Tracking the Adsorption and Electron Injection Rates of CdSe Quantum Dots on TiO2: Linked versus Direct Attachment

Douglas R. Pernik,†‡ Kevin Tvrdy,†§ James G. Radich,†‡ and Prashant V. Kamat*†‡§

†Radiation Laboratory, ‡Department of Chemical & Biomolecular Engineering, and §Department of Chemistry & Biochemistry, University of Notre Dame, Notre Dame, Indiana 46556, United States

ABSTRACT: Understanding CdSe quantum dot (QD) adsorption phenomena on mesoscopic TiO2 films is important for improving the performance of quantum dot sensitized solar cells (QDSSCs). A kinetic adsorption model has been developed to elucidate both Langmuir-like submonolayer adsorption and QD aggregation processes. Removal of surface-bound trioctylphosphine oxide as well as the use of 3-mercaptopropionic acid (MPA) as a molecular linker improved the adsorption of toluene-suspended QDs onto TiO2 films. The adsorption constant K_ads for submonolayer coverage was $(6.7 \pm 2.7) \times 10^{4} \text{M}^{-1}$ for direct adsorption and $(4.2 \pm 2.0) \times 10^{3} \text{M}^{-1}$ for MPA-linked assemblies. Prolonged exposure of a TiO2 film to a CdSe QD suspension resulted in the assembly of aggregated particles regardless of the method of adsorption. A greater coverage of TiO2 was achieved with smaller QDs due to reduced size constraints. Ultrafast transient absorption spectroscopy demonstrated faster electron injection into TiO2 from directly adsorbed QDs ($k_{ET} = 7.2 \times 10^{9} \text{s}^{-1}$) compared with MPA-linked QDs ($k_{ET} = 2.3 \times 10^{9} \text{s}^{-1}$). The adsorption kinetic details presented in this study are useful for controlling CdSe QD adsorption on TiO2 and designing efficient photoanodes for QDSSCs.

INTRODUCTION

Recent environmental and economic concerns have highlighted the urgent need for renewable sources of energy.1 To help satisfy this need, it has been suggested that new advancements should be made to harness energy from the sun, the greatest energy source in our solar system.2–5 Semiconducting nanocrystals known as quantum dots (QDs) are being considered as sensitizers in next-generation photovoltaic devices.6–9 Quantum dot sensitized solar cells (QDSSCs) show promise in improving QDSSC efficiencies.10,11 The phenomena of multiple exciton generation and hot electron injection promote additional interest for QDSSCs, as they raise the theoretical maximum efficiency above the Shockley–Queisser limit of 31%.14–19

The photoanode of a QDSSC consists of semiconductor quantum dots attached to a large band gap semiconductor, such as TiO2, and can be constructed according to a variety of deposition techniques, including colloidal deposition,20 chemical bath deposition,21–23 SILAR,24,25 and electrodeposition.26,27 Colloidal deposition provides a simple and straightforward approach for achieving uniformly sized QDs on a TiO2 surface and is achieved through direct adsorption of QDs on TiO2 or with the assistance of a molecular linker.28,29

Today’s best QDSSCs have only achieved power conversion efficiencies of 4–5%,31 significantly lower than the 10–11% efficiencies reported for dye-sensitized solar cells. Poor efficiency, from a mechanistic standpoint, can be attributed to electron-transfer reactions that compete against the ideal regenerative cycle in these devices.32 Watson and co-workers have demonstrated decreased electron injection rates with increasing chain length in linked QD–TiO2 assemblies.34 Additionally, Bisquert and co-workers have shown that an increasing coverage of TiO2 with CdSe QDs results in an increased incident photon-to-current efficiency (IPCE) for QDSSCs.35 In light of these studies, QD adsorption on TiO2 is a relevant and important area of study for improving QDSSC efficiency.

In this paper, we have investigated the nature of the interactions between CdSe and TiO2 and constructed a kinetic model for CdSe QDs adsorbing onto TiO2. In addition, we have probed the factors that govern QD adsorption rates and discuss how varying adsorption techniques influence charge injection into mesoscopic TiO2.

