Broad-Spectrum Solution-Processed Photovoltaics

by

Alexander Halley Ip

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Electrical & Computer Engineering
University of Toronto

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Abstract

High global demand for energy coupled with dwindling fossil fuel supply has driven the development of sustainable energy sources such as solar photovoltaics. Emerging solar technologies aim for low-cost, solution-processable materials which would allow wide deployment. Colloidal quantum dots (CQDs) are such a materials system which exhibits the ability to absorb across the entire solar spectrum, including in the infrared where many technologies cannot harvest photons. However, due to their nanocrystalline nature, CQDs are susceptible to surface-associated electronic traps which greatly inhibit performance. In this thesis, surface engineering of CQDs is presented through a combined ligand approach which improves the passivation of surface trap states. A metal halide treatment is found to passivate quantum dot surfaces in solution, while bifunctional organic ligands produce a dense film in solid state. This approach reduced midgap trap states fivefold compared with conventional passivation strategies and led to solar cells with a record certified 7.0% power conversion efficiency. The effect of this process on the electronic structure is studied through photoelectron spectroscopy. It is found that while the halide provides deep trap passivation, the nature of the metal cation on the CQD surface affects the density of band tail states. This effect is explored further through a wide survey of materials, and it is found that the coordination ability of the
metal cation is responsible for the suppression of shallow traps. With this understanding of CQD surface passivation, broad spectral usage is then explored through a study of visible-absorbing organolead halide perovskite materials as well as narrow-bandgap CQD solar cells. Control over growth conditions and modification of electrode interfaces resulted in efficient perovskite devices with effective usages of visible photons. For infrared-absorbing CQDs, it is found that, in addition to providing surface trap passivation, ligands must be used to prevent nanocrystal fusion that leads to introduction of band tail states. The most efficient solution-processed infrared solar cells yet reported are achieved through this approach, opening a path towards low-cost photovoltaics with high spectral usage.
Acknowledgments

This thesis is the culmination of five years of research and also a longer journey which I have been fortunate to share with many people that have helped me to get to this point.

I give my sincere thanks to my supervisor, Prof. Ted Sargent, for providing me with the opportunity to work in his group, the means to accomplish my research, and the mentorship and guidance to grow professionally. I also thank all the other professors that have taught my courses, spent time on my committees, and collaborated on projects.

I have been fortunate to work with a large number of fantastic people through the years, and although I won’t be able to name all of them here, I am glad to have shared this experience with them. In particular, the students who were with me almost from the beginning through to the end, André, Lisa, Graham, and David, it has been a crazy ride. Also the senior students who finished before me, when I wondered if I would ever get to this point, Kyle, Ghada, and Illan. Many thanks to Susanna, who helped a great deal early in my PhD studies, and all the other postdocs including Ning, Jiang, Michael, Jeff, and Mingjian. Thanks and best of luck to the students that are in the midst of their research, including Amirreza, Brandon, Bruce, Valerio, and all the rest. Thanks for all the guidance from the senior researchers, Sasha, Sjoerd, Armin, and Larissa. And thanks to all the unsung heroes that keep the lab running, Damir, Remi, Leny, and Jeannie. Again, I cannot name everyone, but I am grateful for contributions from everyone that I had the chance to meet, discuss with and work alongside.

I am grateful to my family, Mom, Dad and Michael, for all their hard work putting up with me for years and giving me the opportunity to make it here. Finally, I give my thanks to my wonderful wife, Malgosia, for her support and devotion, and for keeping me happy, fed and sane through these years.
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Chapter 1
Introduction

Worldwide demand for energy is increasing at an enormous rate. Driven by a high standard of living in developed countries, coupled with the emergence of high population nations aiming to match that standard, society faces a great challenge in supplying the necessary power to keep up with demand. A major problem lies in the reliance on legacy fossil fuels as the primary source of energy. Extraction and consumption of these fuels result in byproducts that are harmful to the environment at large and lead to unpredictable variations in global climate. Furthermore, fossil fuels are a limited resource: increasing demand is leading to an ever more rapid decline in available reserves. Thus, an energy economy based on these sources is unsustainable and irresponsible.

