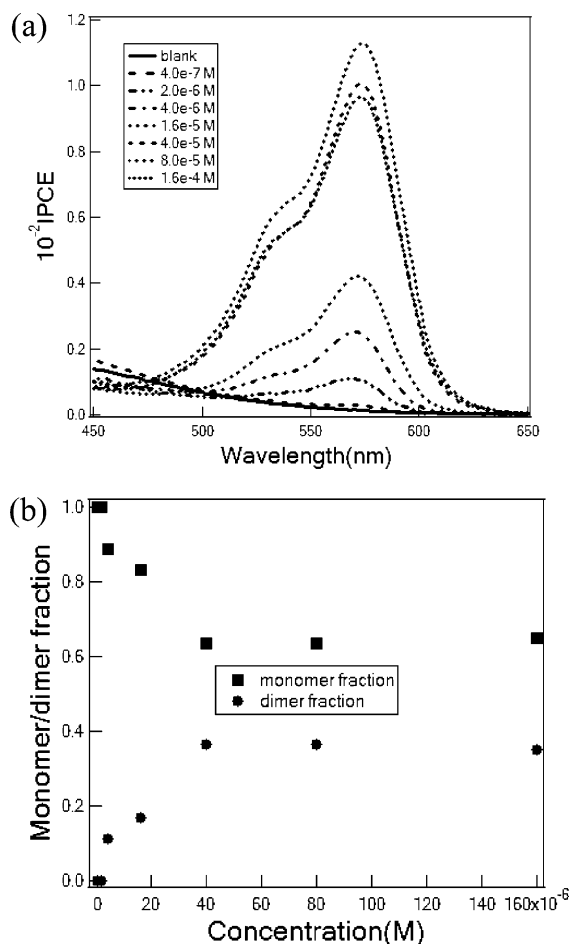


Figure 2. (a) Increase of the sensitized photocurrent with increasing concentration of G15 adsorbed onto rutile (100) electrode and (b) monomer and dimer fractions derived from fitting the photocurrent action spectra.

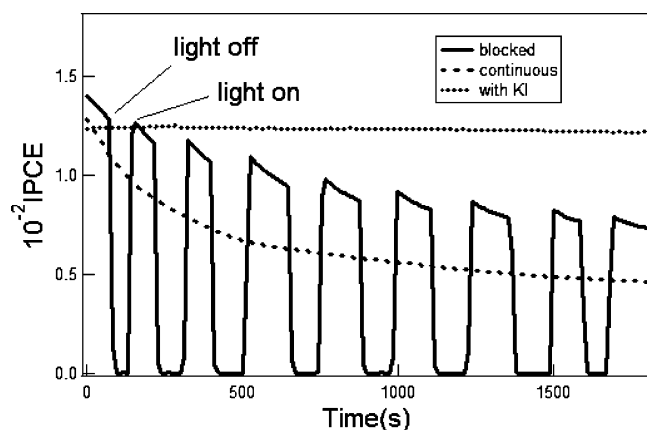


Figure 3. Photocurrent as a function of time for G15 dye adsorbed onto a rutile (100) surface excited at 574 nm. The solid line represents an experiment where the light beam was manually blocked and unblocked as indicated on the graph. The dashed line represents a photocurrent decay plot under continuous illumination. The dotted line shows the photocurrent response with time when KI is used as the regenerator instead of hydroquinone.

hydroquinone was used as the regenerator, a decrease in the photocurrent with time was observed. We interpret this as evidence that hydroquinone and/or the oxidation products of hydroquinone, such as a semiquinone, or more formally a quinone, compete for binding sites with the cyanine dye molecules.¹⁹ There is precedent for this since hydroquinone has been previously used as a regenerator for sensitized semiconductor electrodes, and it was

