Next Generation Photovoltaics: Improvements to Quantum Dot Solar Cells

A Dissertation

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by

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Abstract
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New solar cell technologies such as quantum dot sensitized solar cells (QDSSCs) can help meet the demand for sustainable, clean energy. The investigations presented here demonstrate the optimization of a QDSSC working electrode according to colloidal deposition, electron transfer dynamics for linked and linkerless assemblies, solar paint synthesis with graphene, and CdSe oxidation in a solar paint solvent. CdSe QD size and use of MPA as a molecular linker were studied for their effects on QD adsorption rates onto TiO$_2$. A modified Langmuir model that accounted for particle aggregation was developed to determine adsorption rate parameters for each QD-TiO$_2$ system.

As expected, the use of MPA allowed more QDs to adsorb onto a sintered TiO$_2$ network, as evidenced by a higher equilibrium adsorption constant. However, the use of MPA was found to slow the electron injection into TiO$_2$ due to the greater physical separation between the electron donating and accepting species. Smaller QD particles were able to adsorb onto mesoporous TiO$_2$ in greater numbers than larger QD particles.

When added as a precursor for pseudo-SILAR synthesis, reduced graphene oxide did not affect CdSe growth. Solar cell performance was noticeably impeded by CdSe oxidation in the solvent, and CdSe-based solar paints were found to oxidize more quickly in solvent than on sintered films.
For David Leighton, Alex Griswold, and Uncle Jeff
# Table of Contents

1. Introduction ........................................................................................................................................ 4
   1.1 Current Sustainable Energy Landscape ....................................................................................... 4
   1.2 Solar Cell Mechanics and Design .............................................................................................. 6
   1.3 Specific Research Motivations .................................................................................................... 9

2. Assembly Optimization of QDSSC Working Electrode ................................................................. 10
   2.1 Experimental Design for QD Loading Study ............................................................................. 10
   2.2 Basis for Kinetic Adsorption Model ......................................................................................... 14
   2.3 Development of Modified Langmuir Adsorption Model ......................................................... 19
   2.4 Results of Adsorption Model Fitting: Effect of MPA and QD Size ........................................ 24

3. Effect of Attachment Method on Electron Injection .............................................................. 30
   3.1 Band Theory and QDSSC Electron Injection .......................................................................... 30
   3.2 Effect of Attachment Method on QDSSC Electron Injection Rates ......................................... 32

4. Solar Paint ....................................................................................................................................... 36
   4.1 Introduction to Solar Paint ......................................................................................................... 36
   4.2 Incorporating Graphene in Solar Paint ..................................................................................... 39
   4.3 Degradation of CdSe Solar Paint .............................................................................................. 41

5. Conclusions and Acknowledgements .......................................................................................... 46
   5.1 Conclusions ............................................................................................................................... 46
   5.2 Acknowledgements ..................................................................................................................... 47

6. References ....................................................................................................................................... 48
1. Introduction

1.1 Current Sustainable Energy Landscape

As worldwide energy consumption continues to rise, energy production must increase to meet the growing demand. Currently, the overwhelming majority of the world’s energy needs are met through the burning of fossil fuels. Fossil fuels are seen as an unsustainable source of energy due to their limited supply and their contributions to atmospheric greenhouse gases when burned. An increase in greenhouse gases such as CO$_2$ has been shown to play a role in the increasing temperature of the earth, which has the real potential to dramatically affect human and animal life on earth.\(^1\) Several approaches have been suggested to combat the problem of atmospheric CO$_2$; one such idea is carbon capture and sequestration.\(^2\) By capturing and remotely storing CO$_2$, the byproducts of fossil fuel combustion would not be able to reach the atmosphere and contribute to global warming.

Feasibility aside, this approach still does not address the limited supply of the fossil fuels oil, gas, and coal. Fossil fuels ultimately derive their energy from the sun, but millions of years of pressure were required to convert dead organisms into their modern-day energy forms. In the face of this problem, researchers are actively developing sustainable ways of producing energy.

Several renewable energy sources are being investigated for their potential to address large-scale demand, such as geothermal heat, wind, flowing water, and sunlight. Geothermal heat extraction has the problem of high capital costs, often making it an economically unfavorable option. Despite the relative abundance of wind across the earth, it has the problem of low energy density, making it difficult for wind farms to make any substantial dent in the global energy landscape. Hydroelectric power suffers the opposite problem; while flowing water is high in
energy density, there is a limited supply of waterfalls and fast-moving streams that can be economically converted into hydroelectric generators.

Solar energy appears to have the potential to address global energy needs. Solar flux calculations show that more energy reaches the earth in one hour than the world uses in one year. With solar energy, the problem is one of cheap and efficient energy conversion. Crystalline silicon is the most common type of solar cell in use today. In an attempt to bring down the cost of solar cells, new materials are being investigated such as dye-sensitized solar cells and quantum dot sensitized solar cells. A great deal of academic and industrial research is focused on improving the efficiency of these technologies in order that they might make a dent on the energy market.
1.2 Solar Cell Mechanics and Design

Photovoltaic devices are designed such that electric potential will drive the flow of charge carriers and generate electricity. Today’s most common solar cells are made from bulk crystalline silicon. Silicon is a semiconductor, meaning that its band gap (energy difference between valence and conduction band) is relatively small (less than \(~4\) eV). A semiconductor’s small band gap gives it unique physical properties; in its normal, equilibrium state it acts as an insulator, but if given energy equal to or exceeding its band gap, it will act as an electrical conductor. Crystalline silicon’s band gap is \(1.1\) eV,\(^8\) which allows it to harvest visible light.