EXPERIMENTAL SECTION

Materials. The materials used in QD synthesis were dodecylamine (DDA, Alfa, 98+%), trietylphosphine oxide (TOPO, Acros, 99%), trietylphosphine (TOP, Aldrich, 90%), tetracetylphosphonic acid (TDPAA, PCI Synthesis, Lot #n-TDPA-008001), cadmium oxide (Alfa, 99.998%), and selenium powder (Aldrich, 99.5+%). Titanium dioxide paste (90T, anatase, particle diameter = 20 nm) was obtained from Dyesol, and 3-mercaptopropionic acid (MPA, 99%+) and (3-mercaptopropyl)trimethoxysilane (MPS, 95%) were obtained from Aldrich Chemicals. SiO2 nanoparticles (20 nm diameter, Naico Chemical, 2327) and Parafilm (Pechiney

Received: April 1, 2011
Revised: May 25, 2011
Plastic Packaging) were also used. Toluene (HPLC grade), methanol (ACS grade), hydrochloric acid (ACS Plus grade), acetonitrile (HPLC grade), and sulfuric acid (ACS Plus grade) were also used in this investigation and were obtained from Fisher Chemical.

**CdSe Quantum Dot Synthesis.** CdSe nanoparticles were synthesized according to previously described methods. A 0.05 g portion of CdO, 0.3 g of TDPA, 1 g of DDA, and 2 g of TOPO were heated in a round-bottom flask under nitrogen. At 315 °C, 4 mL of TOP and 0.25 mL of 1 M TOPSe (selenium dissolved in TOP) were injected into the flask, and subsequent heating caused nanocrystal growth, evidenced by a color change from clear to yellow to orange to red. Nanocrystal growth was quenched at the desired size (color) by removing the flask from the heat source. Once the solution cooled to 120 °C, degassed toluene was added, and the solution was transferred into a N2-purged glovebox for future processing and storage. Subsequent syntheses were performed to obtain varying sizes of quantum dots.

**CdSe QD Characterization.** After synthesis, UV—visible absorption spectra were used to characterize the TOPO-capped CdSe nanoparticles, as the wavelength corresponding to the first exciton peak is indicative of the suspension’s average QD size. Wavelengths of 481, 513, 545, and 579 nm corresponded to average particle diameters of 2.6, 3.1, 3.8, and 4.6 nm, respectively.

**Quantum Dot Washing Process.** Washing with methanol was implemented in order to remove unreacted CdO, DDA, TOPO, other reaction precursors, and undesirable byproducts from the quantum dot surface. One wash entailed adding methanol to triple the QD solution’s volume and centrifuging at 10 000 rcf for 10 min. The liquid portion was discarded, and fresh toluene was added to the flocculate, which formed a homogeneous dispersion following mild agitation.

**Preparation of TiO2 and SiO2 Films on Glass Substrates.** Two microscope slides were cut to approximate dimensions of 35 mm × 8 mm, and titanium dioxide paste was applied to them using the doctor-blade method. After application of TiO2 paste, the slides were heated at 450 °C for 1 h to remove organics, and the mass of TiO2 on the glass slides was recorded. The two TiO2 films were then taken into a nitrogen-atmosphere glovebox for QD sensitization. SiO2 films used in transient absorption experiments were also annealed at 450 °C to remove any organics from the films.

**Additional Steps for Linker-Assisted Adsorption Experiments.** The following steps were implemented only for the experiments in which 3-mercaptopropionic acid (MPA) was used as a bifunctional linker to assist in adsorbing quantum dots on TiO2. Inside a nitrogen glovebox, the TiO2 slides were introduced to a pH 2 solution consisting of hydrochloric acid and deionized water for 20 min. The slides were rinsed with deionized water and then rinsed with anhydrous acetonitrile. The TiO2 slides were then immersed in a solution containing MPA (1 M MPA, 0.1 M H2SO4 in anhydrous acetonitrile) for 5 h. The slides were again rinsed with anhydrous acetonitrile and with deaerated toluene before being introduced to the QD—toluene solution.

**Instrumentation.** Absorption data and QD characterization were recorded with a Cary Bio 50 spectrophotometer. A Clark-MXR 2010 (775 nm, 1 mJ/pulse, fwhm = 130 fs, 1 kHz repetition) laser system was implemented for transient absorption measurements with detection software from Ultrafast Systems (Helios). The pump and probe were incident on a quartz 2 mm path length optical cell at an angle < 10° at room temperature. The pump was operated at 95% of fundamental with frequency doubled to 387 nm, and the probe was at 5% of fundamental to generate a white light continuum. The averages of 1000 excitation pulses were used to obtain the transient spectra at a set delay time. Transmission electron microscopy (TEM) was used to characterize the morphology and adsorption characteristics of the nanocrystals on TiO2 using a Titan 80-300 TEM (FEI Company, 300 kV).