To satisfy the growing demand for energy, both now and well into the future, it will be necessary to identify and develop sustainable energy sources. A number of terrestrial options exist, including wind, hydroelectric and geothermal. The most abundant, however, is terrestrial solar energy. The solar resource delivers over 100 000 TW of power to the Earth’s upper atmosphere and is responsible for providing the energy necessary for the natural processes on the planet. This abundant energy source, converted to electricity with a moderate efficiency, could provide a year’s worth of human energy consumption in a mere day.

Development of solar photovoltaic (PV) technology, which will be discussed in more detail in the following chapter, has advanced greatly over the past half-century. Silicon-based solar cells are the current standard for PV. They improved significantly over a time period when energy resources were not the concern they are today, mostly due to silicon’s ubiquity in the booming microelectronics industry. This is despite the fact that silicon is not an ideal material: the bandgap is sub-optimal and indirect, meaning that hundreds of micrometers of materials
thickness are required to fully absorb incident light. Furthermore, high performance silicon cells require stringent, energy-intensive processing conditions, and wafer growth is currently limited in size to 300 mm diameter, which curtails the rapid production of large-area solar photovoltaic energy capture devices.

These considerations have generated significant interest in developing new materials that can better fulfill the promise of a sustainable energy future. A major research front involves the development of solution-processable photovoltaic materials. These can be printed rapidly on large areas and at low cost, reducing the economic barrier to widespread adoption of solar photovoltaics.

Among the materials studied, colloidal quantum dots (CQDs) show particular promise. As discussed in Chapter 3, CQDs are inorganic nanocrystals that can be cast into a film from solution. The optoelectronic properties of CQDs can be rationally tuned simply by varying the nanoparticle size. Thus, they can be engineered to absorb across the entire solar spectrum and hold the potential for very high efficiencies while maintaining low cost manufacturing. They are unique among solution-processed materials for their ability to absorb in the infrared. This is unmatched by other solution-processable photovoltaic materials such as polymers or dyes; thus, CQDs are in a unique position to allow full spectral utilization of sunlight.

In shorter wavelength regions, a number of technologies exist that make excellent use of light in their absorption range. These materials have reached high efficiencies through favourable material properties and intense development. Organolead halide perovskites, discussed in Chapter 7, are an interesting case; these solution-processed materials have ascended in efficiency to over 20% in a small number of years. However, these materials leave the long wavelength portion of the solar spectrum untouched, even though approximately half of the solar irradiance consists of infrared photons.
It would be attractive to combine the excellent short-wavelength performance of these materials with the infrared spectral harvesting of CQDs. However, most work on CQDs has focused on bandgaps optimal for single-junction cells, ~1.3 eV. In Chapter 4, advancement of CQD solar cells with this bandgap through a hybrid passivation scheme is presented. Chapters 5 and 6 explore this process in more detail. Finally, the techniques developed are applied in Chapter 8 to small bandgap, infrared-absorbing quantum dots. An outline of the flow of this thesis is shown in Figure 1.1.

Figure 1.1: Outline of this thesis. The concepts of photovoltaics and CQDs are introduced in Chapters 2 and 3 respectively. A focus is placed on advancing CQD photovoltaics in Chapters 4 through 6. Visible absorbing perovskite PV is demonstrated in Chapter 7, and the potential of a combined approach using infrared sensitive CQDs is explored in Chapter 8.
Energy harvesting through the photovoltaic effect involves the conversion of light directly into electricity, in contrast with most other energy sources, which use heat or fluid flow to drive a turbine connected to an electrical generator. The basic principles of photovoltaic devices can be explained through simple circuit models and the achievable efficiencies can be calculated through detailed balance. Over the past half century, a large number of different materials have been developed for photovoltaic devices, each with distinctive properties and applications.

2.1 Solar Cell Operation

2.1.1 Simple Model of a Solar Cell

In a semiconductor with a bandgap $E_g$, an absorbed photon (with energy $>E_g$) will promote an electron from the valence band ($E_v$) to the conduction band ($E_c$), generating an electron-hole pair. Thus, the energy of the photon has been transferred to the electron. However, to make use of this energy, it is necessary to extract the excited electron. A solar cell is a device with engineered asymmetry used to separate and extract the photogenerated electrons and holes.