However, bulk crystalline silicon makes a poor solar cell. Atomic silicon has four valence electrons in its outer shell and covalently bonds with four other silicon atoms, giving rise to a stable crystal structure with poor conductivity. To get around this problem, impurities are added in a process known as doping. Common dopants are those with three or five valence band electrons. If doped with Group 15 elements such as phosphorus, the resulting silicon is n-type, meaning electrons are the charge carriers. When doped with Group 13 elements such as Boron, the resulting silicon is p-type, meaning its charge carriers are holes (electron vacancies). Today’s crystalline silicon solar cells make use of both p- and n-type silicon, which are joined at a p-n junction. When this junction is formed, electrons rapidly migrate to the p-doped side and holes move to the n-doped side, creating a depletion region. Soon, an equilibrium of electrons and holes is formed on each side of the depletion region and an electric field is established between the two.

The electric field between the p- and n-doped silicon serves to direct the flow of electrons in the solar cell. When light of sufficient energy interacts with the silicon, an electron-hole pair known as an exciton is formed. If this exciton is near the p-n junction’s electric field, electrons
are injected into the n-silicon and holes migrate towards the p-doped side. This flow of electrons is what generates the current in photovoltaic devices.

The same principles behind these single p-n junction silicon solar cells are used in quantum dot sensitized solar cells (QDSSCs). The QDSSC is based on the Grätzel cell design, which used organic sensitizers to harvest light.\(^9\) A QDSSC differs slightly from the Grätzel cell in that it uses quantum dots as sensitizers. Quantum dots (QDs) are inorganic semiconducting nanoparticles that exhibit quantum confinement. Quantum confinement allows the band energetics of these particles to be tuned; as a QD grows larger, its band gap decreases.\(^{10}\) Thus, by using QDs as sensitizers, one is able to gain control over which portion of the solar spectrum he or she wishes to harvest.

QDSSCs make use of a metal oxide electron accepting species such as TiO\(_2\). In the assembly of these devices, a layer of TiO\(_2\) is applied to a conductive material and then quantum dots are deposited. A variety of deposition methods are common, such as colloidal deposition\(^{11}\), chemical bath deposition\(^7, 12, 13\), SILAR\(^6, 14\) (successive ionic layer adsorption and reaction), and electrodeposition\(^{15, 16}\). This part of the setup constitutes the QDSSC’s working electrode, which is connected via an external circuit to a counter electrode. The working electrode (also called the photoanode) and counter electrode can brought close to one another with an electrolyte sandwiched in between them in the construction of an aptly named sandwich cell. The electrolyte serves to replenish the charge carriers as they are drawn off to produce a current. See Figure 1 for a QDSSC overview.
Figure 1. Typical Schematic of a QDSSC. Light interacts with the QD, which causes electrons to be injected into TiO$_2$ and drawn off an external circuit to generate electricity. The electrolyte then replenishes the charge carriers.
1.3 Specific Research Motivations

All facets of quantum dot sensitized solar cells are under extensive research. Much work is under way to develop effective counter electrodes and efficient electrolytes to improve the efficiency of these devices. However, the investigations presented in this dissertation focus on improvements to the QDSSC working electrode for QDs attached to TiO$_2$. An important facet of these studies is the comparisons between direct adsorption and linker-assisted adsorption in which QDs are attached to TiO$_2$ with bifunctional 3-mercaptopropionic acid (MPA) molecules.

The first focus of this work is to maximize CdSe QD adsorption onto TiO$_2$. As an increasing coverage of TiO$_2$ with sensitizer results in improved photovoltaic properties,\textsuperscript{17} understanding the QD adsorption phenomena is an important step towards helping QDSSCs approach market-competitive levels of performance. The second focus of this work is to compare the electron injection characteristics from CdSe QDs into TiO$_2$ for directly adsorbed and molecularly linked quantum dots. By taking an in-depth look of the electronic properties of working electrodes assembled in different ways, researchers will better understand when it is appropriate to use a linker and when direct adsorption might be the better option. And finally, synthesis methods are presented for incorporating reduced graphene oxide in solar paint, a variation on the QDSSC design that incorporates the QD sensitizer and TiO$_2$ in a single layer. CdSe oxidation in this solar paint solvent is investigated as well.
2. Assembly Optimization of QDSSC Working Electrode

2.1 Experimental Design for QD Loading Study

As a greater loading of a large band gap semiconductor with QDs results in improved photovoltaic properties in QDSSCs, a detailed analysis was performed to determine how to achieve the best coverage of TiO$_2$ with CdSe nanoparticles.\textsuperscript{18} The nature of the interactions between CdSe and TiO$_2$ were investigated in a controlled setting.

To track the adsorption of QDs onto TiO$_2$ over time, an experimental setup was used whereby QD adsorption on TiO$_2$ occurred within an optical cell, enabling QD concentrations to be measured over time using a UV-Visible spectrophotometer. Figure 2 shows the schematics of TiO$_2$ slides and QD solution inside the optical cell. A 1 cm x 1 cm x 4 cm optical cell was partially filled with 2.4 mL QD solution in a glovebox maintained with N$_2$ atmosphere. QD concentration in toluene ranged from 1 to 10 µM (moles of quantum dots per liter). The two TiO$_2$ slides were inserted into the optical cell such that the TiO$_2$ surfaces were facing the center of the optical cell, making contact with the QD solution. The TiO$_2$-free ends of each microscope slide were only partially submerged in the QD solution so that small amount of QD solution could hold the TiO$_2$ slides against the walls of the optical cell by the solution’s surface tension. The optical cell was then closed, sealed with Parafilm, and removed from the glove box.
Figure 2. Experimental setup for QD adsorption experiments. Two glass slides with TiO$_2$ films on them were placed on the inner walls of an optical cell. A UV-Visible Spectrophotometer beam passed through the QD-toluene suspension to measure QD concentration in toluene without interference from the glass slides.

Once assembled, the optical cell was placed into a UV-Visible spectrophotometer for a series of absorbance measurements over the course of 48 hours at 15-minute 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 2). The difference in absorbance over time correlated to the amount of QDs adsorbed on the TiO$_2$ films. Blank experiments performed to check the stability of the QD solution exhibited insignificant changes in absorbance.

