ON THE ADVANCEMENT OF QUANTUM DOT SOLAR CELL PERFORMANCE
THROUGH ENHANCED CHARGE CARRIER DYNAMICS

A Dissertation

Submitted to the Graduate School
of the University of Notre Dame
in Partial Fulfillment of the Requirements
for the Degree of

Doctor of Philosophy

by

David R. Baker

Prashant V. Kamat, Director

Graduate Program in Chemical and Biomolecular Engineering
Notre Dame, Indiana
April 2011
ON THE ADVANCEMENT OF QUANTUM DOT SOLAR CELL PERFORMANCE
THROUGH ENHANCED CHARGE CARRIER DYNAMICS

Abstract

by

David R. Baker

The quantum dot solar cell is one of the few solar technologies which promises to compete with fossil fuels, but work is still needed to increase its performance. Electron transfer kinetics at interfaces and limitations of the redox couple within the cell, are responsible for lowering power conversion efficiency. Several techniques which are able to increase electron transfer within the working electrode and at the counter electrode/electrolyte interface are discussed in this dissertation.

Trap sites on the surface of CdSe quantum dots are created when mercaptopropionic acid (MPA) is added to the suspension. The trap sites are emissive creating a loss pathway for photogenerated charges which will manifest as reduced photocurrent. MPA displaces amines on the surface of CdSe creating Se vacancies. Emission properties are controlled by the concentration of MPA. Because trap sites are generated, a more successful method to sensitize TiO₂ films is the SILAR technique which directly grows quantum dots on the desired surface.
Anodically etched TiO\textsubscript{2} nanotubes yield photocurrents 20\% greater than TiO\textsubscript{2} nanoparticles because of longer electron diffusion lengths. Peak incident photon to charge carrier efficiencies of TiO\textsubscript{2} nanotube samples show a doubling of photocurrent in the visible region compared to nanoparticles. The TiO\textsubscript{2} substrates are sensitized with CdS by the SILAR process which is found to utilize both the inside and outside surfaces of the TiO\textsubscript{2} nanotubes.

Etched TiO\textsubscript{2} nanotubes are removed from the underlying titanium foil in order to use spectroscopic techniques. Ultrafast transient absorption shows the extremely fast nature of charge injection from SILAR CdS into TiO\textsubscript{2} nanotubes. Surface area analysis of TiO\textsubscript{2} nanotube powder gives an area of 77m\textsuperscript{2}/g, a value 1.5 times larger than traditional TiO\textsubscript{2} nanoparticles.

By isolating the counter electrode with a salt bridge the effect of the polysulfide electrolyte is found to act as an electron scavenger on the working electrode. Though activity at the platinum counter electrode increases with the presence of polysulfides, the activity is too low to counteract scavenging at the working electrode. Cu\textsubscript{2}S, CoS and PbS electrochemically show promise as alternatives to platinum. Cu\textsubscript{2}S and CoS produce higher photocurrents and fill factors, greatly improving cell performance.
TABLE OF CONTENTS

Figures ................................................................................................................................ iv
Tables ....................................................................................................................................... viii

Chapter 1: Introduction and Background ............................................................................ 1
  1.1 Overview ....................................................................................................................... 1
  1.2 Solar Energy’s Role ..................................................................................................... 1
  1.3 Availability of Solar Energy ...................................................................................... 2
  1.4 Commercial Photovoltaics ....................................................................................... 6
  1.5 Liquid Junction Solar Cells ...................................................................................... 7
    1.5.1 History ............................................................................................................... 10
    1.5.2 Dye Sensitized Solar Cells ............................................................................ 13
    1.5.3 Semiconductor Sensitized Solar Cells ....................................................... 16
    1.5.4 Charge Transfer through Semiconductor Films ....................................... 19
    1.5.5 Photoelectrochemical Techniques ........................................................... 20
    1.5.6 Optical Investigations .................................................................................... 28
  1.6 Areas of Improvement ............................................................................................. 32

Chapter 2: Chemically Controlled Emission of CdSe Quantum Dots .............................. 33
  2.1 Thiols and CdSe Quantum Dots ............................................................................. 33
  2.2 Experimental .......................................................................................................... 35
    2.2.1 CdSe Synthesis ............................................................................................. 35
    2.2.2 CdSe and MPA Mixtures ............................................................................ 36
    2.2.3 Experimental Testing ................................................................................... 37
  2.3 MPA Effects on CdSe Optical Properties .............................................................. 37
    2.3.1 Steady State Emission ................................................................................... 37
    2.3.2 Ligand Exchange Kinetics ........................................................................... 41
    2.3.3 Internal Electron Kinetics ............................................................................ 43
    2.3.4 Implications of Linking Quantum Dots ...................................................... 52
  2.4 Summary .................................................................................................................. 54

Chapter 3: One-Dimensional TiO₂ Nanotube Architectures ............................................. 55
  3.1 One-Dimensional Working Electrodes ..................................................................... 55
  3.2 Experimental .......................................................................................................... 58
    3.2.1 TiO₂ Nanotube (TiO₂-NT) Synthesis ......................................................... 58
    3.2.2 TiO₂ Nanoparticle (TiO₂-NP) Films ........................................................... 58
    3.2.3 Cds SILAR ........................................................................................................ 58
    3.2.4 Experimental Setup ....................................................................................... 59
FIGURES

Figure 1.1 Ultimate efficiency versus semiconductor bandgap. The maximum efficiency (a) determined from Equation 1.1 is shown in blue. The red trace (b) demonstrates the maximum efficiency after shape factors and thermodynamic limitations are accounted. 10

Figure 1.2 Schematic of a liquid junction solar cell. The working electrode (WE) is illuminated from the backside. Excited electrons are transferred to the circuitry and pass through the load after which they reach the counter electrode (CE). Electrons are transferred to the redox couple (R/O) which transfers the electron back to the WE.

Figure 1.3 Two electrochemical cell assemblies (left) two-electrode, and (right) three-electrode. Current is passed between the working electrode (circle) and the counter electrode (bar). Potential is measured in the two-electrode system between the working and counter electrodes whereas in the three-electrode system potentials are measured between the working and a known reference electrode (arrow).

Figure 1.4 A schematic depicting an I-V scan and its components. The y-intercept is the short-circuit current (I_sc), x-intercept is the open-circuit potential (V_oc). The ratio of the box defined by the maximum power divided by the box of I_sc×V_oc is the fill factor.

Figure 1.5 Schematic depicting the three regions commonly observed in V_oc decay measurements: (1) Conduction band scavenging, (2) shallow traps, and (3) deep traps.

Figure 1.6 Ultrafast transient absorption optical arrangement. The fundamental beam is split into the pump and probe beams. The pump beam is converted to the second harmonic and chopped before entering the sample. The probe beam is controlled with a time delay track before being converted to white light and entering the sample. After passing through the sample the transmitted probe beam is collected by a CCD detector.

Figure 2.1 CdSe quantum dots 2.6nm in diameter. Under 366nm UV irradiation the emission changes with varying MPA concentration, (a) 0M, (b) 50µM, (c) 100µM, (d) 500µM, (e) 1mM, (f) 5mM, and (g) 10mM.
Figure 2.2 (A) Steady state photoluminescence spectra and (B) absorbance spectra of 2.6nm CdSe quantum dot solutions with MPA concentrations of (a) 0M, (b) 50µM, (c) 100µM, (d) 500µM, (e) 1mM, (f) 5mM, and (g) 10mM. Absorbance spectra are normalized to the first excitonic peak. The inset of (A) shows the double reciprocal plot corresponding to Equation 2.3 and the band-edge emission at 497nm. Excitation was with 410nm.

Figure 2.3 Normalized photoluminescence spectra of CdSe quantum dots (A) (a,c) with and (b,d) without DDA as a capping ligand (a,b) before and (c,d) after 1mM MPA in solution. (B) Spectra of different sized quantum dots after addition of 1mM MPA. All samples were excited with 410nm.

Figure 2.4 (A) Photoluminescence decays of 3.1nm diameter CdSe quantum dots with 1mM MPA at different wavelengths of the emission spectrum. (B) Stretched exponential lifetimes of the fitted decays from (A), with and without MPA.

Figure 2.5 (A) Contribution of each bi-exponential lifetime at (a,b) band-edge and (c,d) deep-trap wavelengths versus concentration of MPA. (B) Lifetime changes versus concentration of MPA.

Figure 2.6 Transient absorption spectra at different times after excitation of 2.4nm CdSe quantum dots (A) without, and (B) with 1mM MPA. (C) Decay traces of (A) and (B) at 464nm normalized to maximum bleach.

Figure 2.7 Comparison of emission between CdSe quantum dots in 1mM MPA and after precipitation and resuspension in toluene (washed). Emission is normalized to maximum deep-trap intensity.

Figure 3.1 Charge injection and transport in a) TiO2 nanoparticulate substrate, and b) TiO2 nanotube array with semiconductor sensitizers.

Figure 3.2 Illustration of anodically etched TiO2 nanotube formation. Potential is applied after a) titanium is immersed in the fluoride solution. b) TiO2 forms on the surface of the foil, c) pits are formed by the etching process followed by d) further growth of the TiO2 layer in the pits. e) Etching occurs around the etched pits and f) the structure continues to etch into the foil.

Figure 3.3 SEM images of A) a bare TiO2 nanotube array, and B) a TiO2 nanotube array sensitized with 15 SILAR cycles of CdS. TEM image C) of a single CdS sensitized TiO2 nanotube.

Figure 3.4 SEM images of TiO2 nanotube arrays with (a,a’) no CdS, (b,b’) 5 cycles of SILAR CdS, (c,c’) 10 cycles, and (d,d’) 20 cycles. Scale bars in the rightmost images are representative for all images to their left.

Figure 3.5 Diffuse reflectance spectra of (A) TiO2 nanotubes and (B) TiO2 nanoparticles with various depositions of CdS. All spectra are normalized to the first excitonic peak.
Figure 3.6 Characterization of the CdS/TiO₂ nanotube system with (A) XRD of a) TiO₂-NT and b) CdS/TiO₂-NT. (B) EDS analysis of a CdS/TiO₂-NT sample. ..............67

Figure 3.7 Photocurrent versus time measurements for various depositions of CdS on (A) TiO₂ nanotube arrays, and (B) TiO₂ nanoparticle films. Currents were measured under a 0V vs. Ag/AgCl bias........................................70

Figure 3.8 Current-voltage characteristics for various depositions of CdS on (A) TiO₂ nanotube arrays, and (B) TiO₂ nanoparticle films................................................71

Figure 3.9 IPCE spectra of various CdS depositions on (A) TiO₂ nanotube arrays, and (B) TiO₂ nanoparticle films..........................................................73

Figure 4.1 Schematic of (A) aligned TiO₂ nanotube array and (B) randomly oriented nanotubes. SEM images of (C) as formed aligned nanotubes and (D) nanotubes deposited onto carbon paper.................................................................80

Figure 4.2 Schematics of films (A) after sonication and (B) after re-etching the foil. SEM images of (C) sonicated foils and (D) re-etched films corresponding to the cartoons. ........................................................................................................82

Figure 4.3 Absorption spectra of (A) CdS particles on deposited on a clear electrode and (B) CdS SILAR particles on deposited TiO₂ nanotubes. ................85

Figure 4.4 SEM images of (A) deposited TiO₂ nanotubes and (B) deposited TiO₂ nanotubes sensitized via SILAR with CdS, eight cycles.........................86

Figure 4.5 Transient absorption spectra of (A) CdS nanoparticles on an OTE substrate and (B) CdS nanoparticles and TiO₂ nanotubes on an OTE substrate. (C) Peak bleaching decay versus time. All graphs are normalized to peak ΔA for each sample......................................................88

Figure 4.6 IPCE spectra (A) comparing aligned and randomly oriented TiO₂ nanotubes sensitized with CdS. (B) Photocurrent over time, with light on and off, of aligned and random systems, both with and without CdS......................92

Figure 4.7 (A) Open circuit potential measured as the light is turned on and off. After light is turned off (B) electron lifetimes are plotted versus V<sub>OC</sub> determined from the V<sub>OC</sub> decay rate.................................................................93

Figure 5.1 Current-Voltage characteristics of CdS/TiO₂ working electrodes with platinum as a counter electrode in (A) a two-electrode assembly, and (B) a three-electrode assembly.................................................................98

Figure 5.2 Assembly of the salt bridge apparatus with (green) 3M KCl salt bridge separating the counter and working electrode environments. .....................102
Figure 5.3 CdS working electrodes tested in an open system (no salt bridge) with a platinum counter electrode at various concentrations of dissolved sulfur, (A) current-voltage characteristics and (B) electron lifetimes determined from $V_{OC}$ decay rates. .......................................................... 106

Figure 5.4 Photoelectrochemical characteristics, (A) current-voltage traces, and (B) electron lifetimes from $V_{OC}$ decay of CdS working electrodes with a salt bridge isolating the counter electrode. The electrolyte around the counter electrode is changed while the working electrode electrolyte is fixed at 0.1M Na$_2$S. ........... 109

Figure 5.6 Cyclic voltammograms of counter electrode materials, (A) platinum, (B) CoS, (C) Cu$_2$S, and (D) PbS in 10mM Na$_2$S. The working electrode was a platinum disc electrode (1mm radius), reference electrode was SCE, and counter electrode was a platinum flag with a sweep rate of 100mV/s. CoS, Cu$_2$S, and PbS were dropcast onto the disc. The platinum sample was the disc electrode. Sweeps depicted are the fifth of repeated cycles. ................................................................................. 111

Figure 5.7 Current-voltage characteristics of a CdSe/ZnS sensitized working electrode with various materials for counter electrode. The cell was an open system (no salt bridge) with 0.1M Na$_2$S as the electrolyte. .......................................................... 114

Figure 5.8 SEM images of counter electrode materials on OTE, platinized platinum, CoS, Cu$_2$S, and PbS ................................................................. 116
TABLES

Table 2.1 Stretched exponential fitting ................................................................. 47
Table 2.2 Emission decay kinetic fitting .............................................................. 49
Table 4.1 Transient absorption bi-exponential fitting parameters ..................... 89
Table 5.1 Metal-sulfide I-V characterisitic properties ......................................... 115
CHAPTER 1:
INTRODUCTION AND BACKGROUND

1.1 Overview

Significant limitations in quantum dot solar cells are found at interfaces where electrons are transferred. Increasing rates by which electrons cross each boundary directly corresponds to increased photocurrents and power conversion efficiencies. The primary interfaces for electron transfer are the quantum dot/TiO$_2$ interface, boundaries between TiO$_2$ particles in the metal oxide film, the semiconductor electrolyte interface, and the counter electrode/electrolyte interface. To improve cell performance this dissertation examines each process, and develops methods by which electron transfer rates can be enhanced.

1.2 Solar Energy’s Role

Renewable energies need to make a larger impact in the world’s energy portfolio. As fossil fuels continue to be depleted a more stable source of energy is needed to account for the projected increases in energy consumption. It is estimated that by the year 2035 the global energy demand will reach 27TW an increase of 10TW from today.\textsuperscript{1} It is generally agreed that fossil fuels cannot sustain this large increase in power, and we must look to alternative sources not currently available for widespread implementation.
When looking for a more stable and abundant power source nature provides several options. The three accessible choices are hydroelectric, wind, and solar. Hydroelectric can be in the form of dams, tidal, and wave power. Dams have already been installed at most possible sites, and because of transmission limitations tidal and wave power generation is limited to the coasts. Recently, wind power has gained in popularity; however the inconsistencies of wind availability induce stresses on the electrical grid, and can result in unwanted brownouts.

Solar energy has the benefit of being stable and abundant. Over 130,000TW of solar radiation falls upon the Earth. Therefore, it is by far the most abundant source of energy, and if only 0.1% were harvested for electrical power it would easily sustain the world’s energy needs. The challenge for researchers is to develop a system that can convert sunlight into electricity for the same cost as fossil fuels.

During the oil crisis of the 1970’s the first wave of solar research laid the groundwork for today’s scientists and engineers. Many promising studies showed the potential of photovoltaics, but when oil prices fell so did the need for implementing those technologies. With the combination of an increasing environmental movement, fossil fuel decline, and the advent of facile nanofabrication techniques solar power is once again a serious contender for the energy of tomorrow.

1.3 Availability of Solar Energy

Photovoltaics use photons to excite electrons in a photoactive material. The excited electrons are sent to the load, and return to the device to complete the circuit. Semiconductors are the traditional material used in photovoltaics, most notably silicon or gallium arsenide. Due to band structures, limitations are placed on the maximum amount
of solar energy that can be absorbed by a material. Semiconductors absorb photons with energy greater than or equal to their bandgap energy, allowing lower energy photons to transmit through the sample.

The peak of solar radiation intensity is in the visible region, but vast amounts of energy are in the infrared region. Silicon has a bandgap of 1.1eV. Therefore, any photon with energy greater than 1.1eV will be able to excite electrons in a silicon cell, and this still accounts for the visible and part of the infrared energy, and is one reason silicon is so attractive. Bandgap absorption is the primary limitation for solar efficiencies. Assuming that all excited electrons relax back to the conduction band edge the maximum theoretical efficiency can be estimated by assuming the sun is a black body radiator and using Equation 1.1, Figure 1.1.4-10

$$\eta(E_g) = \frac{E_g}{k_B T_s} \int_{E_g/k_B T_s}^{\infty} \frac{x^2}{e^x - 1} dx - \int_0^{\infty} \frac{x^3}{e^x - 1} dx$$  \hspace{1cm} (1.1)

Where $E_g$ is the bandgap of a material, $k_B$ is the Boltzmann constant, and $T_s$ is the temperature of the sun (~6000K).