The asymmetry in a solar cell arises from the use of junctions between different materials. Most commonly, this is a p-n junction as shown in Figure 2.1. When these materials are brought together, a depletion region containing a built-in electric field is formed. This field drives the photogenerated electrons and holes in opposite directions, separating charges.
A solar cell can be modeled with an equivalent circuit in which a current source is in parallel with a diode that restricts the direction of current flow, as shown in Figure 2.2. Under dark conditions, only a small leakage current flows, but illumination turns on the current source and delivers power to a load. If no load is connected, the voltage across the contacts is known as the open-circuit voltage ($V_{OC}$). Likewise, if the contacts are directly connected, the current that flows is known as the short-circuit current ($I_{SC}$). Typically, since the area of illumination is important, the short-circuit current density ($J_{SC}$) is reported.
In the ideal case, a solar cell operates exactly as a diode with an added photocurrent depending on illumination. In reality, parasitic resistances cause the current-voltage characteristics to deviate from this. Series resistance ($R_S$) constitutes any resistive losses in the solar cell, often due to contact resistance or defects within the material itself. It can also be caused by resistance anywhere in the circuit between the cell and the load. Shunt resistance ($R_{Sh}$) refers to any leakage current that bypasses the load, such as shorting between front and back contacts. Low shunt resistance reduces the amount of current that is delivered to the load. For a good solar cell, it is desirable for $R_S$ to be as low as possible while $R_{Sh}$ is as high as possible.

2.1.2 Solar Cell Measurement and Figures of Merit

The most important measurement of a solar cell is a current density-voltage sweep (J-V curve) shown in Figure 2.3. This measurement is performed under illumination using a standard source meant to mimic the solar spectrum. Most commonly, this is the AM 1.5 spectrum, which approximates solar illumination through 1.5 times the atmosphere thickness (or Air Mass) to
represent insolation at temperate latitudes. The power integrated over all wavelengths is 100 mW cm$^{-2}$.

![Diagram of J-V curve]

**Figure 2.3:** Example of a J-V curve. The area of the filled rectangle relative to the larger area defined by the $V_{OC}$ and $J_{SC}$ represents the fill factor. This area is reduced by parasitic resistances.

The J-V curve gives information about the figures of merit introduced in the previous section. At zero voltage, the current density flowing is the $J_{SC}$, while the $V_{OC}$ is the bias at which zero current flows. Of course, the purpose of a solar cell is to generate power and so under real conditions a solar cell will operate at a voltage between these points. The power generated at a given bias is $P(V) = J(V) \times V$. The conditions under which $P(V)$ is maximized is known as the maximum power point (MPP), with the current density and voltage at this point represented by $J_{MPP}$ and $V_{MPP}$ respectively. Ideally, $J_{MPP}$ and $V_{MPP}$ should be as close to $J_{SC}$ and $V_{OC}$ as possible, but parasitic resistances will lead to losses and change the shape of the J-V curve as
indicated in Figure 2.3. These deviations can be captured in a single figure of merit called the fill factor,

$$FF = \frac{J_{MPP} \times V_{MPP}}{J_{SC} \times V_{OC}}$$

The FF can be thought of as a measure of the charge collection efficiency of the solar cell. Finally, the power conversion efficiency (PCE) of the cell is given by:

$$PCE = \frac{J_{SC}V_{OC}FF}{P_{in}}$$

where $P_{in}$ is the incident power per unit area. In order to compare reported PCE values between research groups and companies, there exist accredited laboratories that independently measure cells or modules and certify the performance. Record certified efficiencies for various technologies are compiled and published regularly.\(^{1,2}\)

Another important figure of merit for solar cells is the external quantum efficiency (EQE). This is a spectrally resolved measurement in which the current produced by a given optical excitation is quantified. The EQE is the probability that a photon of wavelength $\lambda$ incident on the solar cell will produce an electron that is delivered to the external circuit:

$$EQE(\lambda) = \frac{J(\lambda)}{qN_{photons}(\lambda)}$$

where $q$ is the fundamental charge and $N_{photons}(\lambda)$ is the number of incident photons of wavelength $\lambda$. Sub-optimal EQE at given $\lambda$ could be due to optical losses (e.g. reflection or parasitic absorption), incomplete absorption (e.g. active layer not sufficiently thick), or ineffective extraction of charge (e.g. carrier recombination at defects or interfaces). To isolate the carrier extraction efficiency, the EQE can be combined with absorption to obtain the internal quantum efficiency, IQE. This is the probability of extracting an electron per photon absorbed by the cell.
2.1.3 Limiting Efficiencies