For each adsorption experiment, absorbance data was collected for 48 hours, and 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:

$$QD_{ads} = \left( \frac{A_0 - A_t}{\varepsilon l} \right) N_A V_{sol}$$  \hspace{1cm} (1)

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 absorbtivity,$^{10}$ $l$ 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 timescales 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 3B) as the concentration of QDs decreased in toluene (Figure 3A). The slight blueshift of these adsorbed QDs is attributed to structural and environmental changes occurring upon adsorption to TiO$_2$.\textsuperscript{17} And third, the absorbance spectra showed no excitonic peak shift within the QD solution over the course of the adsorption experiments, indicating the absence of absorbance changes due to particle ripening or etching.
Figure 3. Absorbance spectra showing CdSe QDs (A) decreasing in concentration in toluene suspension and (B) appearing on films of TiO$_2$. QDs are 3.8 nm in diameter, washed five times, and directly adsorbed onto TiO$_2$. The measured absorbance for the initial scan in (B) is due to light scattering by TiO$_2$ particles, and the blueshift between (A) and (B) has been previously described.$^{17}$
2.2 Basis for Kinetic Adsorption Model

A simple way to analyze QD adsorption on TiO$_2$ is through a Langmuir isotherm, which implies QDs form a sub-monolayer on TiO$_2$ and that adsorption and desorption occur simultaneously.$^{19}$ The forward adsorption processes in which QDs adhere to TiO$_2$ or MPA are commonly used in the construction of QDSSCs. To confirm the reverse process (QD desorption from TiO$_2$), both directly adsorbed and linked CdSe-TiO$_2$ films were immersed in neat toluene for twenty-four hours (Figure 4). A comparison of the absorption characteristics of the two films demonstrates the reversibility of the QD-TiO$_2$ adsorption. After 24 hours, the directly adsorbed QDs completely desorbed from the TiO$_2$ electrode. The molecularly linked QDs experienced a slower desorption rate, as would be expected for particles more strongly bound to TiO$_2$. Because desorption of QDs into fresh toluene is clearly observable, QD adsorption onto TiO$_2$, 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 sub-monolayer adsorption of QDs on TiO$_2$ for both methods of attachment.
Figure 4. Absorbance spectra of CdSe sensitized TiO$_2$ 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.

A question that arises is whether sub-monolayer TiO$_2$ coverage is the only process dominating the adsorption in this system. Previous studies have shown the controlled aggregation of semiconducting nanoparticles$^{20}$ and significant CdSe QD aggregation on TiO$_2$ films after long adsorption times.$^{17}$ Here, further evidence for QD aggregation was found through TEM imaging, as shown in Figure 5. Each sample was prepared by immersing a TiO$_2$ film in QD solution for six hours. A portion of the resulting QD sensitized TiO$_2$ was scraped off of the glass slide, suspended in ethanol, and dropcast onto a TEM grid. This procedure was followed for directly adsorbed (Figure 5A and Figure 5C) and MPA-linked (Figure 5B and Figure 5B) QD assemblies. In B, C, and D, CdSe lattice fringes were measured at 0.351 nm, in
agreement with the (002) spacing for wurtzite CdSe. Although the TiO$_2$ (101) d-spacing of 0.352 nm is very close to this (002) CdSe value, morphology differences were apparent and sufficient for identifying each component. To help demonstrate this point, the sample in Figure 5C was tilted to bring TiO$_2$’s (004) planes into the Bragg angle, verifying TiO$_2$ as the much larger, rod-shaped particle. A and B demonstrate QDs adsorbed on TiO$_2$ as a sub-monolayer, whereas C and D show aggregated QDs on TiO$_2$. The sample in Figure 5A was imaged under brightfield mode to show an overview of individual, spherical QDs directly adsorbed to a cluster of rod-shaped TiO$_2$ particles.
Figure 5. TEM images of CdSe QDs attached to TiO$_2$ by (A and C) direct adsorption and (B and D) MPA-assisted adsorption. Images A and B illustrate sub-monolayer adsorption while C and D are instances of QD aggregation on the TiO$_2$ surface. Image A was taken in brightfield mode and exhibits singly adsorbed spherical QDs on rod-shaped TiO$_2$. All images correspond to a TiO$_2$ in CdSe immersion time of 6 hours.

Figure 6 illustrates the adsorption of QDs with initial Langmuir type sub-monolayer adsorption followed by QD aggregation for both linkerless and linker-assisted adsorption
The mechanism of QD aggregation is of interest, as interparticle interaction could further influence the charge injection process at the metal oxide interface.

Currently, the mechanism behind QD aggregation on the TiO$_2$ surface is not definitively known. Particle aggregation most likely arises from one or more of the following factors: nonpolar interactions between TOPO capping agents of neighboring QDs, van der Waals interactions between QDs, and electrostatic interactions between QDs.

**Figure 6.** CdSe QD adsorption on TiO$_2$ occurs through sub-monolayer formation followed by particle aggregation onto already-adsorbed QDs.
2.3 Development of Modified Langmuir Adsorption Model

To model CdSe QD adsorption on a sintered network of TiO$_2$ nanoparticles, Langmuir second order adsorption and first order desorption processes were used, given by Equations 2 and 3, respectively.\(^{19}\)

\[
[P] + [S] \xrightarrow{k_1} [PS] \quad (2)
\]
\[
[PS] \xrightarrow{k_{-1}} [P] + [S] \quad (3)
\]

P represents CdSe QD particles in toluene solution, S represents sites on the TiO$_2$ network available for CdSe adsorption, and PS represents CdSe QDs that have left solution and are adsorbed onto a TiO$_2$ nanoparticle. The total equilibrium constant for Langmuir type sub-monolayer coverage ($K_{ad}$) is written in terms of the adsorption and desorption rate constants:

\[
K_{ad} = \frac{k_1}{k_{-1}} \quad (4)
\]