Shockley and Queisser employed several more assumptions to the general model described by Equation 1.1 and came to the conclusion that the maximum theoretical power conversion efficiency is 31% for a single semiconductor. This limit is for a device constructed of a single bandgap solar cell. They explain how the 44% derived from Equation 1.1 only applies if the cell is surrounded by a blackbody radiator at the temperature of the sun, ~6,000K, and the cell is at absolute zero. Shape factors, such as the flat plate of a solar cell and the point source of light, are taken into account diminishing
the availability of light. When the temperature of the solar cell is also taken into account
the bandgap can no longer absorb as much due to a finite carrier density in the conduction
band. With the temperature of a solar cell assumed to be 300K, and the angle between the
sun and the normal angle of the cell set to 0 the theoretical maximum of 31% power
conversion efficiency is reached with a bandgap of ~1.2eV, Figure 1.1. Earth’s
atmosphere also plays a significant role in the efficiency of devices as the idealized
blackbody radiator distribution becomes cut by water vapor and other gasses, especially in
infrared wavelengths. The bandgap at the maximum efficiency is close to the bandgap of
silicon (1.1eV) and current maximum efficiencies for silicon have been approaching that
limit.11

Higher efficiencies can be obtained when multiple junctions are employed to
harvest selected sections of the solar spectrum using multiple semiconductors in proper
alignment.12-13 By using multiple semiconductors a larger section of the solar spectrum
can be absorbed, allowing for higher electron energies to be harvested. This type of solar
cell is extensively used in extraterrestrial technologies as they have a much higher
efficiency to weight ratio, imperative for space applications.14
Figure 1.1 Ultimate efficiency versus semiconductor bandgap. The maximum efficiency (a) determined from Equation 1.1 is shown in blue. The red trace (b) demonstrates the maximum efficiency after shape factors and thermodynamic limitations are accounted.¹⁰
1.4 Commercial Photovoltaics

Because of the initial research performed in the 1970’s and 80’s it is common to see commercial applications of photovoltaics. Single crystal silicon is the most widely applied technology in the field. It has the benefit of being stable and has high efficiencies reaching over 25%. The feedstock comes from discarded wafer material from computer chip manufacturers. With the increase in demand for solar power the feedstock is becoming limited and when combined with the high cost of manufacturing, single crystal silicon cells have an uncertain future.

Single crystal silicon solar cells operate on the p-n junction concept. When small amounts of impurities are added to the silicon crystal this has an effect on its Fermi level. For instance, if phosphorous is used to dope silicon more electrons are added to the lattice and the Fermi level shifts to more negative potentials, if boron is added the Fermi level shifts positive. This creates a driving force for photogenerated electrons and holes to separate at the junction and proceed to the load.

To combat the high costs of fabrication, manufacturers have moved to amorphous silicon as a light harvesting material. This approach lowers costs by having a thin layer of absorbing material reducing the amounts of silicon used in the manufacturing process. Amorphous silicon still uses the concept of the p-n junction, but typically the doped layers are extremely thin and surround a layer of undoped silicon. Efficiencies have remained low compared to single crystal, around 12%.

Thin films of other materials have been utilized to improve on the lower efficiency of amorphous silicon. The highest performer has been CdTe thin films, which also employ the p-n arrangement of doped layers surrounding an intrinsic layer (p-i-n...
CdTe cells have been developed since the 1950’s and can yield efficiencies just under 20%. Commercial production has ramped up in recent years though costs remain higher than desired to be competitive with fossil fuels.

The newest entry to the large scale commercial solar production line is thin film copper-indium-gallium-sulfide, or CIGS. CIGS promises to maintain high efficiencies, like CdTe, while reducing costs to around $1/W. This value is seen as a threshold cost by many as to when solar can become commercially competitive. The cost savings arise from simple manufacturing techniques because CIGS can be easily sprayed onto a conductive plastic. Fabrication of CIGS therefore eliminates costly high-vacuum deposition techniques and a roll to roll system is often employed. Though CIGS is a vast improvement, it is still at the threshold, and the availability and cost of indium could impair growth in the energy market.

All the current technologies in the marketplace have improved the accessibility and scope of solar power. However, if photovoltaics are to ever be a significant player in the energy field costs must be reduced even further from where they stand today. Therefore new materials and new architectures must be developed to move forward. One of the most promising developments is the Liquid Junction Solar Cell.

1.5 Liquid Junction Solar Cells

The rest of this dissertation will focus on the liquid-junction solar cell (LJSC). The LJSC is a photoactive electrochemical cell. Like all electrochemical cells all LJSC have a working electrode, a counter electrode, and an electrolyte. Figure 1.2 shows a schematic of how the LJSC is arranged. As photons enter the cell electrons are excited at the working electrode and are collected by a conductive substrate. Electrons pass through the load and
continue to the counter electrode. Redox couples in the electrolyte scavenge electrons from the counter electrode, and through mass transfer the reduced species of the couple diffuses to the working electrode where it is oxidized, completing the circuit.

To optimize performance of the LJSC, materials must be chosen for their electron transfer capabilities and photon absorptivities. Electrolytes must have redox potentials between the conduction band and valence band of the excited semiconductor, and working electrodes must absorb as many incident photons as possible, because absorption is directly proportional to photocurrent.
Figure 1.2 Schematic of a liquid junction solar cell. The working electrode (WE) is illuminated from the backside. Excited electrons are transferred to the circuitry and pass through the load after which they reach the counter electrode (CE). Electrons are transferred to the redox couple (R/O) which transfers the electron back to the WE.
1.5.1 History

The first uses of the LJSC were found in photocatalysis. The seminal work of Fujishima and Honda in 1972 showed that a semiconductor, TiO$_2$, could split water when illuminated with UV light under no external bias.$^{26}$ TiO$_2$ is an important material because of its widespread use in various industries such as sunscreen, food coloring, paints, and zeolites. It has a feedstock that is much more stable than crystalline silicon, tellurium, or indium giving it much greater stability if it is to be used in mainstream energy applications.

Titanium is the ninth most abundant element in the Earth’s crust and most of that is found in metal oxide form.$^{27}$ There are two photoactive polymorphs of TiO$_2$: rutile and anatase. Rutile is thermodynamically the most stable form of TiO$_2$.\(^{28}\) When making single crystalline analyses of photochemical properties for TiO$_2$ rutile is employed.$^{26,29-32}$ Therefore, before the advent of nanocrystalline technologies in photoelectrochemical systems most studies were performed on rutile crystals. In commercial manufacturing rutile is the polymorph most produced due to its high diffractive index and scattering abilities, preferable for a white pigment.$^{33}$ Anatase, though less stable thermodynamically, has been shown to have much greater photoactivity than rutile.$^{34}$

TiO$_2$ is a semiconductor with a wide bandgap of 3.0eV for rutile and 3.2eV for anatase.$^{35}$ The conduction band is made of unoccupied Ti$_{3d}$ states, and the valence band is formed primarily of O$_{2p}$ states.$^{35}$ Rutile has a direct bandgap at the Γ point of the Brillouin zone, and also an indirect bandgap only ~0.03eV larger than the direct gap between the Γ and M points. Anatase has only an indirect bandgap between the Γ and M points. An indirect bandgap is useful for solar applications because it eliminates a radiative
recombination pathway leading to greater probabilities for electron transfer. Of note, the conduction band of TiO$_2$ lies slightly negative of the reduction potential for hydrogen, allowing it to be used for water splitting.$^{36}$

Other metal oxides have been significantly researched for solar applications. After TiO$_2$, ZnO shows the most promise because of the ease of nanofabrication techniques to make nanorods and nanotubes.$^{37-39}$ ZnO is also a wide bandgap semiconductor ($E_g = 3.2$eV), however it has a direct bandgap and emits at 380nm (also deep-trap emission ~530nm). This emissive property, as well as facile single crystal growth, has made ZnO a material sought after for possible lasing properties.$^{40-42}$ In terms of solar energy applications ZnO cannot accept electrons as efficiently as TiO$_2$. However, because of the ease of fabrication, and a slightly more negative conduction band than TiO$_2$, ZnO remains a potential candidate for improving LJSCs.$^{36}$

SnO$_2$ is another ubiquitously used wide bandgap metal oxide in the solar community.$^{43-44}$ Its most common occurrence is in conductive glass. Because a thin layer is relatively conductive when doped with fluorine or indium (∼10Ω/□) most substrates for electrodes are composed of SnO$_2$. Despite the other oxides the cost, availability and electron transfer properties of TiO$_2$ make it the most widely used material.

Because wide bandgap semiconductors can absorb only a small fraction of the sun’s spectrum other materials must be used to capture the remainder of the energy. Since the advent of the LJSC, smaller bandgap semiconductors have been used to capture visible light.$^{45-47}$ These semiconductors, such as CdSe, PbS, or CdS, absorb light with energy greater than or equal to their bandgaps.
One of the most common, and well studied, semiconducting sensitizers is CdS. The bulk bandgap of CdS is 2.7eV, corresponding to light with wavelengths 528nm and shorter. This includes high energy photons in the solar spectrum, but omits all yellow and red light as well as infrared. The benefits of CdS are the ease of synthesis and its driving force for electron transfer to TiO₂. The conduction band of CdS lies 0.5V more negative than the conduction band of TiO₂. This provides a significant driving force for excited electrons to be transferred to TiO₂, increasing the probability of harvesting the excited electron instead of recombining within CdS with photogenerated holes. Cadmium also has a high affinity for sulfides. Cadmium ions will spontaneously react with sulfides to form CdS ($\Delta G_f^\circ = -145.2kJ/mol$) which results in a multitude of deposition techniques used to apply CdS on many substrates.

CdSe is similar to CdS chemically, but the bulk bandgap is 1.7eV resulting in an ability to capture most of the visible spectrum. The conduction band of CdSe is 0.3V more negative than the TiO₂ conduction band, 0.2eV positive of CdS. Most research developments of CdSe have surfaced in nanotechnology. The synthesis of CdSe quantum dots has been researched to the point that one can obtain extremely monodisperse crystals under 5nm in diameter, a control not seen for most materials. Because of its ability to capture most visible photons and the ease of synthesis, CdSe has become a commonplace sensitizer in the LJSC.

Other often used semiconductor sensitizers are CdTe and the lead based chalcogenides PbS and PbSe. All three have bandgaps that allow for near-infrared photon absorption which increases the coverage of the solar spectrum. However, these materials have lower driving forces than CdS and CdSe, although band positions are still
suitable for electron transfer. In the case of PbS and PbSe small particles are required for sensitization because as the size of the particle is reduced quantum confinement pushes their conduction bands negative of TiO$_2$.\textsuperscript{65}

1.5.2 Dye Sensitized Solar Cells

In 1991 Michael Grätzel and Brian O’Reagan published a paper describing the use of a nanoporous TiO$_2$ film sensitized with an organic dye documenting the beginning of the modern dye sensitized solar cell (DSSC).\textsuperscript{66} This DSSC was important for two reasons. First, the efficiency with a sensitizing dye was near 10%, and second the use of a nanocrystalline TiO$_2$ particulate film meant that large surface areas could be sensitized for high absorbances with thin films.

The thin nanocrystalline film differs from single crystal TiO$_2$ in several ways. The porous nature greatly improves the surface area available for sensitizing. It also allows the redox couple electrolyte to penetrate into the film and extract photogenerated holes throughout the thickness of the film. The nanocrystalline morphology allows for thinner films to be applied, resulting in less material and lower costs of manufacturing. Powders of TiO$_2$ are also easier to manufacture than large single crystals.

The use of nanocrystals changes the method by which charge carriers flow through the metal oxide layer. As TiO$_2$ particles are typically 20-50nm in diameter space-charge layers have insufficient room to form causing diffusion to be the primary charge transport mechanism as opposed to internal electric fields found single crystal systems.\textsuperscript{67-71} Diffusion limitations force TiO$_2$ films to be thin (<20µm),\textsuperscript{72} but because of increased surface area photon absorption can remain high.
Unlike semiconductors, which have the ability to absorb photons with a wide range of energies due to band structures, dyes are limited to the distinct HOMO-LUMO energy gap.\textsuperscript{73-74} Absorption centers in the visible range of the solar spectrum are typically made from ruthenium or osmium centered metal-organic porphyrins.\textsuperscript{75} Electrons are excited from the metal center to the ligand $\pi^*$ orbital.\textsuperscript{73,76} By changing the structure of the molecule and the functional groups the absorption properties can be manipulated, but are essentially limited by the absorption mechanism.

In the development of dyes for solar applications the presence of carboxyl groups has been found to have the second most significant impact on cell performance after absorption cross sections.\textsuperscript{77} Carboxyl groups are used as anchoring sites on the TiO$_2$ surface, specifically the anatase (101) surface.\textsuperscript{78} The carboxylate groups bind to titanium surface atoms. With more of such binding groups, dyes can attach more strongly to the TiO$_2$, and thus enable faster electron injection rates. This deposition method forces an upper limit of deposited sensitizer to a monolayer.\textsuperscript{79} Any excess dye on the cell, not in contact with the TiO$_2$, is detrimental to the performance of the cell.

The initial dye reported in the original Grätzel paper was a ruthenium tris(bipyridine) structure.\textsuperscript{66} This dye managed to obtain 7.9\% efficiency. The absorption onset was around 700nm and was able to absorb the visible solar spectrum. New dyes have been developed which are able to extend absorption into the near infrared.\textsuperscript{80-82} The two highest performing ruthenium based dyes are named N719 and N3. These dyes have proven efficiencies over 11\%.\textsuperscript{83} They both have ruthenium centers and many hydroxyl groups to bind to the surface of TiO$_2$. Their absorbances take advantage of most of the energy of the solar spectrum and also provide the highest performance of any LJSC (these
performance terms are described below). The basic structure of the new dyes remains a ruthenium center surrounded by pyridine groups.

Electrolytes are pivotal in the performance of the LJSC. An ideal electrolyte will instantly capture a generated photohole from the working electrode and also instantly scavenge electrons at the counter electrode. To be employed as a steady state device the electrolyte also must transport reduced and oxidized (redox) electrolyte species across the cell between the two electrodes swiftly. In DSSCs the $\Gamma/\Gamma_3^-$ redox couple has endured as the leading performer.\(^{84}\) At the working electrode $\Gamma$ ions are able to harvest photoholes from the HOMO of a dye and oxidize to $\text{I}_2^{*}$.\(^{85-86}\) This intermediate disproportionates into $\Gamma$ and $\text{I}_3^-$. The great benefit of the iodide redox couple is that the oxidized species, $\text{I}_3^-$, has an extremely low affinity for back electron transfer from the working electrode.\(^{85,87}\) This allows photoelectrons to have a higher probability of reaching the back conductive electrode.

The solvent choice is another important factor for the electrolyte. The primary solvent for DSSCs is acetonitrile. This is due to the iodide couple’s equilibrium existing mostly with $\text{I}_3^-$, $K > 10^7 \text{ M}^{-1}$, the overall reaction is Equation 1.2:\(^{85}\)

$$I^- + I_2 \leftrightarrow I_3^-$$  \(1.2\)

In water $K$ is $750 \text{ M}^{-1}$ indicating that after reaction with the photohole the intermediate $\text{I}_2^{*}$ will quickly react in acetonitrile to form $\text{I}_3^-$ limiting chances for electron scavenging. Alternatively, ionic liquids have received attention as solvents due to the fact that they do not leak as easily from a cell, and in some instances have shown a higher open circuit potential.\(^{88-89}\) The much larger electrochemical window (the potential range between
which the electrolyte is reduced or oxidized) of ionic liquids over water or acetonitrile also allows for new materials to be investigated.\textsuperscript{90-92}

1.5.3 Semiconductor Sensitized Solar Cells

Related to the DSSC is the semiconductor sensitized solar cell (SSC). SSCs employ a narrow bandgap sensitizer which is able to absorb photons lower in energy than the metal oxide layer. Semiconductors have properties that make them attractive over dyes. A dye is limited to a monolayer of coverage. This forces researchers to use exotic dyes with extremely high absorption cross sections leaving little room for improvement. Semiconductors have absorption cross sections orders of magnitude larger than dyes, and they can be stacked transferring charge through the semiconductor film to the TiO\textsubscript{2} layer.\textsuperscript{93} The greater flexibility of the semiconductor sensitizer has allowed for a wide range of materials and deposition techniques to flourish.\textsuperscript{69} SSCs have also taken advantage of quantum confinement properties of semiconductors with the inception of quantum dot solar cells (QDSC).\textsuperscript{94-95} Quantum dots allow researchers to fine tune band positions of sensitizers which change absorption properties and electron transfer driving forces.

As mentioned above, a multitude of sensitization techniques have been developed for semiconductor sensitizers. One of the simplest is Successive Ion Layer Absorption and Reaction (SILAR).\textsuperscript{96-98} SILAR involves immersing a substrate into a solution with a desired precursor (e.g. Cd\textsuperscript{2+} from CdSO\textsubscript{4}), allowing this precursor ion to adsorb on the surface of the TiO\textsubscript{2}, then removing the sample, rinsing excess ions off, and immersing in the other precursor ion (e.g. Na\textsubscript{2}S). SILAR works if the reaction for the precursors is spontaneous, such as Cd\textsuperscript{+} and S\textsuperscript{2-}. By using successive cycles the absorption onset wavelength has been shown to red-shift indicating that the semiconductor creates
crystallites in the quantized regime.\textsuperscript{96} Instead of monolayers of sensitizer forming on the surface of the substrate, islands form and grow after repeated cycles.\textsuperscript{99} The simplicity of SILAR has led to its use in sensitizing many materials and also has seen use in areas other than photovoltaics.\textsuperscript{100-102} Because it uses dissolved ions as a construction material nanoporous metal oxide films can be sensitized throughout the pores where a larger pre-formed sensitizer might not penetrate. This allows for thinner TiO\textsubscript{2} films and less loss due to light scattering or reflection.