**Monitoring QD Adsorption on TiO2 Films.** The in situ absorption measurements made use of an experimental setup whereby QD adsorption on TiO2 occurred within an optical cell, enabling QD concentrations to be measured over time using a UV—visible spectrophotometer. Figure 1 shows a schematic of TiO2 slides and QD solution inside the optical cell. A 1 cm × 1 cm × 4 cm optical cell was partially filled with 2.4 mL of QD solution in a glovebox maintained with a N2 atmosphere. The QD concentration in toluene ranged from 1 to 10 μM (moles of quantum dots per liter). The two TiO2 slides were inserted into the optical cell such that the TiO2 surfaces were facing the center of the optical cell, making contact with the QD solution. The TiO2-free ends of each microscope slide were only partially submerged in the QD solution so that a small amount of QD solution could hold the TiO2 slides against the walls of the optical cell by the solution’s surface tension. The optical cell was then capped, sealed with Parafilm, and removed from the glovebox.

Once assembled, the optical cell was placed into a UV—visible spectrophotometer for a series of absorbance measurements over the course of 48 h at 15 min intervals. The optical cell was positioned parallel to the spectrophotometer’s probe beam such that the instrument would only scan the QDs that remained unadsorbed (see Figure 1). The difference in absorbance over time correlated to the amount of QDs adsorbed on the TiO2 films. Blank experiments performed to check the stability of the QD solution exhibited insignificant changes in absorbance.

**RESULTS AND DISCUSSION**

**Verifying QD Adsorption on TiO2.** For each adsorption experiment, absorbance data were collected for 48 h, and the
The decrease in absorbance at the first excitonic peak was monitored over time. The absorbance values at this wavelength were related to the number of CdSe nanoparticles leaving the toluene solution and adsorbing onto TiO$_2$ at each time point according to the following expression

\[ QD_{ads} = \frac{A_0 - A_t}{\varepsilon l} N_A V_{sol} \]

where \( A_t \) represents the absorbance value measured at a given time, \( A_0 \) is the initial absorbance, \( \varepsilon \) is the QD solution’s molar absorptivity, \( l \) is the cell’s path length (1 cm), \( N_A \) is Avogadro’s number, and \( V_{sol} \) is the volume of the solution, which was held constant at 2.4 mL.

Precautions were taken to ensure that decreases in absorbance of the QD solution directly corresponded to QDs adsorbing onto the TiO$_2$ films. First, control experiments consisting of TiO$_2$-free glass slides immersed in a QD solution showed no change in the absorbance spectra of QDs over time, indicating no significant flocculation of QDs from the toluene suspensions or particle degradation on the time scales under investigation. Second, spectral absorbance measurements of the TiO$_2$ films showed that QDs increased in concentration on the TiO$_2$ films with increasing immersion time (Figure 2B) as the concentration of QDs decreased in toluene (Figure 2A). The slight blue shift of these adsorbed QDs is attributed to structural and environmental changes occurring upon adsorption to TiO$_2$. Third, the absorbance spectra showed no excitonic peak shift within the QD solution over the course of the adsorption experiments, indicating the absence of changes in absorbance due to particle ripening or etching.

**Effect of QD Washing on Adsorption to TiO$_2$.** After QD synthesis, excess reaction precursors and undesirable byproducts remain bound to the QD surface. A first methanol wash removes these species from the TOPO-capped CdSe QDs. Murray et al. have described the processes involved in QD washing. Adding methanol to a QD–toluene suspension increases the average polarity of the solvent, causing QDs to flocculate due to attractive van der Waals forces between TOPO-capped QDs. Resuspension in neat degassed toluene then yields monodispersed QDs with less surface-bound TOPO. Whereas Murray and co-workers demonstrated the use of multiple washes to further narrow the QD size distribution, here, we employ methanol washing to remove excess TOPO from the QD surface and thereby improve QD affinity toward TiO$_2$ adsorption. Our washing procedure leaves the particle size distribution largely unaltered. Details on this point are found in the Supporting Information (section S1, Figure S1). A maximum of five wash cycles was optimal to remove excess TOPO, leaving sufficient capping to render stability of QDs in toluene while also allowing QDs to interact with mesoscopic TiO$_2$. Figure 3 shows the dependence of CdSe QD adsorption on the number of washes performed on them for MPA-linked assemblies. Subsequent washes were shown to dramatically increase the number of CdSe nanoparticles that adsorb onto TiO$_2$.