The maximum achievable efficiency for a conventional solar cell is a function of the material bandgap, \( E_g \), and the illumination spectrum.\(^3\) Fundamental losses restrict this maximum. The first loss is due to photons with energy below \( E_g \), as these are transmitted by the cell and do not generate charge carriers. Conversely, photons with energy greater than \( E_g \) are absorbed, but any excess energy beyond the bandgap is lost to heat as the carriers thermalize to the bandedge. Finally, spontaneous emission due to radiative recombination results in losses by the solar cell.

![Figure 2.4: Theoretical efficiency limit for AM1.5 solar spectrum as a function of absorber bandgap. (Adapted from Steve Byrnes, Wikimedia Commons.)](image)

With these losses in mind, the available work that can be performed by the solar cell can be calculated for the AM1.5 terrestrial spectrum as a function of \( E_g \).\(^4\) As shown in Figure 2.4, the maximum PCE is about 33% at a bandgap of approximately 1.34 eV, though the peak is rather broad. Local extrema appear due to spectral variation of the solar spectrum caused by atmospheric absorption. Multijunction cells can reduce the effect of transmissive and thermal
losses, while optical concentration can reduce radiative losses. Through these approaches, the limiting PCE can be more than doubled.

2.2 Overview of Photovoltaic Materials

A wide range of materials have been studied for use in solar cells. These include wafer-based bulk semiconductors as well as emerging solution-processed organics. The National Renewable Energy Laboratory in Golden, CO keeps an updated chart of the record certified efficiencies reported for a wide range of technologies.\(^1\) This chart is reproduced in Figure 2.5. At the upper end of the chart, high-efficiency concentrator cells can be seen. These materials obtain the highest efficiencies but require stringent processing as well as complex tracking systems. In the middle range, commercial single junction technologies are shown, including wafer and thin film technologies. In the bottom right corner, emerging PV technologies can be found. These are generally solution-processed materials with low manufacturing costs but efficiencies that currently lag behind conventional technologies.
Figure 2.5: Chart of the best reported efficiencies for research-scale solar cells. This plot is courtesy of the National Renewable Energy Laboratory, Golden, CO.

### 2.2.1 Wafer-based technologies

Silicon is by far the most widely used photovoltaic material and dominates the commercial PV market.\(^5\)\(^,\)\(^6\) It benefitted greatly from advances in processing technology developed for microelectronics even as sustainable energy sources were not considered a pressing concern. The bandgap of silicon is a slightly less than optimal 1.1 eV, reducing the maximum efficiency to 29%. Additionally, the bandgap is indirect, requiring a hundreds of microns thick optical path length to fully absorb incident light, although nanostructuring can greatly improve the absorption and reduce the required material thickness.\(^7\) In spite of this, the best cells have reached over 25% PCE through improved materials processing and cell architectures. Improved efficiencies and reduced manufacturing costs have reduced the cost per peak watt of silicon to below $1/W, similar to CdTe thin films. Due to the high materials usage in conventional cells,
however, elemental silicon itself represents a relatively large contribution to the cost per watt of silicon solar cells (~$0.01/WP) even though silicon is highly abundant.$^5$

Another wafer based material, GaAs, is nearly perfect for solar conversion. It has a direct bandgap of 1.42 eV, meaning it is highly absorbing and well matched to the solar spectrum. Unsurprisingly, GaAs cells hold the record for the highest efficiency single junction PV cell at 28.8%. Materials and production costs, however, currently restrict the wide-spread use of this material.

A key subcategory of wafer based cells involves III-V multijunction solar cells. These cells stack multiple solar cells with different bandgaps to reduce thermalization losses and improve the PCE. These cells often utilize concentrator systems to further boost performance, and have reached certified efficiencies of 46% using a quadruple junction cell.$^8$ The remarkable efficiencies afforded by these cells unfortunately require extremely complex and expensive manufacturing techniques, limiting their use to applications where power per area is a concern and cost is not. For example, multijunction cells are the technology of choice for applications in outer space.