Top-down approaches are also used for sensitizing with semiconductors. A commonly employed practice is linker assisted deposition.\textsuperscript{103-105} For this, quantum dots are pre-synthesized and attached to the metal oxide layer using a linker molecule. The development of monodisperse quantum dot syntheses allows for specific regions of the solar spectrum to be targeted.\textsuperscript{95} SILAR is not able to have this control over the size of the sensitized layer so presensitized quantum dots allow for tailoring the cell to specific applications. A linker molecule, which has a carboxyl group at one end to bind to TiO\textsubscript{2} and a thiol at the other to typically bind with cadmium,\textsuperscript{106} is employed on presynthesized quantum dots because capping layers commonly found on the surface limit the natural binding.

Electrophoretic deposition has been developed as a facile method to actively deposit quantum dots onto a metal oxide surface without a linker molecule.\textsuperscript{107-110} It has been shown that in a solvent mixture of acetonitrile and toluene, pre-synthesized CdSe quantum dots become negatively charged and move in an electric field.\textsuperscript{109} This allows for faster deposition of quantum dots without a linker than by natural adsorption. However,
quantum dots typically aggregate in this solution and may not be as active or in as intimate contact with the metal oxide layer.

One method used to create even sensitizer coverage over the entire area of a TiO₂ film is chemical vapor deposition (CVD).¹¹¹-¹¹³ This can create monolayers over the surface which SILAR or linker assisted binding cannot. CVD has been employed with catalysts to create nanowires of CdSe and other sensitizers.¹¹⁴-¹¹⁵ Using CVD with catalyst particles for the vapor-liquid-solid technique has been used to generate semiconducting nanowires.¹¹⁶ These wires can be formed on a preexisting structure and greatly improve performance.

The iodide redox couple that works well with DSSCs because of the low back electron transfer is unable to be used in a QDSC because of the oxidative properties of iodide on quantum dots.⁹³,¹¹⁷-¹¹⁸ Upon immersion, QDSC working electrodes will spontaneously degrade until only the white TiO₂ substrate remains. To prevent degradation, Na₂S is used with metal/chalcogenide quantum dots like CdS and CdSe.¹¹⁹-¹²¹ The resulting sulfide/polysulfide (S²⁻/Sₙ²⁻) redox couple is not as effective at preventing back electron transfer as between photogenerated electrons and the I⁻/I₃⁻ couple, however it has the ability to stabilize the quantum dots.

The polysulfide species in the S²⁻/Sₙ²⁻ couple exists in a chain of sulfur atoms with n typically equal to 2 or 4 depending on the pH of the system.¹²² The S²⁻ species reacts with water as seen in Equation 1.3

\[ S^{2-} + H_2O \leftrightarrow HS^- + OH^- \]  \hspace{1cm} (1.3)

Resulting in a pH ~13 for a solution of 0.1M Na₂S and causing most of the polysulfide chains to be two-membered. Despite the conversion of S²⁻ to HS⁻ the reduced
species still has sufficient turnover on the quantum dots to maintain high currents. One large issue with the sulfide electrolyte is that it poisons platinum\cite{123}, which is typically used for counter electrodes in LJSCs. This issue will be addressed in Chapter 5, however the stability that sulfides provide to quantum dots is the most significant attribute of the couple. In recent years new electrolytes have been investigated, such as the cobalt redox couple\cite{124}, but \( \text{S}^{2-}/\text{S}_\text{n}^{2-} \) remains the primary couple for semiconductor sensitizers.

1.5.4 Charge Transfer through Semiconductor Films

In all LJSCs charges must pass through a metal oxide film to reach the conductive backing of the working electrode. In the single crystal scenario charges are driven by internal electric fields formed by band bending\cite{125-127}. In nanocrystalline films particles are too small to allow for a space-charge layer to form\cite{68-70}. To describe the movement of charges researchers have developed what has been termed as the Multiple Trapping Model (MTM) for charge transfer through a nanocrystalline film\cite{128-131}. MTM states that an excited charge will experience many trapping and detrapping events while diffusing to the back conductive contact of a working electrode. Defects in crystal lattices have been shown to be energetic traps for charges in a system\cite{132-133}. When a charge enters into a trap additional energy is required for it to re-enter the conduction band of a semiconductor. Traps have also been shown to be radiative recombination centers in direct bandgap semiconductors\cite{134-136}. Limiting these energetic traps has been a useful technique in improving photocurrents in LJSCs\cite{93,137}. For example, traps in the TiO\textsubscript{2} film have also been shown to fill by illuminating the sample with larger intensities of light\cite{129,138-140}. Bisquert and Peter have shown the effectiveness of this model and how diffusion is the sole method by which charges flow in a nanocrystalline system\cite{141-142}.
Movement of charges in the TiO₂ nanoparticulate film is dictated by electron diffusion lengths. Diffusion lengths are defined by Equation 1.4:

$$L_n = \sqrt{D_n \tau_n}$$  \hspace{1cm} (1.4)

Where $L_n$ is the diffusion length, $D_n$ is the electron diffusivity in TiO₂, and $\tau_n$ is the effective electron lifetime in TiO₂. The longer the diffusion length the further an electron can travel through the film before entering a trap. Values for $D_n$ and $\tau_n$ are often determined as effective values because trap states distort the ideal mobility of charges. To experimentally determine these values researchers typically employ electrochemical impedance spectroscopy (EIS) which modulates potentials at specific frequencies while monitoring the changes in current.\textsuperscript{141} Optimal film thicknesses have been found to be 1/3 of $L_n$.\textsuperscript{72} Therefore a thicker film with higher absorption can be constructed if its diffusion length is enhanced resulting in more charge carriers. To improve solar cell photocurrents many researchers are investigating extending diffusion lengths either by increasing electron lifetimes or diffusivities.\textsuperscript{116,143-145}

1.5.5 Photoelectrochemical Techniques

The goal of any solar cell is to transform incident solar energy into usable work. The maximum power output in a photovoltaic device is determined by sweeping a potential across the cell and measuring the resulting currents with the cell illuminated, a current-voltage (I-V) scan. Figure 1.3 shows the two commonly used experimental arrangements: the two-electrode and the three-electrode systems. The two-electrode system models the real world application, whereas the three-electrode system is useful for determining the electrochemical characteristics of the working electrode.
An I-V scan, demonstrated in Figure 1.4, shows several parameters useful in determining the performance of the cell. The maximum power point is used to determine the power conversion efficiency of the cell. In the two electrode system at zero applied potential the resulting current is called the short-circuit current (I_{SC}). This is the maximum current the cell can generate without an applied bias and is directly related to the maximum number of carriers generated by the cell. Where the trace crosses the voltage axis is termed the open-circuit potential (V_{OC}). In a two electrode system V_{OC} is the potential between the working electrode Fermi level and the counter electrode Fermi level at zero current conditions. In a TiO\textsubscript{2} system the working electrode Fermi level is close to the conduction band and the counter electrode is typically in equilibrium with the redox potential in the electrolyte. This imposes limitations on the ability to manipulate the V_{OC} because in order to improve the system new materials must be chosen, which as described in previous sections, is a difficult task.
Figure 1.3 Two electrochemical cell assemblies (left) two-electrode, and (right) three-electrode. Current is passed between the working electrode (circle) and the counter electrode (bar). Potential is measured in the two-electrode system between the working and counter electrodes whereas in the three-electrode system potentials are measured between the working and a known reference electrode (arrow).
Figure 1.4 A schematic depicting an I-V scan and its components. The y-intercept is the short-circuit current ($I_{SC}$), x-intercept is the open-circuit potential ($V_{OC}$). The ratio of the box defined by the maximum power divided by the box of $I_{SC} \times V_{OC}$ is the fill factor.
Shunt and series resistances can also be determined from the I-V curve. The slope of the I-V trace at ISC belies the shunt resistance or back electron transfer. The slope of the trace at VOC describes series resistance. Given a box drawn on the graph by the ISC and the VOC the amount filled by the box made by the maximum power point is called the fill factor, Figure 1.4. The ideal value for the fill factor is 1. In this case there are no resistance losses across the cell and all photogenerated carriers are captured.

A common test to determine the performance of a solar cell is the current-time trace. In this experiment a constant potential is applied across the cell (typically at ISC potentials) and the photocurrent dynamics are observed as the light is turned on and off. This test reveals the stability of the cell over time; if the cell is degrading a reduction in current is evident. Often a current spike is observed at the instant the light is turned on or off. This spike can be modeled by the Cottrell equation\textsuperscript{146} Equation 1.5:

\[
I(t) = \frac{nF D_o^{1/2} C_o^*}{\pi^{1/2} t^{1/2}}
\]

Where \( n \) is the number of electrons in the redox reaction, \( F \) is Faraday’s constant, \( D_o \) is the diffusion of the oxidized species, \( C_o^* \) is the bulk concentration of the oxidized species, \( I \) is current and \( t \) is time. The Cottrell equation was derived assuming that the concentration of the corresponding species (in this case the reduced species) is zero initially. After a potential step the current spikes and decays with a \( t^{1/2} \) relationship. Being able to see a Cottrell like spike initially in current-time traces indicates that the redox couple boundary layer at the surface of the working electrode is being formed after the light is turned on and reaches equilibrium as the spike decays. In testing p-n junction cells, like thin film
silicon, researchers often employ choppers linked to lock-in amplifiers to reduce noise. In a LJSC, because of the Cottrell spike, this method cannot be used.

A third electrochemical experiment to evaluate solar cells is $V_{OC}$ decay. As previously described in the light $V_{OC}$ is theoretically determined by the difference between the conduction band of TiO$_2$ and the redox potential of the electrolyte.$^{69}$ TiO$_2$ potential is the Fermi level of the working electrode which, because TiO$_2$ has n-type conductivity, is near the conduction band. After light is turned off the Fermi level of the working electrode returns to the equilibrium state; which is equal to the Fermi level of the electrolyte. In an ideal semiconductor there are no states in the bandgap. In reality trap states are contained within the bandgap, and charges must be scavenged by the electrolyte to empty the trap. Bisquert, Hodes and Zaban have shown through $V_{OC}$ decay there are many trap states in between the conduction and valence bands of TiO$_2$.\textsuperscript{131} These trap states determine the rate at which a $V_{OC}$ will decay, and thus the rate at which the decay occurs can yield information useful to charge transport properties described with the Multi-Trapping Model. Bisquert and co-workers adapted an equation used for minority carrier populations in transistors\textsuperscript{147} to relate the $V_{OC}$ decay rate to the electron lifetime in the metal oxide film of the working electrode:\textsuperscript{148}

$$\tau_n(V_{OC}) = \frac{k_B T}{e} \left( \frac{dV_{OC}}{dt} \right)^{-1}$$

(1.6)

Where $\tau_n$ is the electron lifetime, $k_B$ is the Boltzmann constant and $e$ is the charge of an electron. By plotting $\tau_n$ on a log scale versus $V_{OC}$ several regions are typically observed, see Figure 1.5. The first is the constant region which is a constant rate of decay for the $V_{OC}$. This region corresponds to excess electrons in the conduction band being scavenged
by the electrolyte. Since they are all being scavenged at the same potential they all have the same rate of scavenging. The second region is linear on the log scale. This corresponds to shallow trapped electrons that must overcome an energy barrier to raise to the potential of the conduction band before becoming scavenged. The final region is parabolic and is associated with deeply trapped electrons. Bisquert et al. explain that this region is parabolic in accordance with Marcus’ theory of electron transfer.¹³¹
Figure 1.5 Schematic depicting the three regions commonly observed in $V_{OC}$ decay measurements: (1) Conduction band scavenging, (2) shallow traps, and (3) deep traps.
1.5.6 Optical Investigations

Absorption is the most important characteristic of a solar cell. As such, there are many experiments to determine the effectiveness of a cell’s absorption properties. UV-Vis spectroscopy is a steady state technique used to determine the amount of light a sample will absorb. Two modes are used to determine the absorbance of a sample, transmission and diffuse reflectance. Transmission employs the Beer-Lambert law, Equation 1.7:

\[ A = -\log\left(\frac{I}{I_0}\right) \]  

(1.7)

Where \( A \) is the absorbance, \( I \) is the intensity of light transmitting through a sample and \( I_0 \) is the intensity of light incident on the sample. Absorbance therefore is a logarithmic relation to the number of photons absorbed. Scattered light, though not absorbed, will not reach the detector and false values for \( I \) are obtained. Because TiO\(_2\) films are very efficient at scattering, an integrating sphere is used to collect photons scattered off the surface of the film. Diffuse reflectance uses the Kubelka-Munk relationship, Equation 1.8:

\[ f(R) = \frac{(1 - R)^2}{2R} = \frac{K}{s} = \frac{Ac}{s} \]  

(1.8)

Where \( R \) is the reflectance defined as \( R=I_r/I_0 \), with \( I_r \) the intensity of reflected light, \( K \) is the absorption coefficient, \( s \) is the scattering coefficient, \( A \) is absorbance, and \( c \) is the concentration of the absorbing species. For TiO\(_2\) films the scattering coefficient is assumed to be 1.

The response of a solar cell to the solar spectrum is examined using a technique of determining Incident Photon to Charge Carrier Efficiency (IPCE). IPCE is essentially an
external quantum yield for the cell across the active region of the solar spectrum. Efficiencies are calculated using the IPCE equation, Equation 1.9:

\[
IPCE(\lambda) = \frac{1240 \cdot I_{SC}(A)}{P_i(W) \cdot \lambda(nm)} \times 100% 
\]  

(1.9)

In this equation \( P_i \) is the incident power at a particular wavelength \( \lambda \). The number 1240 is the conversion factor \( hc/e \) for converting the number of photons to the number of harvested electrons. In theory a trend in IPCE should follow the same trends found in the absorbance of a cell.\(^{104}\)

Photoluminescence is a common occurrence in materials used to sensitize LJSCs. To improve charge carrier collection efficiencies radiative pathways are commonly reduced by material choice, or by manipulating radiative recombination centers. Emission quantum yields (QY) are determined from steady state photoluminescence spectra. Charge carrier kinetics can be obtained through observing the QY before and after addition of quenchers.\(^{150-152}\) For example Kongkanand et al. showed the decay of CdSe photoluminescence after TiO\(_2\) was added\(^{150}\) to the CdSe film as a quencher.\(^{104}\) The lifetime of photoluminescence can also be obtained which describes the rate at which excited states decay radiatively.\(^{153}\) For most organic dyes, such as chlorophyll and N719, the radiative lifetimes are fitted with single exponentials due to the single pathway for radiative recombination.\(^{154-155}\) Quantum dot emission is typically fitted with multiple exponentials or stretched exponentials due to their recombination centers being non-uniform.\(^{104,156}\) Charge transfer lifetimes can be determined from the difference in photoluminescence lifetimes after a quencher is added,\(^{69}\) Equation 1.10:

\[
k_t = \frac{1}{\tau_{PL+Q}} - \frac{1}{\tau_{PL}}
\]

(1.10)
Where $k_t$ is the charge transfer rate, $\tau_{PL+Q}$ is the average lifetime for the fitted decay of the emitter with quencher and $\tau_{PL}$ is the average lifetime of the fitted decay for the emitter.

Charge transfer rates determined from photoluminescence decay are on the scale of ns. Faster time-scales are often needed for quantum dot sensitizers as electron transfer is commonly on the ps scale.\textsuperscript{157-159} To follow charge transfer on this short time scale transient absorption laser pulse photolysis (TA) is used.\textsuperscript{106,159} Similar to laser flash photolysis an excitation pulse is sent to the sample and followed by a delayed probe beam of white laser light. The absorbance of the sample is measured before and after excitation which yields a change in absorption. A schematic of the process is shown in Figure 1.6. For sensitizer species the change in absorption is directly correlated to the population of excited charges.\textsuperscript{160-162} As the population decays to the ground state the absorbance is monitored. A laser pulse width of $\sim$150fs can resolve the decay of excited sensitizers and track charge transfer to metal oxide substrates.
Figure 1.6 Ultrafast transient absorption optical arrangement. The fundamental beam is split into the pump and probe beams. The pump beam is converted to the second harmonic and chopped before entering the sample. The probe beam is controlled with a time delay track before being converted to white light and entering the sample. After passing through the sample the transmitted probe beam is collected by a CCD detector.
1.6 Areas of Improvement

The three regions of the solar cell, working electrode, counter electrode and electrolyte can all be isolated and improved to increase performance of LJSCs. The three methods by which researchers can improve these regions are to increase short circuit current, increase open circuit potential, and increase fill factor.

As linking quantum dots to TiO₂ films is one of the primary techniques to sensitize a QDSC the interaction between the linker molecule, MPA, and presynthesized CdSe is of importance to the cell’s performance. Thiols are known hole scavengers, and the surface ligand population will be affected by the presence of a new species. Chapter 2 investigates the interactions and consequences MPA has on the surface of CdSe quantum dots, specifically focusing on photogenerated charge carrier dynamics to increase photocurrents.