The same trend was observed for directly adsorbed quantum dots, with an increasing number of washes resulting in a greater number of QDs adsorbing onto TiO$_2$. Data relating adsorption and washing for directly adsorbed QDs and a derivation of the
QDs adsorbed per TiO₂ nanoparticle, a parameter used throughout this study, are described in the Supporting Information (section S2, eqs S1–S4, Figure S2). The use of once-washed QDs resulted in poor attachment in the cases of both direct and linker-assisted adsorption. These results further support the fact that washing improves QD interactions with TiO₂ and MPA. This strong correlation between washing and adsorption highlights the importance of QD pretreatment for successful adsorption onto a TiO₂ surface.

**Establishing a Kinetic Adsorption Model.** A simple way to analyze QD adsorption on TiO₂ is through a Langmuir isotherm, which implies that QDs form a submonolayer on TiO₂ and that adsorption and desorption occur simultaneously. The forward adsorption processes in which QDs adhere to TiO₂ or MPA are commonly used in the construction of QDSSCs. To confirm the reverse process (QD desorption from TiO₂), both directly adsorbed and linked CdSe–TiO₂ films were immersed in neat toluene for 24 h (Figure 4). A comparison of the absorption characteristics of the two films demonstrates the reversibility of the QD–TiO₂ adsorption. After 24 h, the directly adsorbed QDs completely desorbed from the TiO₂ electrode. The molecularly linked QDs experienced a slower desorption rate, as would be expected for particles more strongly bound to TiO₂. Because desorption of QDs into fresh toluene is clearly observable, we assert that QD adsorption onto TiO₂ whether achieved directly or with a linker, is driven by an equilibrium. If this is the only process responsible for QD adsorption, a Langmuir-like kinetic model could accurately model submonolayer adsorption of QDs on TiO₂ for both methods of attachment.

A question that arises is whether submonolayer TiO₂ coverage is the only process dominating the adsorption in this system. Previous studies have shown the controlled aggregation of semiconducting nanoparticles and significant CdSe QD aggregation on TiO₂ films after long adsorption times. Here, we find further evidence for QD aggregation through TEM imaging, as shown in Figure 5. Each sample was prepared by immersing a TiO₂ film in QD solution for 6 h. A portion of the resulting QD-sensitized TiO₂ was scraped off the glass slide, suspended in ethanol, and drop-cast onto a TEM grid. This procedure was followed for directly adsorbed (Figure 5A,C) and MPA-linked (Figure 5B,D) QD assemblies. In Figure 5B–D, CdSe lattice fringes were measured at 0.351 nm, in agreement with the (002) spacing for wurtzite CdSe. Although the TiO₂ (101) d-spacing of 0.352 nm is very close to this (002) CdSe value, morphology differences are apparent and sufficient for identifying each component. To help demonstrate this point, the sample in Figure 5C was tilted to bring TiO₂’s (004) planes into the Bragg angle, verifying TiO₂ as the much larger, rod-shaped particle. Figure 5A,B demonstrates QDs adsorbed on TiO₂ as a submonolayer, whereas Figure 5C,D shows aggregated QDs on TiO₂. The sample in Figure 5A was imaged under bright-field mode to show an overview of individual, spherical QDs directly adsorbed to a cluster of rod-shaped TiO₂ particles.

**Figure 4.** Absorbance spectra of CdSe-sensitized TiO₂ films immersed in fresh toluene over time. Desorption of CdSe in toluene gives evidence for an equilibrium adsorption process. QDs attached by linker-assisted (LA) adsorption exhibit slower desorption than directly adsorbed (DA) quantum dots.