### 2.2.2 Thin film technologies

Solar cells based on semiconductor thin films benefit from reduced materials usage and generally less stringent processing. The active layers are much thinner than those used for crystalline silicon cells, owing to much greater absorption. Rather than a wafer, the absorbing material is deposited on a carrier substrate such as glass or, in some cases, a flexible material. For these reasons, these technologies have potential for lower costs than wafer based cells.
Amorphous silicon, unlike its crystalline analogue, is a direct bandgap material; thus its absorption is strongly increased. The bandgap is not well matched to the solar spectrum and the material has a high defect density, leading to relatively low efficiencies (only ~13% in the best case\(^2\)). In light of this, amorphous silicon is generally only used for low-cost, low-power applications.

Copper indium gallium selenide (CIGS) is a quaternary semiconductor alloy with a tunable bandgap based on the ratio of indium to gallium. It is manufactured through various vapour and solution based processes, including on flexible substrates. For some time, CIGS cells have held the record lab-scale efficiency for thin film technologies, but difficulties in scaling have resulted in low module performance. This was in part due to challenges in maintaining proper stoichiometry throughout a large area film.\(^9\) Module efficiencies have improved lately, and market share has accordingly increased; however, materials scarcity may put a lower limit on the cost. A related material system is the copper zinc tin sulfide (CZTS) semiconductor, which eliminates the use of expensive indium. CZTS has not been as well studied, and thus efficiencies are below 13%.\(^{10}\)

Cadmium telluride (CdTe) is the leading thin film technology with strong absorption and a near ideal bandgap of 1.45 eV. Although lab efficiencies lagged behind CIGS records, superior scalability allowed CdTe modules to enter the market earlier and claim market share. In recent years, the lab efficiencies have rapidly improved to 21.0%, nearly matching the record CIGS efficiencies.\(^2\) Similar to indium and gallium in CIGS cells, the relative scarcity of tellurium may keep the contribution of materials costs similar to silicon despite the much thinner active layers.\(^5\)

### 2.2.3 Emerging technologies

A wide range of materials have seen study as photovoltaic cell candidates but generally have not yet made the leap to commercial modules. Generally, emerging technologies are researched for
their potential as low cost alternatives to current commercial modules. This often implies materials that can be processed using simple solution-based methods without using high temperatures.

The field of organic photovoltaics (OPV) covers a suite of materials including various formulations of small molecules and polymers. These can be processed through low-temperature vapour and solution methods. The absorption is limited by large bandgaps and short carrier diffusion lengths, but these effects are mitigated somewhat through fabrication of multijunction cells and mixed bulk-heterojunction films. A number of OPV companies have been founded, and certified efficiencies have reached over 11%.

Dye-sensitized solar cells (DSSCs), also known as Graetzel cells, make use of a nanoporous scaffold (usually titania) that is sensitized with dye molecules. Often a liquid electrolyte is used to infiltrate the porous structure and regenerate the dye during operation. Similar to OPV, the absorption range of dyes is mostly limited to the visible spectrum. DSSCs have reached efficiencies of approximately 12% and commercial modules have been produced.\textsuperscript{11,12}

Organolead halide perovskites have emerged rapidly in recent years as a photovoltaic technology. Beginning as a replacement for sensitizing dyes on titania scaffolds,\textsuperscript{13–15} their favourable optoelectronic properties have allowed perovskites to reach 20.1% certified efficiency,\textsuperscript{2} nearly matching mature thin film technologies. The meteoric rise in efficiency has sparked considerable interest, and significant focus is now being spent on addressing stability and toxicity concerns.

Colloidal quantum dots (CQDs) are a class of materials consisting of solution-processed semiconductor nanocrystals. They can be made of many different materials and display quantum
size tunability: the absorption range can be adjusted by varying the nanocrystal diameter. CQDs have many unique properties, some of which may allow for photovoltaic efficiencies beyond the Shockley-Queisser limit. This technology will be discussed in more detail in the following chapter.
2.3 References


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Chapter 3
Colloidal Quantum Dots

Colloidal quantum dots (CQDs) are semiconductor nanocrystals which have dimensions small enough that quantum confinement effects alter the optical and electronic properties of the material compared with its bulk analogue. They are synthesized in and processed from solution, thus allowing for low-cost, rapid deposition of active optoelectronic films. Furthermore, CQDs demonstrate relatively efficient multiple exciton generation (MEG). These unique properties make CQDs an attractive material for photovoltaic devices.