At the working electrode higher absorbances and longer diffusion lengths will also increase photocurrent. Materials which can absorb the widest region of the solar spectrum need to be used to capture the most photons. New nanofabricated architectures, such as 1D structures, can improve diffusion lengths in the TiO₂ layer, while also increasing surface area for more sensitizer deposition. This topic will be explored in Chapters 3 & 4.

In comparison to the working electrode, the counter electrode and electrolyte are relatively left untouched by researchers. Because of platinum’s known poisoning by sulfides there is potentially a wide area for improvement. With new electrolytes and new counter electrodes QDSC could increase performance by limiting back electron transfer and reducing overpotentials. Chapter 5 looks into new strategies for the electrolyte/counter electrode interface.
CHAPTER 2:
CHEMICALLY CONTROLLED EMISSION OF CDSE QUANTUM DOTS

2.1 Thiols and CdSe Quantum Dots

One of the most common methods to produce quantum dot solar cells (QDSC) is to molecularly link quantum dots to the metal oxide.\textsuperscript{105,137} Bi-functional linker molecules, such as 3-mercaptopropionic acid (MPA) or cysteine, bind the two components of the working electrode together. Thiol groups have been shown to bind onto surface cadmium states of quantum dots, and carboxylic acid groups are used to chemisorb onto the surface of metal oxides via surface titanium sites on TiO\textsubscript{2}.\textsuperscript{103,106} Though not conductive, these linker molecules are useful in binding quantum dots to the surface where they can pass charges by tunneling.\textsuperscript{163} Without linker molecules quantum dots would have to adsorb to the surface of TiO\textsubscript{2}; a difficult task as CdSe quantum dots are typically coated in hydrophobic ligands.

MPA has been used as an effective method to evenly, and effectively populate TiO\textsubscript{2} surfaces.\textsuperscript{104,159} However, thiols bound to CdSe have been shown to affect surface properties of quantum dots.\textsuperscript{135} Thiols and amines in solution are known hole scavengers quenching quantum dot emission.\textsuperscript{164-165} Once bound, however, they passivate surface dangling bonds, and in the case of amines they can increase quantum yields despite demonstrating quenching properties while in solution.\textsuperscript{166-168} Passivation of the surface is important for CdSe quantum dots as unpassivated surface selenium has been shown to
oxidize and become removed from the nanocrystal creating surface vacancies.\textsuperscript{169} These surface vacancies are known trap sites and prevent fast electron transfer to the metal oxide layer lowering photocurrents.\textsuperscript{170-172}

One of the primary benefits for utilizing quantum dots as a sensitizer is their ability to be tuned for absorption and emission based on their size.\textsuperscript{94-95} Due to quantum confinement effects as the particles become larger their absorption red-shifts as the energy levels defining the bandgap come closer together, as defined by quantum mechanics. This red-shift is also observed in the emission properties as emission from an excited electron relaxing from the conduction band to the valence band (band-edge emission) will also change because the energy levels are dependent on size.

Emission quantum yield (QY) is defined by Equation 2.1:

\[
QY(\%) = \frac{N_e}{N_a} \times 100\%
\]  

(2.1)

Where \(N_e\) is the number of photons emitted and \(N_a\) is the number of photons absorbed by a sample. This definition is also commonly called internal quantum yield. External quantum yield, like IPCE, uses the number of incident photons instead of photons absorbed. The QY of CdSe quantum dots can be manipulated by changing the concentration of species in the colloidal medium.\textsuperscript{173-175} This controls the intensity of emission; however, the wavelengths emitted are fixed by the size of the quantum dot. White emitting quantum dots have seen development due to possibilities for displays and solid state lighting.\textsuperscript{176-179} White emission is typically obtained with what has been termed “magic sized” quantum dots which utilize high emission intensities from deep traps caused by high surface to volume ratios. By increasing surface states deep trap emission
can be comparable in intensity to band-edge emission thereby spreading emission across the visible spectrum. Deep trap emission is often a broad peak because of the many factors defining the energy levels of a trap state.\textsuperscript{180-181} As an ensemble this variety of energy levels yields a broad emission whereas band-edge emission is typically a narrow band due to its defined energy levels. Since the deep trap emission is found mostly in surface states an investigation into the surface interactions of CdSe will be evidenced by changes to the deep-trap emission properties.\textsuperscript{179} This chapter examines the surface interactions between CdSe quantum dots and MPA to determine consequences when linking CdSe to TiO\textsubscript{2}.

2.2 Experimental

2.2.1 CdSe Synthesis

CdSe quantum dots were synthesized using a modified version of the procedure developed by Peng et al.\textsuperscript{182} In a round-bottom three-necked flask 4g of trioctylphosphine oxide (TOPO), 0.6g tetradecylphosphonic acid (TDPA), 0.1g CdO, and various amounts of dodecylamine (DDA) were added. A condenser was placed on the middle neck while the other two were sealed with rubber septa. A thermocouple was inserted through one septum to measure the temperature of solution. A vacuum was pulled through the condenser for 1h while the mixture was heated to a temperature of 100°C and stirred (the TOPO, TDPA and DDA melt). After 1h under vacuum, to remove moisture, dry N\textsubscript{2} was introduced to create an inert atmosphere. The system was heated to 300°C. A syringe containing 0.5mL of 1M trioctylphosphine selenide (TOPSe) and 8mL trioctylphosphine (TOP) injected the selenium precursor into the reaction vessel. As CdSe quantum dots
form the color of the solution turns from clear to yellow and proceeding to red as the quantum dots grow. After the desired color is reached the reaction vessel is cooled to stop the reaction. The resulting solution has toluene added to keep it from solidifying and is stored at 4°C for ~1h to extract excess DDA and TOPO from solution. The quantum dot solution is then centrifuged and the supernatant contains CdSe quantum dots in a toluene solution with some excess ligands that did not solidify. To remove these excess ligands methanol was added until the solution became hazy. TOPO coated CdSe quantum dots are known to be insoluble in a methanol/toluene solution whereas TOPO is soluble. After centrifugation the supernatant was removed and the pellet of quantum dots was resuspended in toluene. This methanol washing was performed three times and CdSe quantum dots were stored in toluene for at least 24h before testing because quantum dots can change size in the first day as they come to equilibrium. Absorption spectra were used to determine the size of the quantum dots.  

2.2.2 CdSe and MPA Mixtures

A linker molecule solution of 1M MPA was dissolved in acetonitrile. From this solution, dilutions of 0.1M and 0.01M MPA were made. To create CdSe-MPA mixtures a stock solution of CdSe was used and aliquots of this were mixed with 10 or 20µL of the MPA solutions yielding solutions with the same concentration CdSe and various concentrations of MPA. The small volume of MPA was used to keep dilution from significantly changing the absorbance of the solutions. Samples were left to equilibrate for 2h before testing.
2.2.3 Experimental Testing

Steady state emission was measured with a Jobin Yvon Fluorlog-3 with samples being excited at a wavelength of 410nm. Photoluminescence decay was measured with a Jobin Yvon single photon counter with excitation created by a 373nm LED. The emission measurements were conducted with solutions in a one-centimeter quartz cell. Transient absorption was conducted using the laser and optical table described in Chapter 1.

2.3 MPA Effects on CdSe Optical Properties

2.3.1 Steady State Emission

Significant changes are seen in emission when MPA is added to CdSe solutions. Under UV irradiation Figure 2.1 shows that the emission becomes red with an increasing concentration of MPA. This is an unexpected result as thiols are known to only change quantum yield not emission wavelength. At 100µM MPA the emission is seen to be almost white. When emission spectra for these samples of 2.6nm CdSe quantum dots and MPA, Figure 2.2, are measured several phenomena present themselves. The first is that the band-edge emission is seen to be quenched with increasing MPA, and the second is that deep-trap emission increases up to 1mM MPA before also being quenched with further addition of MPA. Band-edge emission is the narrow peak at 500nm while the deep-trap emission is a broad peak spreading from 550-750nm peaking at 620nm. As described above, the deep-trap emission origin has been previously determined to stem from surface vacancies of selenium.\textsuperscript{170-172} The deep-trap emission was sufficiently bright with QY commonly 1-5%. In Figure 2.2 band-edge emission without MPA in the system, and therefore negligible deep-traps, gives a QY of 1.3%. The maximum total QY for the
same sample in Figure 2.2A was at 100µM MPA and gave a QY of 2.4%; at 10mM MPA the QY had reduced to 1.1%. Absorption was also seen to change slightly with addition of MPA. Figure 2.2B shows a slight red-shift of the excitonic peak, when normalized, with an increase in MPA concentration. Small red-shifts have been shown to be due to surface complexation of thiols with quantum dots because the S changes the electronic structure of the quantum dot slightly.\textsuperscript{135,184} By changing the solvent medium CdSe quantum dots are suspended in, MPA addition allows for a chemical tuning of the emission properties with little effect on the absorption, a flexibility that can be useful for display applications.
Figure 2.1 CdSe quantum dots 2.6nm in diameter. Under 366nm UV irradiation the emission changes with varying MPA concentration, (a) 0M, (b) 50µM, (c) 100µM, (d) 500µM, (e) 1mM, (f) 5mM, and (g) 10mM.
Figure 2.2 (A) Steady state photoluminescence spectra and (B) absorbance spectra of 2.6nm CdSe quantum dot solutions with MPA concentrations of (a) 0M, (b) 50µM, (c) 100µM, (d) 500µM, (e) 1mM, (f) 5mM, and (g) 10mM. Absorbance spectra are normalized to the first excitonic peak. The inset of (A) shows the double reciprocal plot corresponding to Equation 2.3 and the band-edge emission at 497nm. Excitation was with 410nm.
2.3.2 Ligand Exchange Kinetics

Because the properties of emission are dependent on the surface interaction with MPA an association constant ($K_{app}$) between the two, Equation 2.2, can be determined from the intensity of the band-edge at different concentrations of MPA, Equation 2.3.\textsuperscript{185}

\[
CdSe + MPA \overset{K_{app}}{\leftrightarrow} (CdSe \cdots MPA)
\]

\[
\frac{I^o}{I^o - I} = \frac{I^o}{I^o - I'} + \frac{I^o}{K_{app} (I^o - I') [MPA]}
\]

Where $I^o$ is the initial intensity, $I$ is the current intensity, $I'$ is the intensity with the entire system bound with MPA. The slope of the double reciprocal plot yields $K_{app}$, as seen in the inset of Figure 2.2A. From this plot $K_{app}$ is determined to be 3,730M\textsuperscript{-1} which is similar to values previously seen for species complexing with CdS nanoparticles.\textsuperscript{185-187}

The modified synthesis procedure this chapter describes uses DDA which is not commonly found when producing CdSe quantum dots. DDA is added to the synthesis pot to slow the reaction between Cd and Se ions and allow for more control of the end size. As evidenced by Koole et al., amines are readily displaced by thiols on the surface of ligand coated CdSe quantum dots, while TOPO and TOP are not as easily exchanged.\textsuperscript{188}

To determine what effect DDA had on the deep-trap enhancement by MPA quantum dots of similar size were prepared with and without DDA as a capping ligand. The emission spectra, Figure 2.3A, after MPA has been added without DDA on the surface, shows that there is no deep trap emission despite the band-edge quenching. Meanwhile samples with DDA do show deep-trap emission. This demonstrates the importance of amines for thiol exchange in the creation of Se vacancies on the surface of the CdSe.
Figure 2.3 Normalized photoluminescence spectra of CdSe quantum dots (A) (a,c) with and (b,d) without DDA as a capping ligand (a,b) before and (c,d) after 1mM MPA in solution. (B) Spectra of different sized quantum dots after addition of 1mM MPA. All samples were excited with 410nm.
Se surface states on CdSe quantum dots made with the procedure described for this chapter are passivated by TOP. As mentioned above TOP is not easily displaced by thiols. However, MPA will displace DDA and change the surface environment because when MPA binds to surface Cd the R-S-Cd bond is stronger than R-NH-Cd weakening the Cd-Se bonds on the surface. Once Se is weakened on the surface this increases its chances for oxidation and ejection from the surface creating the vacancy.

As surface interactions are theorized to be the cause of the deep trap enhancement, changing the size of the CdSe quantum dot should change emission properties because the surface to volume ratio is inversely proportional to size. As the quantum dots become larger internal emission (band-edge) becomes more significant. As seen in Figure 2.3B quantum dots of diameter 2.8, 2.8, and 3.6nm were prepared with the same amounts of TOPO, TOP and DDA, but reacted for different amounts of time to yield the various sizes. MPA was added at 1mM and once normalized to band-edge intensity it was seen that the deep trap emission is decreased with decreasing surface to volume ratio. This further shows that deep-trap enhancement is only a surface phenomenon, and does not include internal crystal defects.

2.3.3 Internal Electron Kinetics

The photoluminescence decay dynamics were probed with and without MPA added to the CdSe quantum dot system, Figure 2.4. Stretched exponential kinetics, Equation 2.4, were used to fit decay measurements at wavelengths across the emission spectrum.

\[ y = y_0 + A e^{-[(t-t_0)/\tau]^\beta} \]  \hspace{1cm} (2.4)
Where $y_0$ is the offset value, $A$ is the pre-exponential factor, $t_0$ is the initial time of the decay, $\tau$ is the lifetime, and $\beta$ is the stretching factor. The fitting results are tabulated in table 2.1. Figure 2.4A plots the fitted lifetimes versus wavelength. It is seen that at the band-edge (530nm) the lifetime is reduced with 1mM MPA from 8.0 to 2.6ns. At the deep-trap wavelengths (~625nm) lifetimes do not change in the presence of MPA indicating electrons are being scavenged from the band-edge excited state while trap states remain unaffected. This result explains that the nature of the trap states is unaffected by MPA, however, because of the intensity increase, the population of deep-trap states increases with MPA.

Electron transfer lifetimes can be calculated from the changes in electron lifetime at the band edge, Equation 2.5.

$$k_{ET} = \frac{1}{\tau_{CdSe+MPA}} + \frac{1}{\tau_{CdSe}}$$

(2.5)

Previous studies have used this method to investigate the electron transfer between CdS or CdSe and TiO$_2$. Assuming the new electron transfer pathway is to the trap states and using the lifetime data for band-edge emission (530nm) $k_{ET}$ is found to be $2.6 \times 10^8$ s$^{-1}$, a non-negligible result.

When photoluminescence decays are measured with varying amounts of MPA in solution and fitted with a bi-exponential decay, Equation 2.6:

$$y = y_0 + A_1 e^{-[(t-t_0)/\tau_1]} + A_2 e^{-[(t-t_0)/\tau_2]}$$

(2.6)

The contribution of the fast component is found to increase with increasing MPA concentration and the slow component decreases, table 2.3 and Figure 2.5. This implies that there are two types of emissive states as suggested by Equation 2.2. These drastic changes found in the photoluminescence decay, with and without MPA, are of great
importance because electron transfer lifetimes often fail to take this into account. Because the band-edge wavelengths are used to determine lifetimes MPA quenching must be accounted for when conducting electron transfer rates to TiO$_2$. 
Figure 2.4 (A) Photoluminescence decays of 3.1nm diameter CdSe quantum dots with 1mM MPA at different wavelengths of the emission spectrum. (B) Stretched exponential lifetimes of the fitted decays from (A), with and without MPA.
TABLE 2.1

STRETCHED EXPONENTIAL FITTING

Data for photoluminescence decay traces of Figure 2.4A. All pre-exponential factors, $A$, were set to 10,000 and all offset values, $y_0$, were set to 0.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>t₀ (ns)</th>
<th>B</th>
<th>τ (ns)</th>
<th>t₀ (ns)</th>
<th>β</th>
<th>τ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>7.38</td>
<td>0.467</td>
<td>5.73</td>
<td>7.27</td>
<td>0.404</td>
<td>1.17</td>
</tr>
<tr>
<td>530</td>
<td>7.38</td>
<td>0.526</td>
<td>8.05</td>
<td>7.27</td>
<td>0.424</td>
<td>2.59</td>
</tr>
<tr>
<td>550</td>
<td>7.38</td>
<td>0.515</td>
<td>8.50</td>
<td>7.27</td>
<td>0.426</td>
<td>3.81</td>
</tr>
<tr>
<td>575</td>
<td>7.38</td>
<td>0.465</td>
<td>9.21</td>
<td>7.27</td>
<td>0.391</td>
<td>4.52</td>
</tr>
<tr>
<td>600</td>
<td>7.38</td>
<td>0.438</td>
<td>9.83</td>
<td>7.27</td>
<td>0.389</td>
<td>6.13</td>
</tr>
<tr>
<td>625</td>
<td>7.38</td>
<td>0.429</td>
<td>10.68</td>
<td>7.27</td>
<td>0.396</td>
<td>8.54</td>
</tr>
<tr>
<td>675</td>
<td>7.38</td>
<td>0.427</td>
<td>12.84</td>
<td>7.27</td>
<td>0.408</td>
<td>13.91</td>
</tr>
<tr>
<td>700</td>
<td>7.38</td>
<td>0.429</td>
<td>13.93</td>
<td>7.27</td>
<td>0.413</td>
<td>16.11</td>
</tr>
</tbody>
</table>
Figure 2.5 (A) Contribution of each bi-exponential lifetime at (a,b) band-edge and (c,d) deep-trap wavelengths versus concentration of MPA. (B) Lifetime changes versus concentration of MPA.
TABLE 2.2
EMISSION DECAY KINETIC FITTING

Bi-exponential kinetic fitting of band-edge (540nm) and deep-trap (630nm) emission decay of CdSe quantum dots at different concentrations of MPA. Data is plotted in Figure 2.5.