concluded that it competes with dye adsorption.^{19,20} In addition, the extremely strong adsorption of a structurally similar molecule, catechol, onto TiO₂ surfaces has been studied extensively both experimentally and theoretically.^{21–22} To determine if desorption of the G15 dye from the oxide surface was caused by the competitive adsorption of hydroquinone or the produced quinone, we performed an experiment where the sensitized photocurrent was monitored while periodically blocking the illumination. The solid line in Figure 3 shows that when the light beam was blocked the photocurrent went to zero and, when illumination was restored, the photocurrent returned to the previous value or even to a bit higher value rather than a value obtained from extrapolating the original decay trend using the dashed line in Figure 3. The fact that no photocurrent decrease was observed when no quinone was being produced implies that the displacement reaction may be a complex photoreaction and not a dark reaction. A possible explanation for the photocurrent being larger upon re-illumination would be that the APCE for a dye attached by only one carboxylate leg is lower than the APCE for a dye bound at two sites due to less strong electronic coupling for electron injection. In the dark, when no quinone is being produced, one legged dyes have time to re-establish binding at two sites by finding an unoccupied site or by desorption of a quinone from an adjacent site due to the lower surface quinone concentration during the dark period. We also tested the time dependence of the desorption process at hydroquinone concentrations of 0.45 and 45 mM, but no difference in the desorption rate was observed, providing further evidence that the dyes were replaced by photogenerated quinone that is produced at a constant rate regardless of the hydroquinone concentration. A variation in light intensity by a factor of 2 produced little change in the rate of the decay curves. This result implies that the surface is saturated with the quinone species at low photon flux, effectively presenting a constant surface concentration of the quinone for any of the dye displacement reactions.

Figure 4 shows the decay of the photocurrent for G15 excited at a wavelength of 574 nm and recorded for 1800 s for four different surface concentrations of the dye. The observed current declines monotonically, and we associate this decay with the desorption of the dye. At the monomer absorption maximum of 574 nm, the spectra of Figure 2 show the monomer absorption dominating at this wavelength when compared to the dimer. The photocurrent decay data collected at 530 nm, where the dimer absorption is substantial, are shown in Figure 5. The procedure for renewing the surface following each experiment does not result in decay curves that are exactly reproducible, but the essential magnitude and decay characteristics are retained. There are minor, 10% variations in the amplitude of the current and shape of the decay curves that place limits on the degree to which a quantitative interpretation can be made.

The striking feature of the 530 nm decay curves is the increase in the sensitized photocurrent within the 100 s. An examination of the derivatives of the photocurrent decays at 570 nm show a small presence of a similar increase, but at only 5% of the level observed at 530 nm. Although oxidation of hydroquinone does lead to production of protons at the surface, this initial increase in photocurrent is not attributable to an acid-induced band shift of the TiO₂ since it is not seen uniformly throughout the entire action spectrum. We attribute it to a light-induced surface

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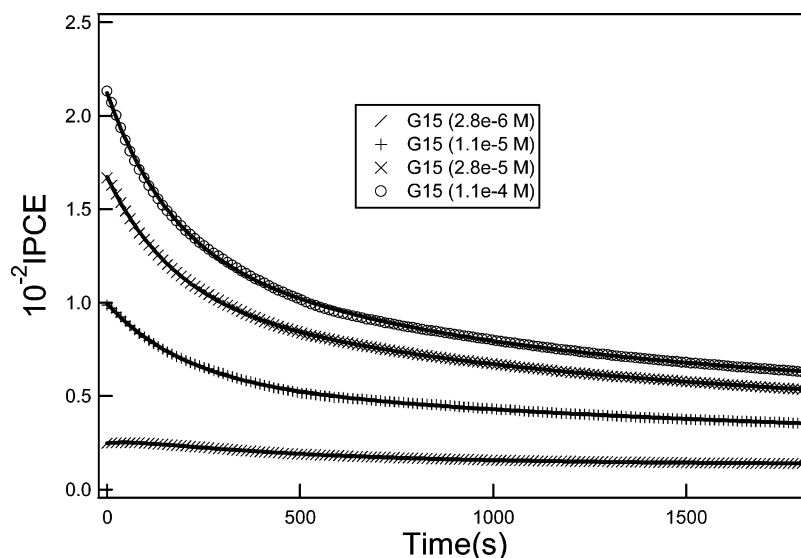


Figure 4. Sensitized photocurrent decay measurements for G15 dye adsorbed on a rutile (100) surface collected by illuminating at the monomer absorption maximum (574 nm). The decrease in photocurrent is due to monomer dye desorption. Solid lines are from fitting.