3.1 Properties of Colloidal Quantum Dots

The intriguing optoelectronic properties of quantum dots are caused by an effect known as quantum confinement. Quantum confinement effects occur when the physical dimension of the system is below the Bohr radius, \( r_B = \frac{\varepsilon \hbar^2}{\mu e^2} \) where \( \mu \) is the reduced electron and hole effective mass, \( \varepsilon \) is the dielectric constant of the semiconductor and \( e \) is the elementary charge. When the radius of the nanocrystal is less than \( r_B \), the energy bands form discrete states and expand the bandgap, as shown in Figure 3.1a.

The lead chalcogenides in particular have Bohr radii in the tens of nanometres, allowing a large range of bandgap tunability. Thus, simply by adjusting the diameter of the CQDs, one can tune the absorption edge precisely to be anywhere across the broad solar spectrum (Figure 3.1b and c). Unlike most solution-processed solar materials, this allows PbS or PbSe quantum dots to harvest solar photons from deep into the infrared. They are therefore very compelling for construction of tandem or multi-junction cells that can potentially exceed the Shockley-Queisser limit.\(^2\)
Figure 3.1: Size tunability of quantum dots. (a) For a bulk semiconductor with a given bandgap, $E_g$ (left), nanocrystals with diameters, $d$, less than the Bohr radius will have an increased bandgap due to quantum confinement. (b) The solar spectrum, with photon flux as a function of photon energy, $E_{ph}$. (c) Example sizing curves for CdSe and PbS quantum dots. The bars represent the range of photons absorbed by CQDs of a given size and material.
An alternative path to exceeding this limit using CQD materials is through multiple exciton generation (MEG). Typically, excess energy from photons whose energy exceeds the bandgap energy is quickly lost as carriers thermalize to the bandedge. MEG provides a pathway to promotion of one or more additional electrons to the conduction band. Confined systems are more amenable to this process than bulk semiconductors (in which the analogous process is known as impact ionization) due to increased carrier interaction and reduced phonon effects.

3.2 Synthesis of Colloidal Quantum Dots and Film Processing

Quantum dots can be formed through a number of processes. Epitaxial quantum dots are produced through consecutive deposition of lattice mismatched materials, leading to interlayer strain that is relieved through formation of quantum dot islands. Solution processed quantum dots can be produced by in situ growth of quantum dot material by chemical bath deposition or successive ionic layer adsorption reaction (SILAR), or through ex situ synthesized CQDs. This work is focused on the latter, in which the CQDs are prefabricated prior to deposition to form solid films.

The synthesis of CQDs is typically performed under inert conditions using organometallic precursors in organic solvents. The most commonly applied synthetic method, particularly for metal chalcogenides such as CdSe and PbS, involves a hot-injection approach, illustrated in Figure 3.2. In this procedure, an organometal precursor (e.g., lead oleate) is heated in a flask. The chalcogenide precursor (e.g., bis(trimethylsilyl) sulfide, or TMS) is then rapidly injected into the solution. This process leads to a brief, local oversaturation of precursor which causes nucleation of nanocrystals seeds. As the precursors are mixed, the concentration drops below the nucleation threshold, preventing formation of new nanocrystals. The formed nuclei then grow through the scavenging of remaining precursor material at elevated temperature. Since there is a single nucleation event and the growth conditions are the same for each quantum dot, a monodisperse population can be achieved. Once all of the precursor is consumed, the nanocrystals undergo a size-focusing process known as Ostwald ripening, in which smaller CQDs give up material to
larger CQDs. Fine control can be achieved over the size of the final CQDs through manipulation of the reaction temperature as well as the reactivity and ratio of the starting precursors. It is also possible to add dopants to the CQDs during synthesis\textsuperscript{6,7}, and, for certain materials, reaction conditions can be adjusted to allow for growth of anisotropic structures such as nanorods, nanoplatelets or tetrapods.\textsuperscript{8,9}

\textbf{Figure 3.2:} Schematic showing the processes occurring during CQD synthesis.