A low theoretical coverage of TiO$_2$ was achieved over the course of the QD adsorption experiments, with less than 10% of the available TiO$_2$ sites covered by CdSe for the majority of the experimental trials. This result shows that adsorption is not limited by the number of available TiO$_2$ adsorption sites for the concentrations of QDs that were used in this investigation. Therefore it is possible to simplify the adsorption model to a pseudo first order relationship:

\[
[P] \xrightarrow{k_1'} [PS] \quad (5)
\]

where Equation 5 assumes a constant number of available TiO$_2$ binding sites. The concentration of QD binding sites on TiO$_2$, $[S_0]$ is then used to relate the second order and pseudo first order adsorption rate constants.
As illustrated in Figure 5, the use of either linkerless or linker-assisted adsorption of CdSe QDs on TiO₂ nanoparticles results in, over time, the aggregation of QDs on the TiO₂ surface. Physically, aggregation is the adsorption of a CdSe QD on a QD that is already adsorbed on a TiO₂ surface. This phenomenon is described by the following relationship:

\[
[P_n S] + [P] \xrightarrow{k_{ag}} [P_{n+1} S]
\]  

(7)

where \(P_n S\) represents any TiO₂ adsorption site with one or several QDs attached, and \(P_{n+1} S\) 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 Equations 3, 5, and 7, the rates of decreasing CdSe QD concentration in toluene due to sub-monolayer adsorption and aggregation processes are given by Equations 8 and 9, respectively:

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

(8)

\[
\frac{-d[P]_{ag}}{dt} = k_{ag} [P] [P_n S]
\]

(9)

where \([P]_{Lang}\) and \([P]_{ag}\) are the concentrations of CdSe QDs which form either a sub-monolayer coverage on the TiO₂ nanoparticulate network \([P]_{Lang}\), or aggregate onto QDs which were already adsorbed to TiO₂ \([P]_{ag}\). The total observable decrease in QD concentration in toluene is then expressed as:
Equation 8 was integrated in order to relate adsorption over time with both starting concentrations of QDs and TiO$_2$ adsorption sites according to a purely theoretical Langmuir-like model. PS is then related to the original concentration of QDs in solution,

\[ PS = P_0 - P \]  

resulting in

\[ \frac{-d[P]_{Lang}}{dt} = k'_1[P] - k_{-1}[P_0 - P] \]  

which is conveniently only a function of $P$. Integration then results in Equation 13, which is the expression that was used to model sub-monolayer adsorption.

\[ [P(t)]_{Lang} = [P_0] - \left( \frac{k'_1[P_0]e^{-(k'_1+k_{-1})t} + k_{-1}[P_0]}{k'_1+k_{-1}} \right) \]  

Experimental deviation from Equation 13 is attributed to QD aggregation onto already-adsorbed QDs and is modeled by Equation 9. By the principle of microscopic reversibility, a reverse aggregation process must also occur, but its rate was assumed to be sufficiently small as to be ignored. Using the trapezoid method of approximate integration on Equation 9 resulted in the following:

\[ [P(t)]_{ag} = [P]_{ag,t-1} + k_{ag}[P]_{t-1}[P_nS]_{t-1}\Delta t \]  

where $\Delta t$ is the time difference between measurements and $t-1$ refers to the time of the measurement previous to the time of the data point of interest. $P$ is the number of CdSe particles
in solution, \( P_nS \) refers to any number of particles adsorbed or aggregated onto individual TiO\(_2\) adsorption sites, and \( P_{ag} \) is the total number of particle aggregates across all TiO\(_2\) adsorption sites. The overall adsorption model consists of the sum of Equations S8 and S10.

\[
[P(t)]_{total} = [P(t)]_{Lang} + [P(t)]_{ag} \tag{15}
\]

To find the rate parameters for any given set of data, constants \( k_1' \), \( k_{-1} \), and \( k_{ag} \) were iterated upon until the sum of the squared error between the model and experimental data was minimized.

After fitting the adsorption data, \( k_1' \) was related to \( k_1 \) by Equation 6 and the resulting \( k_1 \) and \( k_{-1} \) constants were related to \( K_{ad} \) according to Equation 4. Since \( k_{ag} \) does not appear in Equation 4, \( K_{ad} \) is only a measure of sub-monolayer coverage of TiO\(_2\). Figure 7 shows a sample fit of Equations 10 to experimental adsorption data, along with the deconvoluted contributions from Langmuir-like adsorption (Equation 8) and QD aggregation (Equation 9). Figure 7 is a representation of a typical model fit to experimental QD adsorption data.
Figure 7. Theoretical fit of experimental adsorption data. Adsorption due to sub-monolayer formation (Equation 8) and QD aggregation on the TiO$_2$ surface (Equation 9) are added together to obtain the total fit (Equation 10). Linker-assisted adsorption of 2.6 nm diameter CdSe QDs on TiO$_2$ at a concentration of 9.4 µM. QDs were washed five times prior to adsorption.
2.4 Results of Adsorption Model Fitting: Effect of MPA and QD Size

The kinetic model and experimental adsorption data were used to determine adsorption rate constants for QDs on TiO₂. Two factors were investigated separately to determine their affect on QD affinity to TiO₂: MPA usage and QD particle size.

First, QD washing was looked at to see its effect on QD adsorption to TiO₂. Colloidal QDs are typically prepared with capping molecules that allow them to be stable in nonpolar suspensions such as toluene. The capping molecule used in these studies is trioctyl phosphonic acid (TOPO). A post-synthetic process known washing is used to remove excess TOPO as well as excess reaction precursors and undesirable biproducts from the QD surface. Murray et al. have described the processes involved in QD washing.²¹ 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. Re-suspension in fresh solvent then yields monodispersed QDs with less surface-bound TOPO.²¹

It was hypothesized that repeated washing would remove additional TOPO from the QD surface, freeing up more CdSe surface area and making it easier for the QDs to interact with TiO₂. Indeed, this was found to be the case. Figure 8 shows that with increased washing, a greater number of QDs adsorb onto TiO₂ for MPA-assisted adsorption.
Figure 8. CdSe QD adsorption onto TiO$_2$ for QDs washed (a) once, (b) three times, and (c) five times with methanol. Traces represent MPA-assisted adsorption, 3.1 nm average diameter QDs at a concentration of 8.5 µM.