**Figure 5.** TEM images of CdSe QDs attached to TiO₂ by direct adsorption (A, C) and MPA-assisted adsorption (B, D). Images A and B illustrate submonolayer adsorption, whereas images C and D are instances of QD aggregation on the TiO₂ surface. Image A was taken in bright-field mode and exhibits singly adsorbed spherical QDs on rod-shaped TiO₂. All images correspond to a TiO₂ in CdSe immersion time of 6 h.
Kinetic Adsorption Model. To model CdSe QD adsorption on a sintered network of TiO₂ nanoparticles, we first accounted for standard Langmuir second-order adsorption and first-order desorption processes, given by eqs 2 and 3, respectively:

\[ [P] + [S] \xrightleftharpoons[k_1]{} [PS] \]  (2)

\[ [PS] \xrightarrow[k_{\text{des}}]{} [P] + [S] \]  (3)

\( P \) represents CdSe QD particles in toluene solution, \( S \) represents any TiO₂ adsorption site with one or several QDs attached, and \( P + S \) is the same site after the adsorption of an additional particle. It was assumed that the rate of QD aggregation is constant regardless of how many particles are adsorbed or aggregated on the same site.

Using eqs 3, 5, and 7, the rates of decreasing CdSe QD concentration in toluene due to submonolayer adsorption and aggregation processes are given by eqs 8 and 9, respectively:

\[ \frac{-d[P]_{\text{Lang}}}{dt} = k_1' [P] - k_{-1} [PS] \]  (8)

\[ \frac{-d[P]_{\text{ag}}}{dt} = k_{\text{ag}} [P] [P + S] \]  (9)

where \( [P]_{\text{Lang}} \) and \( [P]_{\text{ag}} \) are the concentrations of CdSe QDs that form either a submonolayer coverage on the TiO₂ nanoparticulate network \( ([P]_{\text{Lang}}) \) or aggregate onto QDs that were already adsorbed to TiO₂ \( ([P]_{\text{ag}}) \). The total observable decrease in QD concentration in toluene can then be expressed as:

\[ \frac{-d[P]_{\text{Total}}}{dt} = \frac{-d[P]_{\text{Lang}}}{dt} + \frac{-d[P]_{\text{ag}}}{dt} \]  (10)

Adsorption Kinetic Parameters. Equation 8 was integrated in order to relate adsorption over time with both starting concentrations of QDs and TiO₂ adsorption sites according to a purely theoretical Langmuir-like model. The experimental deviation from eq 8 was then modeled by eq 9, where the concentrations of CdSe nanoparticles and filled TiO₂ sites at each time point were used to build a fit to the data by the trapezoid method of integration. Constants \( k_1' \), \( k_{-1} \), and \( k_{\text{ag}} \) were simultaneously solved for according to an iterative summed squared error minimization process. Additional information on the kinetic model is found in the Supporting Information (section S3).

After fitting the adsorption data, \( k_1' \) was related to \( k_1 \) by eq 6 and the resulting \( k_1 \) and \( k_{-1} \) constants were related to \( K_{\text{ads}} \) according to eq 4. Because \( k_{\text{ag}} \) does not appear in eq 4, \( K_{\text{ag}} \) is only a measure of submonolayer coverage of TiO₂.
The Journal of Physical Chemistry C

Table 1. Rate and Equilibrium Constants for CdSe QDs Adsorbing onto TiO2 from Toluene

<table>
<thead>
<tr>
<th>mode of attachment</th>
<th>$k_1$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_{-1}$ (s$^{-1}$)</th>
<th>$K_{eq}$ (M$^{-1}$ s$^{-1}$)</th>
<th>$K_{ad}$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>direct adsorption</td>
<td>0.42 ± 0.28</td>
<td>(6.2 ± 2.2) × 10$^{-3}$</td>
<td>1.0 ± 0.4</td>
<td>(6.7 ± 2.7) × 10$^3$</td>
</tr>
<tr>
<td>MPA-assisted</td>
<td>0.65 ± 0.23</td>
<td>(1.5 ± 0.5) × 10$^{-3}$</td>
<td>0.9 ± 0.5</td>
<td>(4.2 ± 2.0) × 10$^4$</td>
</tr>
</tbody>
</table>

*a* QDs were washed five times. Uncertainty ranges reflect standard error.