While the hot-injection method has been extremely successful for production of high quality CQD populations, it is restricted in scale. Synthesis occurs in batches which are limited by the nucleating hot-injection step; at larger volumes it becomes difficult to ensure that precursor oversaturation occurs briefly enough to result in a high monodispersity. Thus there has been significant research into alternative growth methods. A heating-up synthesis has been demonstrated using pre-mixed precursors that are heated to a certain temperature to define
nanoparticle size. This approach relies on careful control of temperature and solvent viscosity to produce narrow size distributions.\textsuperscript{10} Another scalable method was reported using a continuous flow approach.\textsuperscript{11} This method can be simply scaled up for mass production, and was shown to result in CQDs of similar quality to batch synthesis methods.

In order to fabricate optoelectronic devices, it is necessary to form films of the CQDs. If good electronic coupling is required for the application, then the original synthesis ligands must be removed. These ligands, which confer colloidal stability in solution, act as electronic insulators in solid state. Typically, a layer by layer (LbL) solid state exchange is used: after casting a thin film of CQDs, a solution containing a shorter, functionalized ligand is introduced. These ligands remove the long, aliphatic ligands from the CQD surface and often serve to densify the film to improve intradot transport.\textsuperscript{12} A wide variety of ligands are used, including short thiols,\textsuperscript{13} halides,\textsuperscript{14} pseudohalides,\textsuperscript{15} and amines.\textsuperscript{16} In some cases, the exchange can be performed in solution so that a well coupled film can be cast without further processing.\textsuperscript{17–19} Post-casting methods can be used to adjust the film properties, such as doping.\textsuperscript{20} Many different thin film methods\textsuperscript{21} can be used to produce CQD films, including spin-coating, dip-coating and spray-coating.\textsuperscript{22} Reduction in film disorder during processing can promote formation of superlattices, in which the CQDs maintain long range order.\textsuperscript{23,24} Improving long range order in films will lead to improvements in charge transport.

### 3.3 Materials

As mentioned previously, II-VI metal chalcogenide semiconductors are the most commonly studied CQD materials. The relatively large Bohr radii of these materials combined with well-studied syntheses means that it is straightforward to produce monodisperse, size-tuned CQD batches for various applications. Cadmium-based CQDs are very common in light emission applications as their tuning range lies across the visible spectrum.\textsuperscript{25} Lead-based CQDs, on the other hand, are very small-bandgap semiconductors in bulk (<0.4 eV), and so they can be tuned across the infrared region.\textsuperscript{2} This makes them particularly attractive for infrared photodetection
and emission purposes. The high terrestrial abundance of elemental lead and sulfur combined with the thin active layers means that materials costs of PbS CQD devices are orders of magnitude lower than those of silicon. Mercury chalcogenides have also been studied for long-wavelength infrared applications.26

Concerns about the use of heavy metals such as Cd have led to searches for alternative CQD materials. Indium phosphide has been used for this purpose to produce high quality light emission,27,28 and copper indium sulfide nanocrystals have also been studied recently in various applications.29,30 Less mature but intriguing non-toxic materials include tin and silver sulfides.31,32 Silicon, while most commonly used in wafer form, can also be used to form size-tunable quantum dots.33

In addition to single semiconductor CQDs, it is common to combine materials in order to further tune their properties. Growth of a shell material around the original CQD core can be used, depending on the relative band alignment, to better confine the electron, hole, or both within the core, as shown in Figure 3.3.34 So-called giant shells have been recently shown to greatly reduce undesirable optical blinking in CQDs.35 Fine control over the shell composition and thickness can be achieved through post-synthesis processing in solution.36 This wide range of materials and forms has led to an array of applications of CQDs.
Figure 3.3: Schematic of two types of core-shell CQDs, and band diagrams showing confinement of both carriers in the core (Type I), or localization of one carrier and extraction of the other (Type II).

3.4 Applications of Colloidal Quantum Dots

3.4.1 Light Emission

Light emission was identified as one of the primary potential applications for CQDs because of the extremely narrow and tunable emission peak caused by the quantum confinement effect. Due to this, light emission is also the most mature application, and a number of commercial products now incorporate CQDs.

CQDs can be used to cover a wide colour gamut and various sizes can be combined to most accurately reproduce natural colours. This has led to the use of QDs as phosphors in state-of-
the-art televisions in which a broadband, high photon energy source is used to excite pixels containing red, blue, and green emitting CQDs. Through use of core-shell structures, non-radiative recombination at surface sites can be reduced and high emission efficiency can be obtained.