<table>
<thead>
<tr>
<th>[MPA]</th>
<th>0M</th>
<th>50µM</th>
<th>100µM</th>
<th>200µM</th>
<th>1mM</th>
<th>2mM</th>
<th>10mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>215</td>
<td>260</td>
<td>275</td>
<td>161</td>
<td>66.2</td>
<td>69.7</td>
<td>45.4</td>
</tr>
<tr>
<td>B₁</td>
<td>12.4</td>
<td>14</td>
<td>14.9</td>
<td>22</td>
<td>28.6</td>
<td>27.4</td>
<td>31.1</td>
</tr>
<tr>
<td>B₂</td>
<td>87.6</td>
<td>86</td>
<td>85.1</td>
<td>78</td>
<td>71.5</td>
<td>72.6</td>
<td>68.9</td>
</tr>
<tr>
<td>τ₁ (ns)</td>
<td>3.39</td>
<td>2.83</td>
<td>3.06</td>
<td>2.64</td>
<td>2.15</td>
<td>2.34</td>
<td>2.25</td>
</tr>
<tr>
<td>τ₂ (ns)</td>
<td>27.3</td>
<td>27.8</td>
<td>28.6</td>
<td>22.8</td>
<td>19.3</td>
<td>20.3</td>
<td>18.5</td>
</tr>
<tr>
<td>&lt;τ&gt; (ns)</td>
<td>26.8</td>
<td>27.4</td>
<td>28.1</td>
<td>22.2</td>
<td>18.6</td>
<td>19.5</td>
<td>17.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>[MPA]</th>
<th>0M</th>
<th>50µM</th>
<th>100µM</th>
<th>200µM</th>
<th>1mM</th>
<th>2mM</th>
<th>10mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>668</td>
<td>851</td>
<td>994</td>
<td>848</td>
<td>464</td>
<td>411</td>
<td>311</td>
</tr>
<tr>
<td>B₁</td>
<td>8.94</td>
<td>8.68</td>
<td>8.73</td>
<td>10.3</td>
<td>14.4</td>
<td>15</td>
<td>17.7</td>
</tr>
<tr>
<td>B₂</td>
<td>91.1</td>
<td>91.3</td>
<td>91.3</td>
<td>89.7</td>
<td>85.6</td>
<td>85</td>
<td>82.3</td>
</tr>
<tr>
<td>τ₁ (ns)</td>
<td>4.3</td>
<td>3.66</td>
<td>3.83</td>
<td>3.82</td>
<td>3.57</td>
<td>3.61</td>
<td>3.44</td>
</tr>
<tr>
<td>τ₂ (ns)</td>
<td>36.7</td>
<td>37.1</td>
<td>38.5</td>
<td>35.5</td>
<td>30.8</td>
<td>30.4</td>
<td>27.5</td>
</tr>
<tr>
<td>&lt;τ&gt; (ns)</td>
<td>36.3</td>
<td>36.8</td>
<td>38.2</td>
<td>35.1</td>
<td>30.3</td>
<td>29.9</td>
<td>26.9</td>
</tr>
</tbody>
</table>
Through ultrafast transient absorption spectroscopy MPA manifests its influence again on the properties of CdSe. Spectra recorded for 2.4nm CdSe quantum dots, with and without, MPA excited with 387nm laser pulses are shown in Figure 2.6. Following the peak bleaching over time, Figure 2.6C shows the difference in ground-state recovery when MPA is added to the system. MPA causes a slower bleaching recovery stemming from the increase of the trap population. Removing electrons from band-edge states is a faster process than from a trap-state (thus the name), and as the population of traps increases the excited electron population, which determines the amount of bleaching, the recovery rate slows. This result shows that MPA changes the structure of the CdSe quantum dot primarily by creating deep-trap states (Se vacancies) on the surface.
Figure 2.6 Transient absorption spectra at different times after excitation of 2.4nm CdSe quantum dots (A) without, and (B) with 1mM MPA. (C) Decay traces of (A) and (B) at 464nm normalized to maximum bleach.
2.3.4 Implications of Linking Quantum Dots

In terms of the QDSC, generating traps on the quantum dot sensitizer is a large drawback for photocurrent. Many research groups have investigated this bottleneck as a route to improve efficiencies.\textsuperscript{93,137,159} MPA is extremely useful for generating dense and even films of CdSe onto TiO\textsubscript{2} surfaces; however the introduction of trap states may overall be a hindrance to photocurrent generation. To overcome this, new linker molecules could be used which do not create surface vacancies on the CdSe, or new techniques to deposit quantum dots like electrophoretic deposition.

The resilience of the MPA-CdSe bond was investigated by precipitating the quantum dots out of a 1mM MPA/toluene solution with methanol, like in the washing steps of synthesis. The quantum dots were resuspended in toluene and the steady photoluminescence was recorded. After normalization of the band-edge emission the deep-trap emission was found to have excellent overlap with the original spectrum, Figure 2.7, indicating the MPA effects are entirely surface bound without influence from MPA in solution. MPA on the surface of CdSe quantum dots has been shown to degrade under illumination due to charges on the quantum dot transferring to the linker molecule and forming radicals. Though the adsorption may not be reversible, MPA can be removed; however the vacancies will remain. MPA therefore may not actually be needed in the operation of the solar cell and acts solely to bring CdSe together with TiO\textsubscript{2} initially. A more effective linker would link CdSe and TiO\textsubscript{2}, but not form trap-sites. A more effective method would be to use bottom-up sensitization procedures which synthesize quantum dots directly on the surface of TiO\textsubscript{2} negating the use of linker molecules entirely.
Figure 2.7 Comparison of emission between CdSe quantum dots in 1mM MPA and after precipitation and resuspension in toluene (washed). Emission is normalized to maximum deep-trap intensity.
2.4 Summary

Addition of MPA was seen to create emissive deep-traps on the surface of CdSe quantum dots coated with TOPO, TOP, and DDA. It was determined that MPA displaces the amine DDA on the surface and as a result Se vacancies are generated which is the source of deep-traps. With increasing concentration of MPA band-edge emission from CdSe was quenched whereas deep-trap emission enhanced up to 1mM MPA before also being quenched. By increasing the size of the quantum dot deep-trap effects were reduced due to smaller surface to volume ratios. By adding MPA photoluminescence decay and transient absorption measurements displayed non-negligible changes, meaning that MPA needs to be accounted for if used to link quantum dots to TiO$_2$. Because of the generation of deep-traps bottom-up synthesis procedures of quantum dots are preferred to pre-synthesis linking.
3.1 One-Dimensional Working Electrodes

As described in Chapter 1 quantum dot solar cells (QDSC) have become increasingly studied due to their promise for increased light harvesting capabilities and selectivity through size control. QDSC have also shown the promise of allowing hot-electron transfer, which would provide higher voltages, along with the possibility of multiple carrier generation for higher photocurrents.\textsuperscript{190-195} Since the early pioneers worked with CdS-TiO$_2$ and similar systems, researchers have investigated many combinations of metal oxide layers, semiconductor sensitizers, and electrolytes, resulting in a good understanding of the inner workings of the photoelectrochemical cell.\textsuperscript{93,95}

One dimensional TiO$_2$ architectures have been utilized to increase diffusion lengths in the metal oxide layer.\textsuperscript{196-198} Longer effective electron lifetimes within one dimensional structures have been found to induce higher photocurrents.\textsuperscript{116,144-145} This is because when electron lifetimes become longer scavenging is reduced, resulting in higher carrier densities. Larger crystal sizes, compared to nanoparticulate films, also allow for further transmission length before contact with crystal boundaries. Boundaries are known trap sites which lower effective electron diffusivities.\textsuperscript{132-133} Common one dimensional TiO$_2$ structures are nanorods templated by Al$_2$O$_3$ nanotubes,\textsuperscript{144,199} hydrothermal nanotubes,\textsuperscript{145,200} and anodically etched nanotubes.\textsuperscript{201-202}
The recent development of anodized TiO$_2$ nanotube (TiO$_2$-NT) arrays has shown promise for many fields such as sensors, hydrogen production, and liquid junction solar cells. TiO$_2$-NT provide for a facile, reproducible and scalable synthesis route. Because of the uniformity of the tubes, and large crystal sizes in TiO$_2$-NT, the diffusion lengths are greatly extended, and make them beneficial nanoarchitectures for charge separation and directing charges to the backing conductive electrode, Figure 3.1.

This chapter explains the deposition of CdS onto TiO$_2$-NT through the successive ionic layer absorption and reaction (SILAR) technique, and compares the TiO$_2$ substrates of nanotubes and the traditional nanoparticulate (TiO$_2$-NP) structures. SILAR is a solution based deposition technique wherein solutions of Cd$^{2+}$ and S$^{2-}$ sensitize the TiO$_2$ surface with CdS quantum dots.
Figure 3.1 Charge injection and transport in a) TiO$_2$ nanoparticulate substrate, and b) TiO$_2$ nanotube array with semiconductor sensitizers.
3.2 Experimental

3.2.1 TiO₂ Nanotube (TiO₂-NT) Synthesis

Titanium foil was cut into strips of 4 × 0.8 cm then cleaned by sonication in a bath of isopropyl alcohol for 1 h for degreasing purposes. After sonication, the foils were stored in acetone. The strips were immersed in a 3-armed electrochemical cell in a solution of 0.27M NH₄F, 5% by volume H₂O, and 95% formamide. The titanium foil acted as a working electrode and platinum gauze was employed as a counter electrode. Potential was ramped at 1 V/s until 20 V was applied between the electrodes. After 12 h at 20 V the titanium foil was removed and rinsed with water. A brief, five second, sonication step in water removed surface deposits from the samples. After sonication and rinsing, the samples were dried in an air stream and then annealed in air at 450°C for three hours. The temperature was ramped, for heating and cooling steps, at 1°C/min.

3.2.2 TiO₂ Nanoparticle (TiO₂-NP) Films

P-25 TiO₂-NP (30 nm average diameter) from Degussa was suspended in methanol at a concentration of 5 mg/ml. The suspension was dropcast onto titanium foils of the same dimension as the previous section. Films were dried in air and annealed at 450°C for three hours. For comparison between the TiO₂-NT and TiO₂-NP, films had similar TiO₂ weights (1 mg/cm²) based on calculations of the TiO₂-NT film.

3.2.3 CdS SILAR

TiO₂ films prepared above were immersed in a solution of 0.1 M CdSO₄ for five minutes. Samples were then rinsed with water and immersed into a solution of 0.1 M
Na₂S for five minutes and rinsed. This comprised one cycle; cycles were repeated until the desired amount of CdS was obtained.

3.2.4 Experimental Setup

Diffuse reflectance absorption spectra were recorded with a Shimadzu UV-3101PC dual beam spectrophotometer. A titanium foil heated to 450°C was used as the reference sample due to the discoloration that occurs when titanium is heated. Photoelectrochemical measurements were obtained using a Princeton Applied Research PARSTAT 2263 potentiostat. In a 3-armed electrochemical cell the titanium foil working electrodes were immersed in an electrolyte of 0.1M Na₂S, with platinum gauze as a counter electrode. A KCl saturated Ag/AgCl electrode was used as the reference electrode for the electrochemical system. The light source was a 150W Xenon lamp with a CuSO₄ 300nm long pass water filter set to illuminate the sample with an intensity of 100mW/cm². For IPCE measurements a Keithley 617 electrometer and a Bauch and Lomb high intensity monochromator were used.

SEM images were obtained with a Hitachi S-4500 FESEM. A JEOL 2010 was used for TEM images. X-ray diffraction measurements were made with a Scintag X1 Advanced Diffraction System. EDS was measured with an Oxford Instruments INCAx-sight Model 7636.

3.3 Comparison of Nanotubes to Nanoparticles

3.3.1 TiO₂-NT Synthesis

Anodized TiO₂-NT are formed by electrochemically etching titanium foil in a fluoride medium. The groups of Grimes and Schmuki have explained the mechanism for
formation as changes in the electric field at the surface of the foil.\textsuperscript{205} Figure 3.2 depicts the formation mechanism. Under applied potential a layer of TiO\textsubscript{2} forms on the surface of the foil, Equation 3.2. TiO\textsubscript{2} reacts with fluoride ions in solution, Equation 3.3, and the resulting TiF\textsubscript{6}\textsuperscript{2-} ions are solublized, and are pushed away by the electric field causing pitting. The pits in the TiO\textsubscript{2} layer cause the electric field to become stronger across the thin pitted region, increasing the etching rate within each pit. As the pit grows into the foil new TiO\textsubscript{2} grows and the electric field becomes concentrated at the tips of the underlying titanium foil. This accelerates etching around the pits, causing the outer wall of the nanotube to form. This formation of pit and tip etching continues into the titanium film and has been shown to etch through the entire film if allowed to proceed unabated.

\begin{equation}
2H_2O \rightarrow 4H^+ + O_2 + 4e^- 
\end{equation}  
\begin{equation}
Ti + O_2 \rightarrow TiO_2 
\end{equation}
\begin{equation}
TiO_2 + 6F^- + 4H^+ \rightarrow TiF_6^{2-} + 2H_2O
\end{equation}

As a conductive backing was desired for cell performance the etching was stopped after the nanotubes reached \(~10\mu m\) in length. From SEM images the outer diameter of the nanotubes was determined to be 80-100nm and the wall thickness was \(~20\)nm. Capillary forces between the nanotubes cause them to draw together as they dry. The brief sonication step which removes surface deposits also rearranges the nanotubes into uniform alignment.
Figure 3.2 Illustration of anodically etched TiO$_2$ nanotube formation. Potential is applied after a) titanium is immersed in the fluoride solution. b) TiO$_2$ forms on the surface of the foil, c) pits are formed by the etching process followed by d) further growth of the TiO$_2$ layer in the pits. e) Etching occurs around the etched pits and f) the structure continues to etch into the foil.
3.3.2 CdS Deposition

Through the SILAR process TiO$_2$-NT and TiO$_2$-NP films were sensitized with CdS. SEM images in Figure 3.3 show TiO$_2$-NT arrays with and without CdS quantum dots. Through this analysis the wide coverage of SILAR CdS is seen and thereby the effectiveness of the SILAR technique. Through extended sonication the CdS/TiO$_2$-NT composite can be removed from the titanium substrate. Once in solution the suspended tubes were dropped onto a TEM grid for characterization. From Figure 3.3C it can be seen that the SILAR CdS was able to penetrate the opening of the TiO$_2$-NT and deposit on the internal surfaces. The high coverage and close contact of the CdS and TiO$_2$-NT is important for creating efficient charge separation under excitation.

By cycling the SILAR process CdS is deposited in two ways: 1) New crystallite formation and 2) growth onto preexisting CdS. Growth was followed with use of SEM imaging. Figure 3.4 shows the surface of TiO$_2$-NT with increasing numbers of SILAR cycles up to 20. CdS is shown to initially form islands. After the initial seeds are formed further deposition occurs on the islands until they are seen to merge into a continuous film after 20 cycles.

Through diffuse reflectance spectroscopy the absorption of CdS particles is seen to red-shift with increasing cycles of SILAR, Figure 3.5. This indicates that the nanocrystals are quantized. After 20 cycles, when the particles merge to form a film, bulk properties are observed and no further red shift is seen with further deposition. TiO$_2$-NP films were sensitized in the same manner and demonstrated similar quantization effects.
Figure 3.3 SEM images of A) a bare TiO$_2$ nanotube array, and B) a TiO$_2$ nanotube array sensitized with 15 SILAR cycles of CdS. TEM image C) of a single CdS sensitized TiO$_2$ nanotube.
Figure 3.4 SEM images of TiO$_2$ nanotube arrays with (a,a’) no CdS, (b,b’) 5 cycles of SILAR CdS, (c,c’) 10 cycles, and (d,d’) 20 cycles. Scale bars in the rightmost images are representative for all images to their left.
Figure 3.5 Diffuse reflectance spectra of (A) TiO$_2$ nanotubes and (B) TiO$_2$ nanoparticles with various depositions of CdS. All spectra are normalized to the first excitonic peak.
3.3.3 Characterization

To further confirm the presence of CdS on the TiO$_2$-NT XRD was used to look for crystalline signatures. XRD of bare TiO$_2$-NT, Figure 3.6A, reveals that the annealed nanotubes consist of the anatase polymorph of TiO$_2$. With 15 cycles of SILAR CdS on the TiO$_2$-NT XRD reveals peaks both from TiO$_2$ and CdS. Broad peaks corresponding to small CdS particles were observed and corresponded to the particles seen in the SEM images of Figure 3.4. Particle size was determined with the Scherrer equation, Equation 3.4, revealed that the CdS crystals were around 2nm in diameter.

$$d = \frac{0.9\lambda}{\beta \cos(\theta)}$$

Equation 3.4

Where $d$ is the diameter of the particle, 0.9 is an empirical shape factor, $\lambda$ is the wavelength of X-rays incident on the sample (0.154nm), $\beta$ is the FWHM of the peak, and $\theta$ is the Bragg angle of the diffracted peak.