The experiment was repeated, this time testing the effect of washing on direct adsorption. The results of this study are seen in Figure 9. As expected, the same trend holds; removal of surface-bound TOPO improves QD affinity for TiO$_2$. However, it should be noted that five wash cycles was found to be optimal; beyond five, the QDs began to lose stability in toluene, eventually making colloidal deposition impossible.
Figure 9. Time dependent CdSe QD adsorption onto TiO$_2$ with QDs washed (a) once, (b) thrice, and (c) five times with methanol. Traces represent directly adsorbed, 2.6 nm average diameter QDs at a concentration of 9.5 µM. Direct comparison should not be made with Figure 8 due to size and concentration differences, although the same relationship between number of washes and adsorption onto TiO$_2$ was observed.

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 removes surface-bound TOPO and that TOPO removal improves QD interactions with TiO$_2$ and MPA. This strong correlation between washing and adsorption highlights the importance of QD pretreatment for successful adsorption on a TiO$_2$ surface.

With the knowledge that five wash cycles is optimal, control studies were set up using QDs that had all been washed five times. The first control study looked at the effect of linker-
assisted adsorption (using MPA) and direct adsorption (without MPA) on adsorption rate parameters. The results of this study 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 TiO$_2$ films.

**Table 1.** Rate and equilibrium constants for CdSe QD adsorbing onto TiO$_2$ from toluene by direct and MPA-assisted adsorption. QDs were washed five times. Uncertainty ranges reflect standard error.

<table>
<thead>
<tr>
<th>Mode of Attachment</th>
<th>$k_1$ (M$^{-1}$ s$^{-1}$)</th>
<th>$k_{-1}$ (s$^{-1}$)</th>
<th>$k_{ag}$ (M$^{-1}$ s$^{-1}$)</th>
<th>$K_{ad}$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Adsorption</td>
<td>$0.42 \pm 0.28$</td>
<td>$(6.2 \pm 2.2) \times 10^{-5}$</td>
<td>$1.0 \pm 0.4$</td>
<td>$(6.7 \pm 2.7) \times 10^{3}$</td>
</tr>
<tr>
<td>MPA-Assisted</td>
<td>$0.65 \pm 0.23$</td>
<td>$(1.5 \pm 0.5) \times 10^{-5}$</td>
<td>$0.9 \pm 0.5$</td>
<td>$(4.2 \pm 2.0) \times 10^{4}$</td>
</tr>
</tbody>
</table>

The larger $k_1$ and smaller $k_{-1}$ for MPA-assisted adsorption indicates QDs experience faster adsorption and slower desorption when MPA was used as a molecular linker. The effects of faster adsorption and slower desorption combine through Equation 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 sub-monolayer adsorption on TiO$_2$ when MPA is used.

Quantum dot aggregation typically dominates adsorption at exposure times greater than ten hours. The significant deviation from Langmuir-like adsorption seen at large times in Figure 7 demonstrates this point. The aggregation rate constant $k_{ag}$ exhibited no noticeable dependence on the method of adsorption; however its uncertainty is large enough to warrant further investigation.

The second control study looked at how QD particle size affects the coverage of TiO$_2$ that can be achieved. 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 TiO$_2$. 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 QDs that adsorbed onto TiO$_2$ after three hours were recorded. The time of three hours was chosen in order to minimize the presence of QD aggregation on the TiO$_2$ 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 TiO$_2$. This discrepancy is possible because $K_{ad}$ is a function of $S_0$, the maximum number of available TiO$_2$ 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 TiO$_2$ adsorption sites. The increased relative adsorption for larger particles is possibly a result of their larger van der Waals forces, which cause stronger electronic interactions with MPA and TiO$_2$.

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 TiO$_2$ surface rather than to achieve a greater mathematical surface coverage. For this reason stronger photovoltaic properties would be expected through adsorption of smaller QDs compared to larger QDs under similar adsorption conditions.
Table 2. Size-dependent adsorption parameters. CdSe QDs washed five times, at an initial concentration 1.0 ± 0.1 µM.

<table>
<thead>
<tr>
<th>QD Diameter</th>
<th>Mode of Attachment</th>
<th>( K_{ad} ) (M⁻¹)</th>
<th>QDs Adsorbed Per TiO₂ Nanoparticle at 3 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6 nm</td>
<td>Direct Adsorption</td>
<td>( 6.5 \times 10^3 )</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>MPA-Assisted</td>
<td>( 6.0 \times 10^4 )</td>
<td>13.0</td>
</tr>
<tr>
<td>4.6 nm</td>
<td>Direct Adsorption</td>
<td>( 9.4 \times 10^3 )</td>
<td>3.2</td>
</tr>
<tr>
<td></td>
<td>MPA-Assisted</td>
<td>( 7.8 \times 10^4 )</td>
<td>7.1</td>
</tr>
</tbody>
</table>

Of course, QD coverage of TiO₂ isn’t the only concern when deciding what size of QDs to use in a QDSSC. Another size-dependent property is the rate of electron injection; charge is injected into TiO₂ more rapidly from smaller QDs than from larger QDs due to an increased conduction band offset."\(^{22}\)
3. Effect of Attachment Method on Electron Injection

3.1 Band Theory and QDSSC Electron Injection

Solids can fall into one of three categories based on their electrical conductivity: insulators, conductors, and semiconductors. A material’s conductive properties are easily explained by band theory. Whereas an individual atom has discrete, clearly defined electronic states, bulk materials have complex overlapping energy states known as bands. When that material gains energy in the form of light or heat, it can access higher energy states in what is known as its conduction band. The energy difference between the valence and conduction bands is known as the material’s band gap. Insulators are materials that have large band gaps; it would require a large amount of energy for a valence band electron to reach the conduction band. Conductors have overlapping valence and conduction bands, allowing electrons to freely conduct throughout the material. A semiconductor has a small band gap. The band positioning of a semiconductor allows it to act normally as an insulator or to act as a conductor when given energy equal to or greater than its band gap.