![Figure 6](image)

**Figure 6.** Theoretical fit of experimental adsorption data. Adsorption due to submonolayer formation (eq 8) and QD aggregation on the TiO2 surface (eq 9) are added together to obtain the total fit (eq 10). Linker-assisted adsorption of 2.6 nm diameter CdSe QDs on TiO2 at a concentration of 9.4 μM. QDs were washed five times prior to adsorption.

shows a sample fit of eq 10 to experimental adsorption data, along with the deconvoluted contributions from Langmuir-like adsorption (eq 8) and QD aggregation (eq 9).

Best-fit adsorption rate and equilibrium constants are found in Table 1. The values of these constants reflect averages of quantum dots sized between 2.6 and 4.6 nm in diameter. All QDs were subject to five wash cycles prior to adsorption on nanoparticulate TiO2 films.

The larger $k_1$ and smaller $k_{-1}$ for MPA-assisted adsorption indicate that QDs experienced faster adsorption and slower desorption when MPA was used as a molecular linker. This result is in agreement with what was qualitatively demonstrated by desorption into fresh toluene (Figure 4). The effects of faster adsorption and slower desorption combine through eq 4 to result in nearly an order of magnitude increase of $K_{ad}$ for linked QDs over directly adsorbed QDs. This result indicates a stronger driving force for submonolayer adsorption on TiO2 when MPA is used.

Quantum dot aggregation typically dominated adsorption at exposure times greater than 10 h. The significant deviation from Langmuir-like adsorption seen at large times in Figure 6 supports this hypothesis. The aggregation rate constant $k_{agg}$ exhibited no noticeable dependence on the method of adsorption; however, the uncertainty in $k_{agg}$ is large enough to warrant further investigation.

The amount of surface-bound TOPO on CdSe also affected the kinetic parameters. Thrice washed QDs had $K_{ad}$ values between 25% and 50% of the $K_{ad}$ values given in Table 1. Quantum dots that were washed only once experienced such poor adsorption that equilibrium parameters could not be determined in either the direct adsorption or linker-assisted adsorption cases (see Figure 3).

A summary of factors that improve QD adsorption on TiO2 is found in the Supporting Information (section S4).

**Effect of QD Size on Adsorption Parameters.** Physical intuition would lead one to believe that a greater number of smaller particles could adsorb onto a fixed surface area than larger particles. Indeed, this was found to be the case for CdSe QDs on TiO2. Four kinetic adsorption experiments were set up at the same starting QD concentration to probe adsorption size dependence. For each of these experiments, $K_{ad}$ as well as the normalized number of QDs that adsorbed onto TiO2 after 3 h were recorded. The time of 3 h was chosen in order to minimize the presence of QD aggregation on the TiO2 films. The results of these four experiments are presented in Table 2. Interestingly, $K_{ad}$ was found to be larger for larger particles even though they experienced a lower number of QDs adsorbing onto TiO2. This discrepancy is possible because $K_{ad}$ is a function of $S_{np}$ the maximum number of available TiO2 adsorption sites, which, in turn, is based on the quantum dot’s physical cross section. As larger QDs have greater cross sections, their increased adsorption (manifest as a larger $K_{ad}$) was only greater relative to the number of available TiO2 adsorption sites. We expect the increased relative adsorption for larger particles to be a result of their larger van der Waals forces, which cause stronger electronic interactions with MPA and TiO2.

In a QDSSC, photocurrent is inherently limited by the number of QDs on the surface of the photoanode. It is, therefore, more desirable to have a greater number of particles adsorb onto a TiO2 surface. For this reason, we expect stronger photovoltaic properties to be generated through adsorption of smaller QDs compared to larger QDs under similar adsorption conditions.

**Electron Injection Rate Dependence on Method of Adsorption.** In the following section, we probe how linked versus linkerless QD attachment, once achieved, affects a commonly studied property of nanostructured interfaces: electron-transfer kinetics. Electron-transfer rates were determined using ultrafast transient absorption spectroscopy, a pump—probe technique that provides spectral and kinetic information about the samples’ electronically excited state.