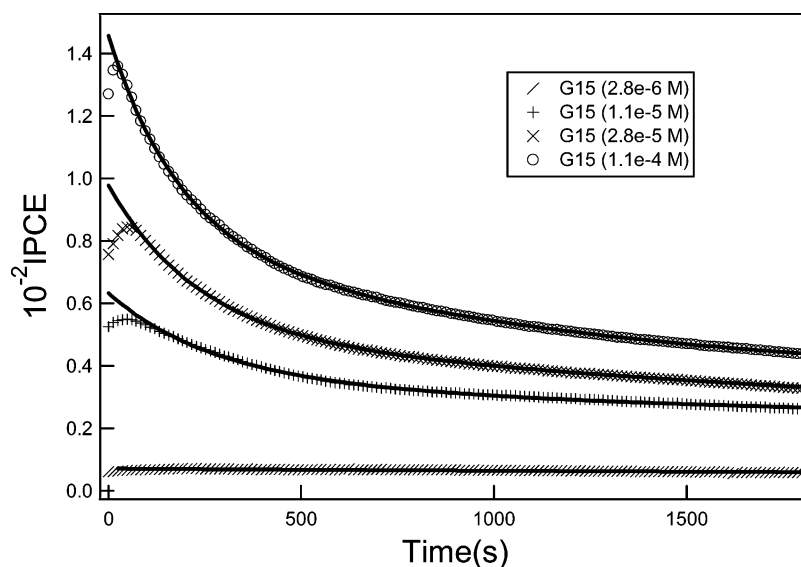


Figure 5. Sensitized photocurrent decay measurements for G15 dye adsorbed on a rutile (100) surface collected by illuminating at the dimer absorption maximum (530 nm). The solid curves are the fits to the long-term decays using data from times greater than 50 s.

reorganization of monomer dye to create more of the blue-absorbing aggregate at the surface.

Discussion

The photocurrent decay curves at 530 and 574 nm give evidence of a dynamic detachment and rearrangement process of the carboxylate linkages of the G15 dye on the surface. The kinetics of the photocurrent curves can be modeled to gain a self-consistent picture of these processes. We see the complement of dye on the surface as falling into one of two manifolds: dimer or monomer.

Surface dimers are composed of two dye molecules that are sufficiently close that they can dimerize through van der Waals forces to give a blue-shifted absorption spectrum similar to that shown in the insert of Figure 1 for a similar dye in solution. The ΔG of dimerization will differ for the two cases of dye in solution and dye on the surface because the geometric constraints from the surface attachment of the dyes through the carboxyl functions can preclude the closest approach of the chromophores. The molecules composing surface dimers can remain in close contact or can spread apart to become two monomer dyes with the balance

between these two populations being determined by the ΔG of dimerization, which should be sufficiently large to greatly favor the dimer form. For the carbocyanine dye with the spectrum of Figure 1, this ΔG is -7.4 kcal/mol,¹⁸ which should be more positive than the ΔG of dimerization of the dye on the surface since the entropic component of ΔG should be much more negative in solution than on the surface. We expect that only the open monomer configuration should be subject to the desorption reaction with quinone. However, the closed dimer has four carboxyl attachment points and a van der Waals dimerization interaction to keep it intact on the surface and resistant to desorption during the time span of these experiments.

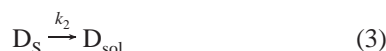
It is reasonable to expect two types of monomers on the surface: one that has only one bound carboxylate group and one that has both carboxylate groups bound. The former can be displaced in one step by the quinone produced at the surface and latter will require two sequential reactions with the quinone for displacement from the surface.

The surface fractional coverage of dye θ by these various forms of the dye can then be expressed as

$$\theta = \theta_1 + \theta_2 + \theta_3 \quad (1)$$

where θ_1 is the fractional coverage dyes with a single surface bond, θ_2 is the fractional coverage of monomers with two surface attachments, and θ_3 is the fractional coverage of dimers.

A simple kinetic model can be used to interpret the form and rate of the photocurrent decays of Figures 3 and 4. One first begins with the displacement of the monomeric dyes by the quinone on the surface. These attached monomeric dyes will be displaced and dissolve into the electrolyte once the titanium–carboxylate bonds dissociate according to the following reaction scheme:



where D_T and D_S refer to dyes originally bound with two carboxylate groups (θ_2) and those bound with one carboxylate group, respectively. D_T becomes D_{ST} after losing one bond with rate k_1 , and k_{-1} is the reattachment rate constant. D_{ST} and D_S are essentially the same but only the D_{ST} portion of the one-legged dye is in equilibrium with D_T . After breaking one more bond with a rate constant of k_2 , these dyes become dissolved in the electrolyte (D_{sol}). k_1 and k_2 are seen to be pseudo-first-order rate constants in the concentration of quinone.