A conduction band electron is free to move to the conduction band of other materials as long as the potential energy for such a transition is favorable. In other words, the electron can only move down energy levels. This injection of an electron from one material to another is an important area of research for QDSSCs. Specifically, in QDSSCs electrons need to be injected from the electron accepting QD into the TiO₂ support structure so it can contribute to producing an electric current. This electron injection process needs to occur faster than the process of natural electron-hole recombination in the QD.
Quantum dots are nanoscale semiconductors. They are made of materials that are semiconductors even in bulk. As a QD’s particle size decreases, the material begins to exhibit quantum effects and its band gap increases. It has been demonstrated that with an increasing TiO$_2$–QD conduction band offset (as QD size decreases), electrons inject more rapidly into TiO$_2$. Upon first glance, this is a useful result with real-world implications for how to improve efficiency in QDSSCs. However, quantum dots need to be synthesized to a fairly narrow size range in order to harvest a substantial portion of the solar spectrum. This illustrates the need for further investigations in improving electron injection speeds in QDSSC.
3.2 Effect of Attachment Method on QDSSC Electron Injection Rates

Electron injection rates were compared in CdSe QDSSC electrodes that had been assembled by linker-assisted adsorption and by linker-free adsorption. 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. When a CdSe nanoparticle absorbs light, an exciton is produced and its characteristic absorption band disappears. This disappearance of the absorption band shows up as a negative, or bleached, signal in transient absorption spectroscopy. As charge carriers recombine or are transferred to neighboring acceptors, the characteristic absorption band reappears. By exciting a sample of CdSe QDs on TiO$_2$ and measuring the absorbance of the sample at intervals after the photoexcitation, the rate of electron injection from CdSe can be learned.

CdSe (3.1 nm in diameter) attached to SiO$_2$ (both by direct adsorption and with the use of (3-mercaptopropyl)-trimethoxysilane (MPS) as a molecular linker) was used as a control for this investigation, as SiO$_2$ is electronically insulating to CdSe. Therefore, the CdSe-SiO$_2$ sample provided data for how rapidly the electrons and holes would naturally recombine in CdSe QDs. A biexponential model was used, where the fast time component ($\tau_1$, 1-3ps) was assigned to electron trapping events,$^{23}$ and the slow time component ($\tau_2$, tens of ps) was assigned to the electron transfer time window. Assuming the only difference between QDs attached to SiO$_2$ or TiO$_2$ is the added pathway of electron transfer, the apparent electron transfer rate of both linked and directly attached QDs to TiO$_2$ nanoparticles was calculated using the following relationship$^{24}$:

$$k_{ET} = \frac{1}{\tau_{2,\text{TiO}_2}} - \frac{1}{\tau_{2,\text{SiO}_2}}$$ (16)
where $\tau_{2, \text{TiO}_2}$ and $\tau_{2, \text{SiO}_2}$ are the excited state lifetimes of CdSe QDs attached to TiO$_2$ and SiO$_2$, respectively.

The decay in the bleached signal is showcased in the various traces in Figure 10 B-E which represent 1, 10, 100, and 1000ps following the initial excitation event. Using the slower lifetime from a two-exponential best-fit of this kinetic data (Figure 10F, red curves) in conjunction with Equation 16, apparent electron transfer rates for both linked and linkerless QD-metal oxide junctions were calculated. A full list of best-fit parameters, including calculated electron transfer rates, is found in Table 3.

**Figure 10.** Absorbance spectrum of (d=3.1nm) CdSe quantum dots in toluene solution (A), and transient absorption spectral traces of attached to SiO$_2$/TiO$_2$ in a linkerless (B)/(C) and linked (D)/(E) fashion. Transient signal decreases with increasing pump-probe delay time: 1ps (red), 10ps (blue), 100ps (teal), 1000ps (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 TiO$_2$ acceptor.
Table 3. Summary of biexponential best-fit results (Figure 10F, red lines) of d=3.1nm CdSe quantum dots attached to TiO\textsubscript{2} and SiO\textsubscript{2} nanoparticles in both a linkerless and linked fashion. Apparent electron transfer rate constants were calculated using Equation 16.

<table>
<thead>
<tr>
<th>Mode of Attachment</th>
<th>Species</th>
<th>$A_1$ (s$^{-1}$)</th>
<th>$\tau_1$ (s)</th>
<th>$A_2$ (s$^{-1}$)</th>
<th>$\tau_2$ (s)</th>
<th>$k_{ET}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Adsorption</td>
<td>CdSe-SiO\textsubscript{2}</td>
<td>0.36 (±0.01)</td>
<td>2.1 (±0.2) $\times 10^{-12}$</td>
<td>0.72 (±0.01)</td>
<td>280 (±16) $\times 10^{-12}$</td>
<td>7.2 $\times 10^9$</td>
</tr>
<tr>
<td></td>
<td>CdSe-TiO\textsubscript{2}</td>
<td>0.51 (±0.01)</td>
<td>3.1 (±0.2) $\times 10^{-12}$</td>
<td>0.53 (±0.01)</td>
<td>94 (±14) $\times 10^{-12}$</td>
<td></td>
</tr>
<tr>
<td>MPA-Assisted</td>
<td>CdSe-MPS-SiO\textsubscript{2}</td>
<td>0.28 (±0.02)</td>
<td>1.6 (±0.2) $\times 10^{-12}$</td>
<td>0.77 (±0.01)</td>
<td>303 (±22) $\times 10^{-12}$</td>
<td>2.3 $\times 10^9$</td>
</tr>
<tr>
<td></td>
<td>CdSe-MPA-TiO\textsubscript{2}</td>
<td>0.36 (±0.01)</td>
<td>2.6 (±0.2) $\times 10^{-12}$</td>
<td>0.68 (±0.01)</td>
<td>180 (±9) $\times 10^{-12}$</td>
<td></td>
</tr>
</tbody>
</table>