The nanocrystals seen in Figure 3.4 are larger than the XRD data predicts, indicating that the crystals on TiO$_2$ are actually aggregates of CdS. Further characterization with EDS was employed to determine the atomic proportions of the CdS crystals, Figure 3.6B. It was found that Cd and S are in a 1:1 stoichiometric ratio on a 15 cycle sample.
Figure 3.6 Characterization of the CdS/TiO$_2$ nanotube system with (A) XRD of a) TiO$_2$-NT and b) CdS/TiO$_2$-NT. (B) EDS analysis of a CdS/TiO$_2$-NT sample.
3.3.4 Photoelectrochemical Performance

Using a three electrode photoelectrochemical cell a comparison was performed between TiO$_2$-NT and TiO$_2$-NP as substrates for SILAR CdS. Under a bias of 0V vs. Ag/AgCl, the photocurrents of CdS/TiO$_2$-NT and CdS/TiO$_2$-NP samples were measured with light on and off, Figure 3.7. The samples’ response to illumination was swift. Once illuminated, the CdS/TiO$_2$-NT demonstrated a superior ability to produce photocurrent. Without sensitization of CdS both TiO$_2$-NT and TiO$_2$-NP yielded little photocurrent, indicating all current was generated by the CdS. In both samples photocurrent was found to increase with increasing deposition of CdS. During the initial 10 cycles of deposition, currents rose with respect to the increased amount of CdS deposited. After 15 cycles, however, the rise in photocurrent slowed with increased amounts of CdS. The maximum deposition of CdS, beyond which there is no noticeable increase in photocurrent, coincides with the merging of CdS islands into a continuous film on the TiO$_2$ surface. As also seen by Vogel, Pohl, and Weller in a previous CdS SILAR study further deposition of CdS fails to impact the photocurrent because the larger and thicker films are less efficient at transferring electrons to the TiO$_2$ substrate than the smaller nanocrystals.$^{96}$ Smaller quantum dots have been shown to have faster electron transfer rates to TiO$_2$ than larger dots.$^{159}$ Two explanations for this size dependence are that 1) the driving force for an electron between the conduction band of CdS and the conduction band of TiO$_2$ is larger with a small CdS particle due to quantization effects making the conduction band of the CdS more negative, and 2) As the conduction band of the quantum dot becomes more negative more states in the TiO$_2$ conduction band are available for transfer.$^{207}$
I-V characteristics in Figure 3.8 confirm the increased photocurrents of the TiO$_2$-NT substrate over TiO$_2$-NP observed in Figure 3.7. As explained in Chapter 1, the open circuit potential ($V_{OC}$) is dependent on the materials chosen for the cell. In this study the $V_{OC}$ is determined by the conduction band of the TiO$_2$ and the redox potential of the electrolyte. Since both systems are designed with the same materials the open circuit potentials observed, -1.1V vs. Ag/AgCl, are similar.

Under white light illumination and a bias of 0V vs. Ag/AgCl the maximum photocurrent observed for the CdS/TiO$_2$-NP system was 5.14mA/cm$^2$ ± 0.03mA/cm$^2$. For the CdS/TiO$_2$-NT system maximum photocurrent was 6.18mA/cm$^2$ ± 0.04mA/cm$^2$. This increase in photocurrent represents a 20% enhancement in charge carrier harvesting efficiency with the one-dimensional architecture. The power conversion efficiencies of these cells (as measured in a two electrode arrangement) are relatively low (<0.5%) due to overpotentials caused by sulfur poisoning of the platinum counter electrode. Record QDSC are able to obtain over 3% power conversion efficiency. To overcome these losses the reader is referred to Chapter 5.
Figure 3.7 Photocurrent versus time measurements for various depositions of CdS on (A) TiO$_2$ nanotube arrays, and (B) TiO$_2$ nanoparticle films. Currents were measured under a 0V vs. Ag/AgCl bias.
Figure 3.8 Current-voltage characteristics for various depositions of CdS on (A) TiO$_2$ nanotube arrays, and (B) TiO$_2$ nanoparticle films.
Photocurrent action spectra were measured to compare the photoresponses of CdS/TiO$_2$-NT and CdS/TiO$_2$-NP, Figure 3.9. From the Incident Photon to Charge Carrier Efficiency (IPCE) graphs it is clear that the nanotube architecture is superior to the nanoparticle film as it yields double the IPCE in the visible regime. This increase in photocurrent is because of the TiO$_2$-NT’s ability to harvest and transport electrons at high rates as seen previously with photoluminescence effects. The size quantization effects of the CdS by the SILAR method are also evident in the IPCE traces as the photocurrent onsets are observed to red-shift with increasing cycles of deposition. The bulk bandgap of CdS is 2.4eV which corresponds to an absorption of 517nm. After 20 cycles of deposition bulk properties are reached as evidenced by Figure 3.5. It is interesting to observe active photocurrent generation occurs with CdS/TiO$_2$-NT more than 50nm red of this. It is unknown exactly what causes this activity, but could be caused by unique absorption properties of aligned one dimensional structures, or as an earlier study by Gerischer and Lübke explained, disorder in the CdS.211
Figure 3.9 IPCE spectra of various CdS depositions on (A) TiO$_2$ nanotube arrays, and (B) TiO$_2$ nanoparticle films.
The trend of photocurrent increasing with higher depositions of CdS is also observed with the IPCE plots up to 10 cycles. After ten cycles photocurrents decrease, as was also observed by Vogel et al.\textsuperscript{96} This is attributed to the charge injection efficiency decreasing with particle size. White light photocurrents are able to remain high because new regions of the solar spectrum are utilized. Beyond 20 cycles overall photocurrents also decline due to thicker layers of CdS resulting in higher rates of recombination within the CdS film. The increase and decrease of photocurrents seen in white light illumination and IPCE for both CdS/TiO\textsubscript{2}-NT and CdS/TiO\textsubscript{2}-NP systems is indicative of the CdS particles aggregating on the surface independent of substrate.

3.4 Summary

CdS sensitized solar cells, based on nanotubular and nanoparticulate substrates, were compared on the basis of photoelectrochemical performance. The directionality of the nanotube system proved beneficial as it was able to more efficiently separate electron-hole pairs generated in the CdS quantum dots. After sensitization, a 20% increase in photocurrent was observed for TiO\textsubscript{2}-NT substrates over similarly sensitized TiO\textsubscript{2}-NP substrates. IPCE spectra were also able to demonstrate the higher photocurrents in the TiO\textsubscript{2}-NT system, seen as a doubling of the maximum IPCE efficiency. As similar materials were used in both systems no change in \(V_{OC}\) was observed.
CHAPTER 4:
REMOVAL AND REDEPOSITION OF ANODICALLY ETCHED NANOTUBES

4.1 Limitations of the Etched TiO₂ Nanotube

The etched TiO₂ nanotube described in Chapter 3 was shown to increase photocurrents in quantum dot solar cells (QDSC). Through increases in diffusion length, photocurrents were found to improve by 20%. This significant improvement would be beneficial except the titanium foil backing causes several problems that need to be addressed before the technology can be more deeply researched and used in everyday applications.

The process of anodically etching TiO₂ nanotubes results in the titanium foil etching on all sides. In use as a solar cell only one side can be illuminated at a time. Because light cannot penetrate the titanium foil, geometry limits the active yield to one half. By not allowing light to penetrate, the titanium foil also inhibits many spectroscopic techniques commonly employed to investigate electron transfer kinetics. By removing nanotubes from the titanium foil the full capacity of the nanotubes can be reached. Once removed, nanotubes can be cast onto new substrates such as transparent glass electrodes. Transparent working electrodes are needed in practical QDSC because illumination from the backside creates charge carriers closest to the backing electrode, the optimal geometry for a cell. Also, once removed from the titanium surface and in solution, spectroscopic techniques can be applied to the nanotube-quantum dot system. Recycling
of the titanium foil is also possible once the active arrays are removed, a benefit extremely attractive for future commercial applications.

A process that can remove the nanotubes while retaining their useful diffusion length properties would create a more applicable cell. There have been previous efforts to remove the nanotubes, though typically focusing on keeping the inherent alignment from the etching process for membrane purposes, and not solar applications.\textsuperscript{212-213} The alignment does not necessarily need to be retained for higher photocurrents. Other TiO\textsubscript{2} one dimensional structures have shown longer diffusion lengths despite their random alignments.\textsuperscript{214-215} Yanagida et al. have demonstrated that hydrothermally synthesized TiO\textsubscript{2} nanotubes (which are inherently random in orientation) have longer effective electron lifetimes than nanoparticulate films.\textsuperscript{215} Longer electron lifetimes directly relate to higher photocurrents by increasing the probability that an electron will be collected at the backing conductive electrode. This chapter describes the removal of anodically etched TiO\textsubscript{2} nanotubes, using removed tubes to make QDSC. Also spectroscopic techniques are used to determine electron transfer rates, as well as surface area analysis of nanotube powders.

4.2 Experimental

4.2.1 Etching of TiO\textsubscript{2} Nanotubes

To etch TiO\textsubscript{2} nanotubes in titanium foil a similar procedure was followed as in Chapter 3. Differences were found in the etching medium and etching time. The prepared titanium foils were etched at 60V in an electrolyte solution composed of 2 vol % H\textsubscript{2}O, 0.3 wt % NH\textsubscript{4}F in ethylene glycol. Ethylene glycol has a lower dielectric constant than
formamide (36 vs. 84 respectively) resulting in a more conductive electrolyte with faster etching rates. Ethylene glycol etches titanium at 15\(\mu\)m/h whereas formamide etches at 2\(\mu\)m/h. Etched foils were removed from solution after 1.5h. The post-etching procedure was the same as in Chapter 3.

4.2.2 Removal of TiO\(_2\) Nanotubes

TiO\(_2\) nanotubes were removed from the titanium foil backing by extended sonication. Sonication was applied to the prepared samples in water for 50 min with a Fischer Scientific FS30 sonicator. After sonication titanium foils were removed from the nanotube suspension. The suspension was then dried on a hot plate and the resulting nanotube powder was removed from the container and weighed. To determine the surface area of the nanotubes a Quantachrome Instruments Autosorb-1 was used with the dry nanotubes. For storage, nanotubes were resuspended at 1mg/mL in methanol. Deposition of nanotubes onto substrates was conducted by two methods: 1) electrophoretic deposition (EPD), and 2) dropcasting. For optical characterization, films were cast onto fluorine-doped tin oxide conductive glass electrodes (OTE). Photoelectrochemical tests of deposited nanotubes used titanium foils, heat treated at 450\(^\circ\)C due to coloration, as substrates. For EPD, solutions of acetonitrile/methanol, at a 4/1 ratio and in an electric field of 125V/cm, deposited nanotubes onto the positive electrode. Dropcast films were deposited to a concentration of 0.5mg/cm\(^2\), similar to the weight calculated for as formed nanotubes.

4.2.3 Sensitization of CdS

As in Chapter 3 TiO\(_2\) films were sensitized with CdS using the Successive Ion Layer Absorption and Reaction (SILAR) technique. Nanotube films were immersed in
0.1M CdSO₄ for 5min then rinsed to expel excess Cd²⁺ ions, then immersed in 0.1M Na₂S for 5min, rinsed again; the cycle was repeated eight times. CdS was used as formed without annealing.

4.2.4 Characterization

Photoelectrochemical tests of nanotube films on heat treated titanium foils used a Keithley 2601 source-meter unit. The light source was a 150W Xenon lamp with an aqueous CuSO₄ 310nm cutoff filter to remove harmful UV radiation. Samples were positioned at 100mW/cm² in a 3-armed glass electrochemical cell. Platinum gauze was the counter electrode in the two-electrode, 0.1M Na₂S system. The third arm of the cell was sealed, and the entire system was purged of oxygen by bubbling nitrogen for ten minutes before testing. SEM images were obtained from a Hitachi S-4500 FESEM.

Transient absorption tests of films on OTE were conducted with an ultrafast transient absorption laser set-up described in Chapter 1. Briefly the sample was excited with 150fs pulses of 387nm light chopped to allow five pulses through and five blocked. White light pulses probe the absorption of the sample at known times after excitation and without excitation.

4.3 Performance and Properties of Removed Nanotubes

4.3.1 Removal of Etched TiO₂ Nanotubes

Anodically etched TiO₂ nanotubes were sonicated in water for an extended (>10min) time. The length of time in sonication was found to have a significant impact on the dispersal of nanotubes in solution, determined from SEM imaging of recast films. Initially nanotubes are separated from the surface of the titanium foil in aligned sections.
Through further sonication these sections disperse into individual nanotubes. Figure 4.1 demonstrates the differences between nanotubes prior to disassembly, and nanotubes which have undergone 50min of sonication and have been dropcast onto carbon paper. Both sets of nanotubes have diameters of ~80nm, though the lengths of the separated nanotubes have been reduced from 10µm to ~1µm.
Figure 4.1 Schematic of (A) aligned TiO$_2$ nanotube array and (B) randomly oriented nanotubes. SEM images of (C) as formed aligned nanotubes and (D) nanotubes deposited onto carbon paper.
The titanium foils removed from the sonication bath were imaged to determine what remained on the surface. Two regions were seen to dominate the surface. Figure 4.2 shows an SEM image and a schematic of the surface demonstrating smooth TiO$_2$ areas and deposits of TiO$_2$ in shapes resembling circles of similar diameter to the removed nanotubes. These ring deposits are only slightly above the surface and are assumed to be the base of the original nanotubes. The smooth region is likely the barrier layer of TiO$_2$ formed between the nanotubes and the titanium metal. The foils were etched a second time in the same fashion as the initial etching procedure and imaged again. Two surface regions were observed again. A smooth region was present as well as areas of fully formed nanotubes. The “footprints” left over from sonication therefore acted as templates for further etching while the barrier layer disallowed formation of nanotubes. The shape of the footprints is hypothesized to allow the applied electric field to form on the surface much like in the original etching procedure giving way to etching of nanotubes into the foil. The smooth barrier layer does not result in an electric field conducive to nanotube formation and most likely etches uniformly into the foil. By this effect it is possible to recycle the titanium foil and obtain a higher yield of product (removed nanotubes) than with a single etching step.
Figure 4.2 Schematics of films (A) after sonication and (B) after re-etching the foil. SEM images of (C) sonicated foils and (D) re-etched films corresponding to the cartoons.
By removing the nanotubes characterization can be applied independent of the titanium foil. BET surface area analysis was conducted on dry TiO\textsubscript{2} nanotube powder. Previous reports estimated the surface area of etched TiO\textsubscript{2} nanotubes to be 285 m\textsuperscript{2}/g.\textsuperscript{216} The presence of the titanium foil prohibits an accurate determination of nanotube mass yielding an estimate with a high amount of error. The sonication and drying technique yields a powder of nanotubes which is what most BET apparatuses are designed to test. Through the procedure described in this chapter ~0.3 mg/cm\textsuperscript{2} of nanotubes were obtained from the initial etching step. Analysis determined that anodically etched TiO\textsubscript{2} nanotubes have a surface area of 77.0 ± 2.9 m\textsuperscript{2}/g. Assuming a smooth cylindrical wall, 8 µm length, 100 nm outer diameter, and a 15 nm wall thickness one can calculate the surface area to be 34 m\textsuperscript{2}/g. This indicates that there is extra surface area due to roughness though not as much as previously believed.

4.3.2 Redeposition and Photoelectrochemical Characterization

TiO\textsubscript{2} nanotubes were deposited through two common procedures for depositing particles onto a substrate: 1) electrophoretic deposition (EPD) and 2) dropcasting. EPD was determined to be cumbersome due to nanotubes falling out of solution and their low mobility. To deposit a sample the electric field could only be applied for a limited time (30-60s) before the solution needed to be stirred and resuspended. This cycling, on-off, had to be repeated several times to deposit the entire contents of a solution. Surface hydroxyl groups on the TiO\textsubscript{2} provide a negative charge giving rise to electrophoretic mobility. No preferential alignment was observed upon SEM imaging.

The dropcast method worked well to create homogenous films. A volume of 20 µL/cm\textsuperscript{2} or less was required per drop to obtain the even films; otherwise nanotubes
would aggregate in solution. Films were air dried and annealed at 400°C to sinter the TiO₂ nanotubes. Photoelectrochemical tests of the two methods compared performance and no significant difference was determined, also both methods yielded equally homogenous films. Because of the ease of deposition dropcasting was the preferred method by which to deposit nanotubes.

4.3.3 Electron Transfer Properties from CdS to TiO₂ Nanotubes

TiO₂ nanotubes deposited onto OTE were sensitized with CdS by the SILAR process. To compare to pure CdS, OTE electrodes had colloidal CdS dropcast onto them; blank OTE do not provide a significant amount of surface area for SILAR to yield detectable absorbances.