Since there is no dye dissolved in the electrolyte, and under continuous illumination quinone will be continually produced at the surface, we assume the path from single carboxylate bound dyes to dissolved dyes is irreversible. The following rate equations can be written assuming a fast equilibrium between D_T and D_{ST} :

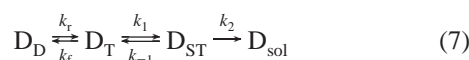
$$-\frac{d[D_T]}{dt} = -\frac{d[D_{ST}]}{dt} = k_2[D_{ST}] = k_2 \frac{k_1}{k_{-1}} [D_T] = k_2 K [D_T] \quad (4)$$

$$-\frac{d[D_S]}{dt} = k_2 [D_S] \quad (5)$$

where K is the equilibrium constant between D_T and D_{ST} (k_1/k_{-1}). After integration, we obtain the original monomer surface coverage as a function of time t (in seconds)

$$\theta(t) = \theta_1^0 \exp(-k_2 t) + \theta_2^0 \exp(-k_2 K t) \quad (6)$$

For dimers, the desorption process is more complicated. With the equilibrium constant K_{dm} (k_f/k_r) representing the closed/open ratio for the dimer, the desorption of dimer molecules can be represented by the following sequence of reactions:



The dimer form of the adsorbed dye molecules is in equilibrium with the two legged D_T monomers, which can then desorb as discussed above. It is clear that with $K_{dm} > 10^4$, the surface concentration of D_T will be very small and very little dimer will be desorbed by the quinone within the time frame of these experiments. θ_3 will remain constant during the exposure time of these experiments.

Therefore, eq 6 should be corrected to

$$\theta(t) = \theta_1^0 \exp(-k_2 t) + \theta_2^0 \exp(-k_2 K t) + \theta_3 \quad (8)$$

We measured the dye desorption rate by following the sensitized photocurrent at a particular wavelength as a function of time in an electrolyte containing no dye. Assuming the sensitized photocurrent is proportional to dye surface coverage, we express the photocurrent as a function of time in eq 9 by multiplying by constants to convert coverage per unit time to photocurrent density the same way as reported previously.²³

$$J(t) = \epsilon_m(\lambda) L_p \Phi_s A F N_0 \{ \theta_1^0 \exp(-k_2 t) + \theta_2^0 \exp(-k_2 K t) + \epsilon_d(\lambda) \theta_3 / \epsilon_m(\lambda) \} \quad (9)$$

In the above equation, $\epsilon_m(\lambda)$ is the monomer light absorption cross section for the dye at wavelength λ , $\epsilon_d(\lambda)$ is the corresponding value for the dimer, L_p is the photon flux in $\text{mol cm}^{-2} \text{s}^{-1}$, Φ_s is the photochemical yield for electron transfer from the excited dye to the TiO_2 , assumed to be constant and near unity for all forms of the dye on the surface, A is the illuminated surface area of the TiO_2 electrode in cm^2 , and F is the Faraday constant. N_0 is the full monolayer coverage on the surface ($1.4 \times 10^{-10} \text{ mol/cm}^2$) determined using the photocoulometric measurement reported previously.²⁴

In principle, the fitting of the decay curves of the photocurrent at 530 and 574 nm to eq 9 should yield the same values for the kinetic and thermodynamic constants. In practice, a common best fit approach was necessary. For each solution concentration, the 530 and 574 nm decays were fit to eq 9 to obtain K , k_2 , and Θ_3 . The value of Θ_3 was changed for each of the two decay curves separately, and then the curves were refit until the best fit was obtained for K and k_2 for both decay curves taken together. The values from the best fit of the three higher concentration curves are given in Table 1 as the range of the results from Figures 2 and 3. These results were derived using the extinction coefficient for monomer and dimer dye given in the inset of Figure 1.

At the smallest concentration ($2.8 \times 10^{-6} \text{ M}$), the photocurrent can only be fit by a single-exponential function. We interpret this to indicate that at small coverages most of the dyes can get two legs down so there are virtually no dyes on the surface that are bound with only one carboxylate group. Since the coverage is very small, the rearrangement from monomers into dimers should also be negligible. In such a case, we are only able to derive values for the product of K and k_2 .

A comparison of the Θ values in Table 1 reveals a surface populated with significant amounts of each of the possible forms of the attached dye, which can vary with different total surface coverage of the TiO_2 . Yet, the k_2 and K constants in Table 1 are very consistent over the higher concentration ranges, ranging from 3.8 to $5.2 \times 10^{-3} \text{ s}^{-1}$ for k_2 . This implies a single pathway for desorption of the dye such as might be described in eqs 2 and 3. The equilibrium constant K of about 0.10 reveals that the reattachment rate k_{-1} of eq 2 is 10-fold faster than the rate constant for the desorption of the one-legged dye in the presence of quinone. At low surface coverages, only the slow decay $k_2 K$ is observed, consistent with the presence of only the two-legged D_T species on the surface. It should be noted that a numerical analysis was also done for the decay mechanism of eqs 2 and 3 instead of the closed analytical form derived in eq 9, since it is not entirely clear that the equilibrium K is fast compared with respect to k_2 . The derived rate constants that fell within the range of results in Table 1 and the results were not sufficiently different as to