Under this analysis, apparent electron transfer rate constants for CdSe QDs attached to TiO\textsubscript{2} 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 TiO\textsubscript{2} nanoparticles involves tunneling through the QD-metal oxide junction, it was expected that the transfer rate in the case of directly adsorbed QDs would be greater than that of those attached with a linker molecule. Previously, Watson and coworkers reported an increase in electron transfer rate from CdS QDs to TiO\textsubscript{2} nanoparticles with decreasing mercaptoalkanoic acid chain length.$^{25}$ However, their investigation was limited to nanosecond time resolution and did not report QDs directly attached to TiO\textsubscript{2}. Here, with picosecond time resolution, the electron transfer dynamics were probed 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 three. In terms of the probability of electron tunneling, which decreases exponentially with increasing distance,$^{26}$ an even greater enhancement of $k_{ET}$ was expected with direct attachment. It is possible that while the enhancement observed here was

34
due to an increasingly intimate contact between the QD and TiO$_2$ species, even linkerless attachment resulted in contact that may have been hindered by a physical or energetic barrier.
4. Solar Paint

4.1 Introduction to Solar Paint

The end goal for this research is to help develop a solar cell technology that can provide clean energy on a large scale. It would be foolish to ignore practicalities such as cost when designing a solar cell. Various research groups have had successes with printable photovoltaics and low-cost materials for use in large-area solar cells.\textsuperscript{27-31} One particular application for nanoscale semiconductors has recently emerged: solar paint. Solar paint is a one-layer approach that has the potential to meet the demand as an economically viable solar cell technology. The Kamat group has recently demonstrated the feasibility of solar paint by producing a solar cell with a power conversion efficiency exceeding 1\% based on a simple layer paintbrush approach under ambient conditions.\textsuperscript{32}

Figure 11 illustrates the simple principle behind solar paint. Whereas a traditional QDSSC requires several assembly steps, with this approach both the large bandgap semiconductor and the sensitizer are contained in one layer of the paste.
Figure 11. A layer of solar paint can be applied to a conductive surface and produce electricity when illuminated. The sensitizer and large bandgap semiconductor are both contained in the paste to simplify the traditional QDSSC design.\textsuperscript{32} 

This recent work in the Kamat group tested several different materials in a water/t-butanol paste. First, bulk CdS with TiO\textsubscript{2} and/or ZnO were used, achieving power conversion efficiencies between 0.57 and 0.89. Then, CdS and CdSe pastes were developed using a pseudo-SILAR (Successive Ionic Layer Adsorption and Reaction) method. This method produced a painted CdS-TiO\textsubscript{2}/CdS-TiO\textsubscript{2} solar cell with an efficiency of 1.08 percent.\textsuperscript{32} The preparation steps for the pseudo-SILAR method are shown in Figure 12.
Figure 12. Pseudo-SILAR solar paint preparation process. Reaction precursors are mixed and centrifuged in each cycle to create CdS and CdSe nanoparticles.\textsuperscript{32}

There are several opportunities to improve on solar paint. Further optimization and use of different semiconductor nanoparticles should help to boost the efficiency of these devices.
4.2 Incorporating Graphene in Solar Paint

Graphene is a popular material that is under extensive research due to its high electron and hole mobility. By incorporating reduced graphene oxide (RGO) to solar paint, it was expected that RGO would act as nano-channels for electron transport, helping to improve the solar paint efficiency. As graphene is inexpensive, has high electrical conductivity at room temperature, and is soluble in polar solvents, it is a good candidate for use in solar paint.

Pastes were prepared with a slight modification on the previously demonstrated pseudo-SILAR method: in each cycle Cd\(^{2+}\) precursor ions were added to the TiO\(_2\) slurry, which was centrifuged, decanted, and resuspended in solvent before Se\(^{2-}\) ions were added. Rather than add RGO to previously prepared pastes, it was included in the TiO\(_2\)-solvent slurry before the pseudo-SILAR steps were performed. By this method, it was expected that CdSe particles would seed and grow on the TiO\(_2\) particles and on RGO alike. Thus, the RGO would be better incorporated into the TiO\(_2\)-CdSe network.

Adding RGO to the TiO\(_2\) slurry appeared to have no negative affect on CdSe growth. Figure 17 (found later in section 4.3) demonstrates that the absorption spectra for films made from three pastes are identical, independent of the amount of RGO incorporated in the slurry.
**Figure 13.** CdSe growth is present with (right) and without (left) RGO in the TiO₂ slurry.

**Figure 14.** Three pastes containing (left) 0 mg/mL reduced graphene oxide, (middle) 0.025 mg/mL reduced graphene oxide, and (right) 0.1 mg/mL reduced graphene oxide. Each paste was prepared with two sets of alternating cycles of 0.5 mL of Cd²⁺ and Se²⁻ precursors.
4.3 Degradation of CdSe Solar Paint

Thin films were prepared from the three pastes pictured in Figure 14 by sintering at 200 °C under nitrogen on indium-doped tin oxide (ITO) conductive glass. 0.25 cm² working area sandwich cells were prepared using a Cu₂S-RGO counter electrode and a polysulfide electrolyte. Current versus potential measurements as well as cell performance parameters are shown in Figure 15 and Table 4, respectively.

**Figure 15.** Current versus potential curves for three CdSe/TiO₂ pastes with 0 mg/mL RGO (top left), 0.025 mg/mL RGO (top right), and 0.1 mg/mL RGO (bottom) added as precursors to the slurries.
Table 4. Cell performance parameters.