Absorption spectra of TiO₂/CdS and CdS films are shown in Figure 4.3. The absorption onset for both samples occurs at 520nm indicating a CdS bandgap of 2.4eV for both films. In Figure 4.4 pristine and sensitized TiO₂ nanotubes are imaged with the TiO₂/CdS films coated evenly with aggregates ~10nm in diameter.
Figure 4.3 Absorption spectra of (A) CdS particles on deposited on a clear electrode and (B) CdS SILAR particles on deposited TiO₂ nanotubes.
Figure 4.4 SEM images of (A) deposited TiO$_2$ nanotubes and (B) deposited TiO$_2$ nanotubes sensitized via SILAR with CdS, eight cycles.
Transient absorption spectroscopy was used to determine the electron transfer rate between CdS and TiO₂ nanotubes. Films of CdS, with and without TiO₂ nanotubes, were excited with laser pulses with wavelengths of 387nm. Due to oxidation of metal chalcogenide materials under UV excitation in air all transient absorption experiments were performed under a vacuum.²¹⁷ CdS demonstrates a bleaching event between 480-540nm of the visible spectrum, Figure 4.5. The broad bleaching peak is due to the non-uniformity of CdS crystals. As time progresses after excitation, the bleaching recovery is assumed to be due to electron-hole recombination within the CdS crystals, Equation 4.1.

\[
CdS + h\nu \rightarrow CdS(h^+ + e^-) \rightarrow CdS \tag{4.1}
\]

\[
CdS(h^+ + e^-) + TiO_2 \rightarrow CdS(h^+) + TiO_2(e^-) \tag{4.2}
\]

The addition of TiO₂ nanotubes to the film provides another pathway for excited electrons, Equation 4.2, and therefore the bleaching recovery is faster. Figure 4.5C follows the change in absorption at the bleaching peak over time and compares the CdS film to TiO₂/CdS. The multi-exponential decay was fitted to determine recovery lifetimes, Equation 4.3:

\[
y = y_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \tag{4.3}
\]

Where \( y \) is the signal \( y_0 \), \( A_1 \), and \( A_2 \) are fitting parameters, and \( \tau_1 \) and \( \tau_2 \) are fitted lifetimes. Table 4.1 tabulates the fitted parameters.
Figure 4.5 Transient absorption spectra of (A) CdS nanoparticles on an OTE substrate and (B) CdS nanoparticles and TiO$_2$ nanotubes on an OTE substrate. (C) Peak bleaching decay versus time. All graphs are normalized to peak $\Delta A$ for each sample.
TABLE 4.1

TRANSIENT ABSORPTION BI-EXPONENTIAL FITTING PARAMETERS

Bi-exponential kinetic fits for traces from Figure 4.5C of ultrafast bleaching for CdS and CdS+TiO\textsubscript{2} systems.

<table>
<thead>
<tr>
<th></th>
<th>CdS</th>
<th>CdS+TiO\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(y_0)</td>
<td>-0.15</td>
<td>-0.062</td>
</tr>
<tr>
<td>(A_1)</td>
<td>-0.54</td>
<td>-0.67</td>
</tr>
<tr>
<td>(\tau_1) (ps)</td>
<td>7.3</td>
<td>2.9</td>
</tr>
<tr>
<td>(A_2)</td>
<td>-0.40</td>
<td>-0.44</td>
</tr>
<tr>
<td>(\tau_2) (ps)</td>
<td>81.5</td>
<td>31.5</td>
</tr>
</tbody>
</table>
As electron transfer to TiO$_2$ nanotubes is considered to be the primary cause for the faster bleaching recovery electron transfer rates can be calculated from the fitted lifetimes, Equation 4.4:

$$k_{ET} = \frac{1}{\tau_{TiO_2-CdS}} - \frac{1}{\tau_{CdS}}$$  \hspace{1cm} (4.4)

Upper and lower limits are given by determining electron transfer rates with fast and slow recovery lifetimes ($\tau_1$ and $\tau_2$). Rates of $2.0 \times 10^{10}$ s$^{-1}$ and $2.1 \times 10^{11}$ s$^{-1}$ were determined indicating the ultrafast charge injection. For comparison MPA linked CdSe quantum dots transfer electrons to TiO$_2$ on the order of $10^7$ to $10^{10}$ s$^{-1}$.\textsuperscript{159}

4.3.4 Photoelectrochemical Comparison

To determine the performance loss associated with changing the TiO$_2$ nanotube substrate from aligned to random photocurrents were measured between as formed TiO$_2$ nanotubes and TiO$_2$ nanotubes deposited on heat treated titanium foils. Both films were tested with and without CdS; random films contained the same weight of TiO$_2$ as calculated for the aligned films.

Photocurrent action spectra (IPCE) of aligned and random nanotube systems are shown in Figure 4.6A. Both films demonstrate a photocurrent onset at 550nm, matching their absorption spectra (Figure 4.3). By randomizing the orientation of TiO$_2$ nanotubes for a CdS substrate the IPCE shows little loss in photocurrent. Upon illumination with white light, Figure 4.6B, photocurrents are seen to be less in the randomized substrate for both sensitized and bare TiO$_2$ nanotubes. The initial spike in photocurrent when the light is turned on is due to the redox species reacting at the surface of the working electrode, the current spike decays according to the Cottrell equation.\textsuperscript{146} After attaining steady state photocurrent levels the aligned system with CdS showed 1mA/cm$^2$ whereas randomized
nanotubes produced 0.8mA/cm². Without CdS sensitization aligned nanotubes produced four times the photocurrent as random nanotubes. After sensitization the rise in photocurrent is the same for both alignments indicating charges are transported through both random and aligned systems equally.

Open circuit potentials (V_{OC}) in the random nanotube film were found to decay faster than in the aligned array, Figure 4.7. The faster decay demonstrates a greater rate of scavenging by the electrolyte as described by the electron lifetime determination of open circuit potential decay process described in Chapter 1.

It is clear that the random orientation induces faster electron back-transfer. The faster electron lifetime of the deposited tubes arises for two reasons. First there is no barrier layer on bare titanium foil. TiO₂ barrier layers are known to reduce electron backtransfer from conductive substrates.²¹⁸ The second reason for faster kinetics is that the random orientation has higher porosity causing the electrolyte to be in more intimate contact with the film creating fewer mass transfer limitations. The changes in mass transfer limitations account for the initial spike of the photocurrent and the slow rise to equilibrium for the aligned array’s photocurrent. Increased electron back transfer accounts for the reduction in photocurrent; this can be overcome by applying a thin TiO₂ compact layer to the surface of the titanium foil if needed. Overall, the randomization of the TiO₂ nanotube substrate does not significantly impair the performance of the cell.
Figure 4.6 IPCE spectra (A) comparing aligned and randomly oriented TiO$_2$ nanotubes sensitized with CdS. (B) Photocurrent over time, with light on and off, of aligned and random systems, both with and without CdS.
Figure 4.7 (A) Open circuit potential measured as the light is turned on and off. After light is turned off (B) electron lifetimes are plotted versus $V_{OC}$ determined from the $V_{OC}$ decay rate.
4.4 Summary

Etched TiO$_2$ nanotubes were removed from the titanium backing by sonication. Titanium foils were found to be able to re-etch after the initial nanotubes had been removed providing a footprint of the original structure remained. In powder form etched nanotubes are able to provide a more accurate BET surface area analysis and in solution electron transfer properties from CdS, deposited by SILAR, could be determined. Photoelectrochemical experiments determined the alignment of nanotubes does not play a factor in transporting electrons, but increased electron back-transfer lowers photocurrents. By removing etched TiO$_2$ nanotubes various new applications can be devised through new experiments and new substrates.
CHAPTER 5:
COUNTER ELECTRODE-ELECTROLYTE INTERFACE

5.1 Counter Electrode and Electrolyte Bottlenecks

Oxidized species of redox couples are commonly added to electrolytes to rid the system of diffusion limitations between the working electrode (WE) and the counter electrode (CE). In the case of the iodide redox couple (I/I₃⁻), iodine is added to a lithium iodide solution to make I₃⁻. Dye sensitized solar cells (DSC) are able to perform closer to an ideal cell, larger fill factors (FF), than quantum dot solar cells (QDSC) because of two reasons: 1) the iodide redox couple is very active with platinum, and 2) back electron transfer from the WE to the redox couple is limited. The low back electron transfer rate stems from the formation of I₃⁻ from the intermediates I⁻ I₂⁻, Equation 5.1. The intermediates react to form I₃⁻ quickly, especially in an acetonitrile solvent, and I₃⁻ is a poor scavenger of electrons, except on an active surface like platinum where it becomes very reactive. However, due to iodide’s oxidative properties on quantum dots the iodide couple cannot be used in QDSC. The polysulfide redox couple (S²⁻/Sₙ²⁻) does have an intermediate like the iodide couple, Equations 5.2-4, but unlike I₃⁻, Sₙ²⁻ is also responsible for increased electron scavenging from working electrodes.⁹³

\[ I^- + I_2^- \leftrightarrow I_3^- \]  \hspace{1cm} (5.1)

\[ CdSe(h^+) + S^{2-} \rightarrow CdSe + S^- \]  \hspace{1cm} (5.2)
\[ S_{n}^{2-} + e^- \leftrightarrow S_{n}^{2-} + S^- \]  \hspace{1cm} (5.3)

\[ S^- + TiO_2(e^-) \rightarrow S^{2-} + TiO_2 \]  \hspace{1cm} (5.4)

Despite the many intermediates which are able to scavenge electrons from the working electrode the redox couple remains fixed with \( S^{2-}/S_{n}^{2-} \) for stability purposes. This causes researchers to look elsewhere to improve cell performances.

Since the initial development of the semiconductor sensitized solar cell, both before and after the advent of quantum dots, the vast majority of research energy has been directed at the WE. Short-circuit currents (\( I_{SC} \)) of QDSC have been improved to more than 12mA/cm\(^2\) under one sun of irradiation (AM 1.5), which is greater than half the photocurrent commonly observed in dye-sensitized solar cells\(^{93,208-209} \). Power conversion efficiencies have, however, remained low (~3%) due to lower FF. The FF of dye sensitized cells is commonly above 80\% whereas with QDSC the highest FF is around 60\%.\(^{93} \) In terms of efficiency FF has just as much impact as \( I_{SC} \) or open-circuit potential (\( V_{OC} \)). Because the goal is to produce power, efficiency is related to FF by Equation 5.5:

\[ \eta = \frac{P_{\text{max}}}{P_{\text{inc}}} = \frac{FF \cdot I_{SC} \cdot V_{OC}}{P_{\text{inc}}} \]  \hspace{1cm} (5.5)

Where \( \eta \) is the power conversion efficiency, \( P_{\text{max}} \) is the maximum power generated, and \( P_{\text{inc}} \) is the incident power, FF is therefore proportional to overall efficiency, and an extremely important characteristic.

Resistances and overpotentials are the most common causes of low FF\(^{93,219-220} \). Series resistance is commonly found in the underlying conductive glass layers, typically
8-15Ω/□. Resistances in electrolytes are minimal due to the high concentrations of electrolytes, and metal oxide layer resistances are dictated by the amount of trap sites, as discussed earlier. In all, overall series resistance is on the order of 100Ω. A large portion of which is charge transfer resistances, or overpotentials, at the electrode-electrolyte interface.

The development of nanoporous films with high surface areas, as well as surface modifications, helps to overcome overpotentials at the WE. However, the CE material of choice remains platinum, which has been shown to rapidly create a surface layer of chemisorbed sulfide in the common polysulfide electrolyte of the QDSC. This sulfide layer is the primary overpotential barrier observed in the system and limits electron transfer at the counter electrode. Figure 5.1 shows I-V characteristics of a QDSC in a two-electrode system and three-electrode configuration. In the three-electrode system, potentials are measured between the WE and the reference electrode with current passing between the WE and CE. In a two-electrode system, the CE is the reference and the energy (potential) of the electrons in the current are directly measured. With a platinum CE it is common to find extremely low FF (<20%) because of the overpotential.
Figure 5.1 Current-Voltage characteristics of CdS/TiO₂ working electrodes with platinum as a counter electrode in (A) a two-electrode assembly, and (B) a three-electrode assembly.
The sulfide layer on the surface of platinum has been studied from the beginning of liquid-junction solar cell research; once it was determined that QDSC needed a polysulfide redox couple. The mostly standard electrolyte, 1M Na$_2$S, 1M S, and 0.1M NaOH, is often used by the research community for several reasons.$^{222-223}$ S$_2^-$ (from Na$_2$S) is the reduced species of the polysulfide redox couple, responsible for scavenging holes from the surface of the quantum dots without degrading the quantum dots.$^{121}$ As stated above, sulfur is added to the system because it reacts with sulfide to create the polysulfide species (the oxidized species) to reduce mass-transfer limitations at the CE, Equation 5.6. NaOH is added to assist in long-term stability of CdSe.$^{222,224}$

$$S^{2-} + S_n \rightarrow S_{n+1}^{2-} \quad (5.6)$$

To overcome inherent overpotentials due to platinum-sulfide layers, alternatives to platinum at the counter electrode have been studied.$^{93,103,225}$ After the realization that most metals react with sulfur to create a metal-sulfide surface, conductive metal-sulfide materials were investigated for use as alternative CE.$^{123}$ These studies showed promise for materials like Cu$_2$S and CoS, but failed to directly compare which perform the best in a QDSC. Hodes et al. reported that Cu$_2$S is an extremely capable CE, but it suffers from stability issues.$^{226}$ The common problem is that Cu$_2$S flakes off surfaces, and can deposit onto the surface of CdSe. CoS films also showed similar instability. Recently, however, the Bisquert group has used brass reacted with polysulfide solutions (on the suggestion of the 1980 Hodes study) as a counter electrode, and their fill factors have improved in a two-electrode system to over 0.6.$^{208}$
This chapter looks into the effect the standard electrolyte has on the system in an effort to investigate the interactions focusing primarily on the counter electrode. It also examines alternatives to the platinum counter electrode and quantitatively compares their performances electrochemically and photoelectrochemically.

5.2 Experimental Techniques

5.2.1 CdSe SILAR Synthesis

WEs were sensitized with CdSe SILAR on TiO₂ and passivated with ZnS. TiO₂ films were formed by immersing a 0.9×5 cm² fluorine-doped tin oxide optically transparent electrode (OTE) into a 40mM aqueous solution of TiCl₄ at 70°C for 30min. This creates a thin “compact layer” of TiO₂ on the surface of the OTE. A transparent layer of Solaronix Ti-Nanoxide T/SP TiO₂ paste was applied on top of the “compact layer” by the “doctor-blading” method and the film was annealed at 450°C for 1h. A scattering layer of DyeSol 18NR-AO paste was doctor-bladed on top of the annealed film and the resulting film was annealed again at 450°C for 1h. To interconnect the various layers of the films, electrodes were soaked in a 40mM TiCl₄ solution at 70°C for 30min and annealed a third time at 450°C for 1h.

To sensitize the TiO₂ film, CdSe was deposited by the SILAR process. CdSe SILAR was developed by the Grätzel group with a 30mM Cd(NO₃)₂ solution in ethanol as the Cd precursor. The Se precursor was made by dissolving SeO₂ in ethanol under an N₂ atmosphere. After dissolution, NaBH₄ was added to reduce Se from a 4+ oxidation state to 2-. The Se and Cd precursors were stored in a glovebox under N₂ atmosphere for
SILAR deposition. Films were sensitized in a glovebox with 6 cycles of CdSe SILAR. The electrodes were washed with ethanol and dried following each immersion step.

Once CdSe SILAR films were deposited, samples were capped with three SILAR layers of ZnS as a protective coating to prevent CdSe from converting to CdS. The Zn precursor solution was aqueous 50mM zinc acetate and the sulfide precursor was aqueous 50mM Na₂S. This process was conducted in air with 5min immersion steps.

5.2.2 Salt Bridge Isolation

To accurately assess the electrolyte interactions with CE a salt bridge was employed to separate the WE and CE environments physically while retaining electrical contact, as shown in Figure 5.2. The salt bridge was constructed with 0.5wt% agar in a 3M KCl solution. The salt bridge filled the base of a glass tube. After solidifying, an electrolyte solution and a CE could be placed above the salt bridge. This assembly could be inserted into the electrochemical cell with a WE and electrolyte. The WE for the salt-bridge tests used CdS SILAR (10 cycles) on DyeSol 18NR-T TiO₂ paste.
Figure 5.2 Assembly of the salt bridge apparatus with (green) 3M KCl salt bridge separating the counter and working electrode environments.
5.2.3 Alternative Counter Electrode Synthesis

Cu$_2$S, PbS, and CoS nanoparticle films were deposited on OTE at 0.25mg/cm$^2$ to create alternative CEs. Cu$_2$S nanoparticles were formed by sonicating a 70% Cu, 30% Zn brass foil in an aqueous solution of 1M Na$_2$S and 1M S. In a polysulfide solution copper spontaneously forms a black thin film of Cu$_2$S on the surface of the brass. Sonication removes the Cu$_2$S formed on the surface of the brass and then exposes new brass surfaces for further reaction with polysulfide. After sonication for 1h the brass foil is removed, the solution is centrifuged and the supernatant is discarded. De-ionized water was used to resuspend the Cu$_2$S particles and the solution was centrifuged again. This washing procedure was repeated three times to remove residual polysulfide from the suspension. The resulting nanoparticles were dried in a vacuum, weighed and stored at 10mg/mL in ethanol.

CoS and PbS nanoparticles were prepared by mixing aqueous solutions of CoCl$_2$ and Pb(NO$_3$)$_2$ respectively with aqueous solutions of Na$_2$S. The resulting precipitates were washed three times and dried in a vacuum oven. After being dried and weighed, CoS was stored at 10mg/mL and PbS was stored at 5mg/mL, both in ethanol. The counter electrode for salt-bridge testing was a platinum gauze electrode. For the tests comparing counter electrodes, nanoparticles were dropcast to a film concentration of 0.25mg/cm$^2$ for Cu$_2$S, CoS, and PbS onto OTE. Pt OTEs were “platinized” by spreading H$_2$PtCl$_6$ (8wt% in H$_2$O) over the OTE and heating to 450°C for 30min.