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Table 1. Monomer Desorption Coefficients and Equilibrium Constant of G15 with Rutile (100)

conc. (M)	K	k_2 (s ⁻¹)	θ_1	θ_2	θ_3
2.8×10^{-6}		$1.1-3.5 \times 10^{-4}/K$		0.04–0.11	
1.1×10^{-5}	0.09–0.17	$3.8-4.6 \times 10^{-3}$	0.12–0.18	0.077–0.087	0.08–0.09
2.8×10^{-5}	0.09	$4.3-5.2 \times 10^{-3}$	0.30–0.36	0.26–0.33	0.10–0.11
1.1×10^{-4}	0.14	$4.2-4.9 \times 10^{-3}$	0.39–0.46	0.35–0.37	0.18–0.23

change the qualitative nature of the conclusions drawn from the constants in Table 1.

The initial increase in photocurrent at 530 nm, where the dimer extinction coefficient is greater than the monomer, is attributed to the transformation of monomer dyes into a dimer that has a higher absorbance at this wavelength. The rearrangement of monomers into dimers increases the dimer coverage and, at excitation wavelengths where the dimer extinction coefficient is greater than that of the monomer, increases in dimer coverage should result in a net increase in current upon illumination. This is indeed what is observed and appears to be the only reasonable explanation for an increase in photocurrent while dye desorption is occurring.

Within 100 s of exposure, all of the monomer dye that can rearrange to form this aggregate has done so. The size of this subpopulation of dye on the surface is proportional to the difference between the photocurrent at time zero in Figure 3 and the fit to the long-term decay of the photocurrent extrapolated to zero time, also shown in Figure 3. For the decays at the three higher concentrations, this difference ranges from 0.001 at 2.8×10^{-5} M to 0.002 at higher concentrations. This increase should be proportional to the change in the extinction coefficient of the monomer molecule as it rearranges to the dimer: ($\epsilon_{\text{dim}}(\lambda) - \epsilon_{\text{m}}(\lambda)$). However, the use of the literature ϵ values in Figure 1 for the monomer and dimer did not lead to physically reasonable analyses of the photocurrent decay curves. Given the geometric constraints placed upon the dimer by the surface lattice of attachment points, the spectrum and extinction coefficients of this unique dimer aggregate may differ greatly from the solution example of Figure 1. Given the 0.001–0.002 increase over the three higher solution concentrations, we conclude that the number of sites where such a monomer/dimer rearrangement can occur is defined and limited and is preferentially occupied at surface coverages below 0.5. If all of the θ_3 values derived for the 1.1×10^{-5} M concentration were to be attributed to this unique aggregate, a lower limit for ($\epsilon_{\text{dim}}(\lambda) - \epsilon_{\text{m}}(\lambda)$) can be calculated to be $7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, which is high, but not unreasonable.

Such a sharply peaked absorption spectrum for a dimer has been reported for carbocyanine dyes on nanocrystalline TiO₂ surfaces.²⁴

We have previously studied the sensitization of single-crystal oxide surfaces with the ruthenium based dye N3. N3 binds to the surface very strongly and no desorption was observed within the experimental time frame used herein even when hydroquinone was used as the regenerator.^{10,25} The G15 dye studied herein yields initially higher IPCE values than those measured for N3 on the same crystal surface (rutile (100)) probably due to the higher extinction coefficient of the G15 dye ($1.5 \times 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ vs $1.42 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for N3). However if hydroquinone is used as a regenerator desorption of the G15 dye occurs and the binding sites are rapidly occupied by quinone. More than half of the originally adsorbed dyes are lost in about 20 min, demonstrating the vital importance of choosing the right regenerator for optimal performance of a dye cell. To fabricate a more efficient organic dye-sensitized TiO₂ solar cell, a highly absorbing and inexpensive sensitizer needs to be developed that binds as strongly as the N3 dye together with the use of an appropriate regenerator.

Conclusion

We have studied the displacement of the dicarboxylated thiocyanine dye G15 from the single-crystal rutile (100) surface by the oxidation products of the hydroquinone regenerator. In addition, the rearrangement of the G15 dye from monomer to dimer was observed, revealing the dynamic attachment and detachment reactions of the dye to the surface. The kinetic constants of these processes were found to be consistent with a two-step desorption mechanism.

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