<table>
<thead>
<tr>
<th>Type of Paste Used</th>
<th>$V_{OC}$ (V)</th>
<th>$I_{SC}$ (mA)</th>
<th>Fill Factor</th>
<th>% Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe+TiO$_2$+0 mg/mL RGO</td>
<td>0.149</td>
<td>0.0107</td>
<td>0.32</td>
<td>0.0020</td>
</tr>
<tr>
<td>CdSe+TiO$_2$+0.025 mg/mL RGO</td>
<td>0.134</td>
<td>0.0082</td>
<td>0.31</td>
<td>0.0014</td>
</tr>
<tr>
<td>CdSe+TiO$_2$+0.1 mg/mL RGO</td>
<td>0.134</td>
<td>0.0085</td>
<td>0.32</td>
<td>0.0014</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.072</td>
<td>0.0085</td>
<td>0.37</td>
<td>0.0009</td>
</tr>
</tbody>
</table>

The performance of these cells was quite poor, evidenced by the power conversion efficiencies on the order of 0.001 percent. It is important to note that these films were sintered five days after the pastes were made. It was suspected that CdSe degradation played an important role in these cells performing so poorly and that the films were behaving similarly to a pure TiO$_2$ working electrode. As a semiconductor, TiO$_2$ can function as a working electrode on its own, but its large band gap makes it a poor light harvester. A TiO$_2$ film sandwich cell was prepared and tested as a baseline. As seen in Table 4, the TiO$_2$ cell performed only slightly worse than the partially degraded CdSe on TiO$_2$-RGO films, supporting the hypothesis of CdSe degradation.

Further pieces of observational and spectroscopic support the CdSe degradation hypothesis.

Figure 16 shows that CdSe-TiO$_2$ pastes lose their color when stored in oxygen-rich solvents for extended periods of time (compare to Figure 14).
Figure 16. The same pastes as in Figure 14, shown here two weeks later. Each paste has lost its color.

Additionally, scattering UV-Visible Spectroscopy was used to see the shift in absorbance of these pastes before and after degradation. Figure 17 shows the results of these measurements. In each case, the broad CdSe peak flattens significantly.
Figure 17. UV-Visible Spectroscopy traces of films made from three CdSe/TiO$_2$ pastes with 0 mg/mL RGO (top left), 0.025 mg/mL RGO (top right), and 0.1 mg/mL RGO (bottom) added as precursors to the slurries. After 21 days new films were made from the same pastes; all three pastes have degraded, as evidenced by the significant flattening of the broad peak at 430-680 nm. All traces have been normalized to their TiO$_2$ peaks (~350 nm).
Of course, the mechanism of CdSe degradation is of interest. Based on the final color of the pastes in Figure 16, it is likely that CdSe reacts with oxygen to produce one or more of the following products: CdO (dark brown), selenium(IV) oxide (grayish pink), or selenium(II) oxide (brownish black). It appears that a paste's solvent (t-butanol and water) mediates this oxidation process. Figure 18 demonstrates that once a film has been sintered, CdSe will not oxidize on the same timescales as when it is in solvent.

**Figure 18.** CdSe does not degrade quickly on sintered films. Each scattering UV-Visible absorbance trace has been normalized to its CdSe peak (~480 nm). Traces are offset on the y-axis to allow both traces to be fully distinguishable.
5. Conclusions and Acknowledgements

5.1 Conclusions

Quantum dot solar cells can feasibly make a dent in the future energy market. The findings presented here contribute to the fundamental understanding of quantum dot sensitized solar cells. In particular, this work takes a look at several practical aspects such as how to maximize QD coverage on a working electrode, the effect of molecular linkers on electron injection from CdSe QDs into TiO$_2$, and solar paint oxidation.

As expected, QDs were found to adsorb onto TiO$_2$ more readily when MPA was used as a molecular linker than when they were directly adsorbed. More small QDs could adsorb onto TiO$_2$ compared to larger QDs from comparable concentrations in toluene suspensions. Electrons injected from QDs into TiO$_2$ more rapidly when linker molecules were not used to attach the two species than when they were molecularly linked.

Finally, paint-based solar cells have recently emerged as a variation on the Grätzel cell design, incorporating the sensitizer and electron accepting species in a paste that is applied in one layer. Reduced graphene oxide was successfully incorporated into CdSe/TiO$_2$/t-butanol/water slurries without affecting CdSe growth by pseudo-SILAR synthesis. However, performance was impeded by CdSe degradation in the solvent. Dissolved oxygen is believed to oxidize CdSe in the solar paint solvent; however atmospheric oxygen is slow to oxidize sintered films of CdSe on TiO$_2$. 
5.2 Acknowledgements

I would like to first thank Dr. Prashant Kamat for giving me the freedom to take on sizable projects and for letting me develop into a better scientist as my projects evolved organically. Second, I must thank Dr. Kevin Tvrdy for his top notch mentoring. Kevin was my role model in lab and was the first to open my mind to the possibility of pursuing a scientific career. I want to thank the other graduate and undergraduate students in the Radiation Laboratory for their friendships and scientific guidance, but they should understand that Kevin is my favorite. Sorry, Doug Hines.

I’d like to thank my family for their continued 100% support of my pursuits. I also want to acknowledge the friends that I’ve made at Notre Dame outside of lab including my wonderful friends in the Glee Club. Specifically, Tim Schumer has been an excellent friend, lab partner, and co-Vice President of the Glee Club with me.

I want to thank the Slatt family for the Fellowship for Undergraduate Research in Energy Systems and Processes, which I received in the spring of 2010. I also want to acknowledge the U.S. Department of Energy for supporting much of the research in the Radiation Laboratory.

Although it’s difficult to put a name to the specific person I’d like to thank for this, I want to acknowledge whichever unseen powers gave me the opportunity for undergraduate research at Notre Dame. Throughout my time in the Radiation Laboratory I had access to a wealth of resources including journal subscriptions and top-of-the-line scientific instruments. I suppose it’s appropriate to thank Notre Dame as a whole for having an integral mission of excellence in scientific research.

I look forward to continuing similar work next year in the Korgel group at the University of Texas at Austin.
6. References