Table 2. Size-Dependent Adsorption Parameters

<table>
<thead>
<tr>
<th>QD diameter (nm)</th>
<th>mode of attachment</th>
<th>$K_{ad}$ (M$^{-1}$)</th>
<th>QDs adsorbed per TiO2 nanoparticle at 3 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>direct adsorption</td>
<td>6.5 × 10$^3$</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>MPA-assisted</td>
<td>6.0 × 10$^4$</td>
<td>13.0</td>
</tr>
<tr>
<td>4.6</td>
<td>direct adsorption</td>
<td>9.4 × 10$^3$</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>MPA-assisted</td>
<td>7.8 × 10$^3$</td>
<td>7.1</td>
</tr>
</tbody>
</table>

*a* CdSe QDs were washed five times, at an initial concentration of 1.0 ± 0.1 μM.
Figure 7. Absorbance spectrum of (d = 3.1 nm) CdSe quantum dots in toluene solution (A), and transient absorption spectral traces of CdSe QDs attached to SiO2/TiO2 in a linkerless (B)/(C) and linked (D)/(E) fashion. The transient signal decreases with increasing pump—probe delay time: 1 ps (red), 10 ps (blue), 100 ps (teal), 1000 ps (magenta). Transient absorption kinetic traces of (B)—(E) at the characteristic first excitonic peak of CdSe (F) demonstrate the quenching of the excited state in the presence of the TiO2 acceptor.

Table 3. Transient Absorption Biexponential Best-Fit Results for CdSe Quantum Dots Attached to TiO2 and SiO2 Nanoparticlesa

<table>
<thead>
<tr>
<th>mode of attachment</th>
<th>species</th>
<th>$A_1$</th>
<th>$\tau_1$ (s)</th>
<th>$A_2$</th>
<th>$\tau_2$ (s)</th>
<th>$k_{ET}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>direct adsorption</td>
<td>CdSe—SiO2</td>
<td>0.36 (±0.01)</td>
<td>2.1 (±0.2) x 10$^{-12}$</td>
<td>0.72 (±0.01)</td>
<td>280 (±16) x 10$^{-12}$</td>
<td>7.2 x 10$^9$</td>
</tr>
<tr>
<td></td>
<td>CdSe—TiO2</td>
<td>0.51 (±0.01)</td>
<td>3.1 (±0.2) x 10$^{-12}$</td>
<td>0.53 (±0.01)</td>
<td>94 (±14) x 10$^{-12}$</td>
<td></td>
</tr>
<tr>
<td>MPA-assisted</td>
<td>CdSe—MPA—SiO2</td>
<td>0.28 (±0.02)</td>
<td>1.6 (±0.2) x 10$^{-12}$</td>
<td>0.77 (±0.01)</td>
<td>303 (±22) x 10$^{-12}$</td>
<td>2.3 x 10$^9$</td>
</tr>
<tr>
<td></td>
<td>CdSe—MPA—TiO2</td>
<td>0.36 (±0.01)</td>
<td>2.6 (±0.2) x 10$^{-12}$</td>
<td>0.68 (±0.01)</td>
<td>180 (±9) x 10$^{-12}$</td>
<td></td>
</tr>
</tbody>
</table>

a Results are based on the red lines in Figure 7F for d = 3.1 nm CdSe QDs. Apparent electron-transfer rate constants were calculated using eq 11.

Following photoexcitation of CdSe, the characteristic CdSe absorption band (Figure 7A) bleaches, which is manifested as negative absorbance in the transient spectral profile (Figure 7B—E). As carriers either recombine or are transferred to neighboring acceptors, this bleaching signal recovers and can be traced in real-time through delay-stage control of the pump—probe time differential. This decay in transient signal is showcased in the various traces in Figure 7B—E, which represent 1, 10, 100, and 1000 ps following the initial excitation event. CdSe QDs (3.1 nm diameter) were attached to a nanoparticulate SiO2 film by direct adsorption and through the use of (3-mercaptopropyl)trimethoxysilane (MPS) as a molecular linker. Because SiO2 is electronically insulating and will not undergo electron transfer from CdSe QDs, we were able to probe the QD relaxation kinetics.