5.2.4 Photoelectrochemistry

Cells were tested in either salt bridge assemblies or open assemblies (no salt bridge). WEs were illuminated in a backside alignment where the light travelled through
the OTE and contacted the bottom side of the film first. All measurements were conducted with an incident power of 100mW/cm² filtered to AM 1.5 from a 150W Xe lamp. The photoelectrochemical scans were made with a Princeton Applied Research PARSTAT 2263 potentiostat.

5.2.5 Electrochemical Activity Testing

The electrochemical behavior of the various CE materials was established in a three electrode arrangement with a platinum foil as a CE, an SCE reference electrode, and a Pt disc electrode (1mm radius) for WE. Metal sulfide suspensions were dropcast onto the surface of the Pt disc (0.25mg/cm²). All cyclic voltammograms were recorded at a scan rate of 100mV/s.

5.3 Charge Transfer at the Counter Electrode/Electrolyte Interface

5.3.1 Influence of Polysulfide on the QDSC Performance

Figure 5.3A shows the changes to an I-V scan with increasing concentration of polysulfide. Because the exact concentration of polysulfide is difficult to determine because of the existence of various polysulfide species, the concentrations are described in terms of dissolved sulfur. With increases in polysulfide concentration a decrease in FF, $I_{SC}$, and $V_{OC}$ is observed.

The positive change of $V_{OC}$ is expected due to the Nernstian potential shift with increased polysulfide concentration as dictated by Equation 5.7:

$$E = E^\circ + \frac{RT}{nF} \ln \left( \frac{[S_n^{2-}]}{[S_2^{2-}]} \right)$$  (5.7)
Where $E^{\circ'}$ is the formal potential for the sulfide couple, $R$ is the gas constant, $T$ is the absolute temperature, $n$ is the number of electrons in the reaction, and $F$ is Faraday’s constant. Thus, as the concentration of $S_n^{2-}$ increases the redox potential becomes more positive.

At higher polysulfide concentrations photocurrent would be expected to rise due to the reduction of mass transfer limitations. Instead, a decrease in photocurrent is observed with increasing polysulfide concentrations. This behavior indicates that an additional inhibiting pathway is more pronounced than overcoming mass transfer limitations. The most likely pathway is back-transfer to the electrolyte as described by Equation 5.4. As the back transfer of photogenerated electrons to the redox couple is the dominant additional pathway it should be possible to monitor this process by following electron lifetimes using $V_{OC}$ decay measurements. Figure 5.3B shows the effective electron lifetime ($\tau_n$) vs. $V_{OC}$ as calculated using the process described in Chapter 1.
Figure 5.3 CdS working electrodes tested in an open system (no salt bridge) with a platinum counter electrode at various concentrations of dissolved sulfur, (A) current-voltage characteristics and (B) electron lifetimes determined from $V_{OC}$ decay rates.
At the initial moment after the light is turned off and $V_{OC}$ starts to decay lifetimes become reduced from ~2s to 0.1s when the concentration of sulfur is increased from 0M to 0.2M. The faster electron lifetimes with increasing concentration of sulfur is observed for the duration of decay to the ground state. The shape of each curve in Figure 5.3B is the same, indicating that the electronic states in the TiO$_2$ layer of the WE are unchanged by the electrolyte. The reduction of $\tau_n$ therefore indicates that $S_{n}^{2-}$ does significantly scavenge electrons from the WE because the electron lifetimes are reduced by more than an order of magnitude.

5.3.2 Salt Bridge Isolation

To investigate the role of redox couples at specific electrodes rather than the system as a whole, a salt bridge was introduced to physically isolate the WE and CE environments while retaining electrical connectivity. This allows electrolytes to be changed in one half of the cell without disturbing the other.

Platinum activity was measured with and without excess polysulfide; the results are shown in Figure 5.4. In the I-V scan it is seen that $I_{SC}$ increases with increasing concentration of polysulfide. $I_{SC}$ of the 0M system was -1.4mA/cm$^2$ whereas with 0.1M sulfur added to the counter electrode environment $I_{SC}$ was -2.4mA/cm$^2$. Additionally, when the system is changed to the iodide redox couple a similar trend is observed with photocurrents increasing from -1.0mA/cm$^2$ to -3.7mA/cm$^2$ (at -0.5V) when the oxidized species of the redox couple ($I_3^-$) is introduced. The polysulfide system, at a concentration of 0.1M sulfur, nearly doubles the photocurrent, while the iodide system demonstrates a fourfold increase with a concentration of 0.04M $I_2$. This increase in photocurrent shows how in the liquid junction solar cell charge transfer dynamics at the counter electrode, as
well as mass transfer limitations, greatly dictate the overall performance of the cell. It should be noted that in Figure 5.4 that the $V_{OC}$ of the polysulfide and iodide systems are shifted due to the redox potential difference between them.

Electron lifetimes were also determined for the QDSC containing a salt bridge. Figure 5.4B demonstrates electron lifetimes when maintaining the same redox couple in the WE compartment at 0.1M Na$_2$S, while varying the redox couple in the counter electrode compartment. It is observed that the only difference between the different CE systems is the potential at which the traces in Figure 5.4B fall. The shapes and the position on the lifetime axis are all identical, indicating that the lifetime of electrons in the WE is unperturbed by the variation of redox couples in the CE compartment.
Figure 5.4 Photoelectrochemical characteristics, (A) current-voltage traces, and (B) electron lifetimes from $V_{OC}$ decay of CdS working electrodes with a salt bridge isolating the counter electrode. The electrolyte around the counter electrode is changed while the working electrode electrolyte is fixed at 0.1M Na$_2$S.
5.3.3 Alternative Counter Electrodes

To overcome the limitations of platinum overpotentials, Cu₂S, CoS, and PbS were chosen as possibilities due to their reactivity in sulfide media and semiconducting properties. Others have reported on these metal sulfide electrodes in the past, but a direct comparison of their activity has yet to be performed.\textsuperscript{103,123,221,225,227} Figure 5.6 shows cyclic voltammograms (CV) of a platinum disc electrode (1mm radius) with and without the sulfides dropcast onto its surface. Each curve is the fifth cycle in the CV, and the electrolyte was 0.1M Na₂S, corresponding with the findings of the previous section. Recording the fifth cycle ensured reproducible CV performance. All potentials are vs. SCE. Currents with metal-sulfides deposited on the surface of the platinum disc electrode are all at least one order of magnitude greater than the bare platinum electrode. This implies that the turnover of species at the surface of metal-sulfides is much greater than on platinum. The peaks around -1V vs. SCE and -0.2V vs. SCE are attributed to the sulfide layer formation and removal, respectively. Peaks observed in between these two have been attributed to polysulfide species shrinking in length as determined by Allen and Hickling.\textsuperscript{221} The polysulfide peaks are not found on platinum unless there is a high concentration of polysulfide in the bulk solution. The metal-sulfide species can exhibit these peaks in sulfide solutions without excess polysulfide present thus indicating their ability to easily perform redox processes. In a QDSC with a $S^{2-}/Sn^{2-}$ redox couple a CE must be able to perform redox chemistry efficiently. The poisoning of platinum and its low activity in sulfide media, seen in Figure 5.6, demonstrates that it is a poor choice for a CE in a QDSC.
Figure 5.5 Cyclic voltammograms of counter electrode materials, (A) platinum, (B) CoS, (C) Cu$_2$S, and (D) PbS in 10mM Na$_2$S. The working electrode was a platinum disc electrode (1mm radius), reference electrode was SCE, and counter electrode was a platinum flag with a sweep rate of 100mV/s. CoS, Cu$_2$S, and PbS were dropcast onto the disc. The platinum sample was the disc electrode. Sweeps depicted are the fifth of repeated cycles.
CEs were photoelectrochemically tested in two-electrode cell without a salt bridge (open system) with 0.1M Na$_2$S as the electrolyte, and CdSe capped with ZnS on TiO$_2$ as the WE. I-V comparisons were made between a platinized OTE and OTE with the nanoparticulate metal sulfides dropcast onto the surface at 0.25mg/cm$^2$. After illumination for 4 cycles at 25mV/s, Figure 5.7 shows the I-V curves corresponding to each CE material, and Table 5.1 gives the $V_{OC}$, $I_{SC}$, FF, and efficiencies. Recording of the fourth cycle was chosen because the systems had come to equilibrium at this point. A scan rate of 25mV/s was selected to limit the surface capacitance formation which can cover the peaks from the sulfide layer formation and removal. Cu$_2$S and CoS are seen to have the highest FF (0.34 and 0.27) and $I_{SC}$ (4.17 and 4.24mA/cm$^2$ respectively). PbS and platinized OTE yield significantly lower performances with FF of 0.21 and 0.15 respectively, and $I_{SC}$ of 1.48 and 1.09mA/cm$^2$ respectively. PbS has been shown previously to degrade in polysulfide media,\textsuperscript{228} and after the 4 cycles it was not as active compared to the initial scans. When the I-V scans are compared to the CVs of Figure 5.6, it can be seen that an effective counter electrode needs to be responsive with polysulfide species, but also have high currents with the oxidation and reduction of the sulfide surface layer. PbS demonstrated the best ability to undergo charge transfer with polysulfide as observed by the CV peak at -0.4V vs SCE in Figure 5.6, but the removal of the sulfide film, represented by the peak at -0.2V vs. SCE, was diminished. The low response to removing the sulfide film corresponds to low solar cell performance when employed as a counter electrode. Platinum’s lack of activity as seen by low currents in Figure 5.6 hindered its performance whereas Cu$_2$S and CoS showed relatively high activity in all regions of the CV. The slightly larger FF for Cu$_2$S is likely to stem from the
nanostructure of the particles. SEM images in Figure 5.8 show that CoS is composed entirely of small particles (~5nm) forming a film on the OTE surface whereas Cu$_2$S is composed of small particles (~10nm) and larger directionalized crystals (~1µm) that may play a role in increased charge transfer through the film, as described in Chapters 3 and 4. The directionality of the Cu$_2$S particles is promising for future works looking to enhance charge transfer within the counter electrode. The small particles of CoS likely contribute to the stability of films observed compared to Cu$_2$S which commonly detached if washed.
Figure 5.6 Current-voltage characteristics of a CdSe/ZnS sensitized working electrode with various materials for counter electrode. The cell was an open system (no salt bridge) with 0.1M Na$_2$S as the electrolyte.
TABLE 5.1

METAL-SULFIDE I-V CHARACTERISTIC PROPERTIES

Metal-sulfide counter electrodes and their I-V characteristic properties corresponding to Figure 5.7.

<table>
<thead>
<tr>
<th>Counter Electrode Material</th>
<th>$V_{oc}$ (V)</th>
<th>$I_{sc}$ (mA/cm$^2$)</th>
<th>FF</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>-0.45</td>
<td>1.09</td>
<td>0.15</td>
<td>0.07</td>
</tr>
<tr>
<td>Pb</td>
<td>-0.48</td>
<td>1.48</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td>Cu</td>
<td>-0.40</td>
<td>4.17</td>
<td>0.34</td>
<td>0.56</td>
</tr>
<tr>
<td>Co</td>
<td>-0.41</td>
<td>4.24</td>
<td>0.27</td>
<td>0.48</td>
</tr>
</tbody>
</table>
Figure 5.7 SEM images of counter electrode materials on OTE, platinized platinum, CoS, CuS, and PbS.
5.4 Summary

The working and counter electrode interactions with redox couples and their influence on the performance of QDSC were investigated. It was found that polysulfide species in the electrolyte scavenge photogenerated electrons from the working electrode and offset any beneficial effects at the counter electrode. As an alternative to platinum, PbS, Cu$_2$S and CoS were considered as counter electrodes and their electrochemical performance was compared in a QDSC arrangement. It was found that Cu$_2$S and CoS exhibit better electrochemical activity towards the S$^{2-}$/S$_n^{2-}$ redox couple.
CHAPTER 6:
CONCLUSIONS AND OUTLOOK

Charge carrier dynamics within quantum dot solar cells (QDSC) were enhanced by developing new sensitization procedures, utilizing nanoarchitectures and by using new materials. Quantum dot sensitizers linked with mercaptopropionic acid (MPA) showed deep-trap emission if amines were used in their synthesis. By changing the sensitization method electrons can be directly transferred to a TiO$_2$ layer without becoming trapped on the surface of the quantum dot. Also, by changing the metal oxide layer from nanoparticulate films to aligned one dimensional nanostructures photocurrents are increased due to longer electron diffusion lengths. Even after randomizing the nanotubes the one dimensional CdS/TiO$_2$ films retained high photocurrents. Electrons were seen to be scavenged from CdSe/TiO$_2$ working electrodes by polysulfide species in the redox couple electrolyte. By omitting these oxidized redox species the system yielded lower electron back-transfer and higher power conversion efficiencies. Alternative counter electrode materials were developed to overcome overpotential losses at the traditional platinum-sulfide interface. Cu$_2$S and CoS were found to improve photocurrents and fill factors improving the overall performance of the cell.

The sensitization process for QDSC was chosen to be a bottom-up approach after it was found that linker molecules create trap sites on the surface of colloidal CdSe nanoparticles. Trap sites are created by the thiol group of MPA replacing amine ligands.
on quantum dot surfaces. Amines, such as dodecylamine and hexadecylamine, are commonly used in quantum dot syntheses to slow reactions and increase emission quantum yields. Though it is a common procedure to sensitize TiO$_2$ films, the addition of MPA introduces a loss pathway, as evidenced by increases in deep-trap emission. Deep-traps are known to stem from Se vacancies on the surface of CdSe quantum dots and the introduction of MPA therefore is seen to change the surface environment causing surface Se atoms to oxidize and be removed. The properties of a quantum dot linked to a TiO$_2$ surface are therefore changed after the initial synthesis. Any work performed on quantum dots to increase their performance as sensitizers is possibly hampered by the creation of deep-trap states.

By changing the concentration of MPA and amount of amines on the surface deep-trap emission could be finely controlled. A quantum dot solution, which originally emits with blue light, can be changed to appear red by the addition of MPA as the deep-trap emission overwhelms the band-edge. Several studies are looking to use quantum dot emission as displays. Prior to this chemical control, the only possibility to change emission wavelengths came from changing crystal size during synthesis.

One-dimensional architectures have been shown in the past to provide longer electron diffusion lengths by limiting crystal boundaries. Etched TiO$_2$ nanotubes were used to introduce a one-dimensional structure that was facile to prepare and simple to sensitize. Using the simple SILAR sensitization process to deposit CdS quantum dots, photocurrents were improved over nanoparticulate systems by 20%. The etching process is facile in that it applies a potential across two electrodes, one of which is a titanium foil.
The process is similar to electroplating, and can therefore be easily scaled for manufacturing purposes.

Removing the TiO₂ nanotubes by sonication allows for more flexible substrates to be utilized in photovoltaic applications, once again creating a scalable process for commercializing QDSC. Since the nanotubes were found to have larger surface areas than nanoparticles, and CdS was able to effectively sensitize the entire surface of the nanotubes, inside and out, etched TiO₂ nanotubes have the potential to significantly impact power conversion efficiencies of future QDSC.

Back-electron transfer has been a serious concern in the QDSC field because of polysulfide’s abilities to harvest electrons. Through the development of the salt bridge isolation technique the exact effects of polysulfide at the counter electrode are deemed to be beneficial because diffusion limitations are removed. It was determined that any introduction of polysulfide to the system creates more losses due to scavenging than can be overcome by removal of diffusion limitations at the counter electrode therefore the recommended electrolyte is 0.1M Na₂S.

Because platinum becomes poisoned by sulfides overpotentials in the system are created and significantly hamper performance. To overcome this, new materials for counter electrodes were compared electrochemically. The semiconducting metal-sulfides Cu₂S, CoS, and PbS all showed much higher electrochemical activity in a sulfide medium generating currents an order of magnitude higher than platinum. When incorporated into a photoelectrochemical assembly Cu₂S and CoS translated their increased activity to I-V characteristics, generating higher currents and fill factors. PbS was found to degrade eventually. These materials showed that the counter electrode plays a significant role in
the overall performance of the QDSC and in the near future developments in mechanical
stability should allow these counter electrodes to make the QDSC much more efficient
than today.

The future of the QDSC rests in more efficient electron transfer in the working
electrode, solid state electrolytes, and developing new counter electrodes to further
increase activity. The incorporation of facile nanofabrication techniques and new material
development can be used to increase power conversion efficiencies giving the quantum
dot solar cell a bright future. Currently the QDSC relies on cadmium based quantum dot
technologies. The toxicity of these materials limits their applicability to larger energy
market. New materials like silicon or iron-oxide quantum dots should be investigated
further to create cheaper and safer components. One problem that has plagued the liquid
junction solar cell has been leakage of the electrolyte. Developing a solid electrolyte with
fast electron and hole transfer properties would eliminate this issue and possibly provide
a more flexible cell. The platinum counter electrode as already described will not work
for the QDSC system. From the data presented in this dissertation it should be clear that
new counter electrode materials can greatly enhance performance and need to be further
investigated perhaps incorporating new materials such as graphene and carbon nanotubes
to increase currents. Already the QDSC has the ability to produce a competitively priced
energy harvester per Watt, and it has the potential to make a significant impact in the
future with only minor improvements.
REFERENCES


(11) Green, M. A. *Prog. Photovoltaics* 2009, 17, 183.


(50) *Photocatalysis: science and technology*; Masao Kaneko, I. O., Ed.; Springer, **2002**.


(208) Gonzalez-Pedro, V.; Xu, X. Q.; Mora-Sero, I.; Bisquert, J. ACS Nano 2010, 4, 5783.