By attaching the same batch of QDs to TiO2, a material that readily accepts electrons from the CdSe conduction band, we were able to probe the relaxation kinetics with the additional pathway of electron transfer. The kinetic traces of each film are shown in Figure 7F. Here, we fit the first 100 ps following the creation of the transient state to a biexponential model, assigning the fast time component ($\tau_1$, 1—3 ps) to electron-trapping events and the slow time component ($\tau_2$, tens of picoseconds) to the electron-transfer time window. Assuming the only difference between QDs attached to SiO2 or TiO2 is the added pathway of electron transfer, we were able to calculate the apparent electron-transfer rate of both linked and directly attached QDs to TiO2 nanoparticles using the following relationship:

$$k_{ET} = \frac{1}{\tau_2,\text{TiO}_2} - \frac{1}{\tau_2,\text{SiO}_2}$$

where $\tau_2,\text{TiO}_2$ and $\tau_2,\text{SiO}_2$ are the excited-state lifetimes of CdSe QDs attached to TiO2 and SiO2, respectively. Using the slower lifetime from a two-exponential best fit of our transient kinetic data (Figure 7F, red curves) in conjunction with eq 11, we calculated the apparent electron-transfer rates for both linked and linkerless—QD TiO2 junctions. A full list of best-fit parameters, including calculated electron-transfer rates, is provided in Table 3.

Under this analysis, apparent electron-transfer rate constants for CdSe QDs attached to TiO2 nanoparticles in a linked and linkerless fashion were 2.3 $\times$ 10$^9$ s$^{-1}$ and 7.2 $\times$ 10$^9$ s$^{-1}$, respectively. Given that the mechanism for electron transfer in the case of CdSe QDs on TiO2 nanoparticles involves tunneling through the QD—metal oxide junction, we expect the transfer rate in the case of directly adsorbed QDs to be greater than that of those attached with a linker molecule. Previously, Watson and co-workers reported an increase in electron-transfer rate from CdS QDs to TiO2 nanoparticles with decreasing mercaptoalkanoic acid chain length. However, their investigation was limited to nanosecond time resolution and did not report QDs directly attached to TiO2. Here, with picosecond time...
resolution, we were able to probe electron transfer on the ultrafast time scale, the region that showcases the majority of temporal transient dynamics.

It is interesting to note that, despite the presumably intimate contact for directly adsorbed QDs, $k_{ET}$ increased by only a factor of 3. In terms of the probability of electron tunneling, which decreases exponentially with increasing distance, we expected a greater enhancement of $k_{ET}$ with direct attachment. We speculate that, although the enhancement observed here is due to an increasingly intimate contact between the QD and TiO$_2$ species, even linkerless attachment results in contact that may be hindered by a physical or energetic barrier. Although identification of such a barrier is purely speculative, we anticipate that some surface-bound TOPO interferes with maximum overlap between the QD donating and TiO$_2$ accepting states.

■ CONCLUSIONS

The power conversion efficiency of quantum dot sensitized solar cells can be enhanced with greater absolute coverage of the TiO$_2$ photoanode with sensitizer. The present results provide insights into QD adsorption, which is an integral part of QDSSC optimization. First and most importantly, QD washing with methanol allows for greater adsorption due to removal of excess TOP from the QD surface. Second, increasing the QD concentration in toluene leads to greater coverage of TiO$_2$, as predicted by the Langmuir model. Third, a greater number of smaller nanoparticles absorb onto TiO$_2$ from a given concentration of QDs in toluene, and consequently, a larger photocurrent is expected with this improved QD loading. Finally, QD aggregation onto already-adsorbed QDs begins to dominate submonolayer adsorption at times greater than 10 h. Faster electron injection into mesoscopic TiO$_2$ was observed from directly adsorbed quantum dots over MPA-linked assemblies. Efforts are currently under way to quantify the effect of particle aggregation on electron-transfer kinetics. The fundamental information presented in this work will aid in constructing quantum dot sensitized solar cells with greater efficiency.

■ ASSOCIATED CONTENT

Supporting Information. Effect of washing on the QD size distribution, derivation of QDs adsorbed per TiO$_2$ nanoparticle, effect of washing on adsorption for directly adsorbed QDs, additional information on the kinetic adsorption model, and summary of points for improved QD adsorption on TiO$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: pkamat@nd.edu.

■ ACKNOWLEDGMENT

The research described herein was supported by the Office of Basic Energy Science of the Department of Energy. D. R. Pernik wishes to acknowledge the Vincent P. Slatt Fellowship for Undergraduate Research provided by the Notre Dame Energy Center. This is contribution NDRL 4884 from the Notre Dame Radiation Laboratory.

■ REFERENCES