Currently, significant research is being carried out that seeks to develop electrically-driven CQD-based light-emitting devices (LEDs) that do not require a separate optical excitation source. Device optimization has led to QD-LEDs on par with vacuum-deposited organic LEDs, as well as high efficiency short-wavelength IR sources.

### 3.4.2 Sensing

The rich surface chemistry of CQDs can be exploited for a number of sensing applications. A well-studied application of CQDs involves their use as fluorescent markers. By functionalizing CQD surfaces with certain ligands, the dots can be made to bind to certain features *in vivo* and tracked non-invasively. Common biomarkers, such as green fluorescent protein, have broad emission spectra and poor tunability. This limits the number of different biomarkers that can be used as it becomes difficult to separate the different signals. CQDs, which exhibit very narrow emission peaks, can be multiplexed and easily distinguished.

As biosensing agents, CQDs are again specifically functionalized and used as fluorescent markers *in vitro*. Following a photon excitation, the QDs will fluoresce efficiently, unless they are quenched by resonant energy transfer to a nearby acceptor. Quenching can occur when an analyte of interest binds to the molecules (such as nucleic acids or antibodies) decorating the surface of the CQD followed by the binding of a specifically functionalized quencher. In this case, the reduction of CQD emission can be used to indicate the presence of the target species.
The high surface to volume ratio of CQDs also makes them attractive for gas sensing applications. In a CQD film there are many binding sites for gas molecules, and their presence can greatly affect the optoelectronic properties. For example, PbS CQDs, stripped of native ligands using a NaNO$_2$ exchange, were used to produce fast and sensitive electronic sensors for NO$_2$ and H$_2$S gas.$^{41,42}$

3.4.3 Transistors

The use of transistors in electronic circuits has allowed for expansive growth of consumer electronic devices in many form factors. As demand for lightweight and flexible devices increases, solution processable materials are of interest for next-generation circuits.

CQDs have been demonstrated for use in field-effect transistors (FETs) that can be fabricated on flexible substrates.$^{43}$ High mobilities and band-like transport have been demonstrated using carefully chosen ligands for highly coupled films.$^{44,45}$ These structures also allow for in depth characterization of nanocrystal solids.$^{46}$

3.4.4 Photodetection

The high absorptivity of CQD solids makes them a very attractive material for light sensing applications. Additionally, the size tunability makes it possible to fabricate sensors for specific bands of photons. The ability to deposit CQDs from solution makes it possible to produce new form factors not accessible by traditional wafer based photodetectors.

The most common material for photodetection is PbS, owing to its broad infrared absorption range, though HgTe$^{47}$ and CdSe$^{48}$ photodetectors have also been demonstrated. Photodetectors can take different forms, and PbS CQDs have been used in fast photodiodes.$^{49}$
photoconductors\textsuperscript{50,51} and phototransistors\textsuperscript{52–54}. Furthermore, photodetectors have been able to exploit multiple exciton generation\textsuperscript{55}.

In an early report on PbS CQD photodetectors, a small photovoltaic effect was also demonstrated\textsuperscript{56} This was the first demonstration of solution-processed infrared PV, and sparked significant research over the next decade.

## 3.5 Review of Colloidal Quantum Dot Photovoltaics

### 3.5.1 Cell Architectures

Solar cells using CQDs generally fit into three categories\textsuperscript{57}: (i) as an array in a p-i-n structure, (ii) as sensitizers on TiO\textsubscript{2} as in a dye-sensitized solar cell, and (iii) embedded within a semiconducting polymer (Figure 3.4). All of these structures, and extensions thereof, have seen great progress since the early 21\textsuperscript{st} century. This thesis will focus on the development of the first architecture, involving an array of CQDs used to absorb photons and transport charges. Other forms will be briefly reviewed here.

Hybrid polymer-CQD cells were among the earliest demonstrated devices, with CQDs acting as acceptors in place of typical fullerenes in a bulk-heterojunction device. Quantum confined CdSe nanorods were blended with poly(3-hexylthiophene) (P3HT) to achieve 1.7% power conversion efficiency (PCE) under AM1.5G simulated solar illumination\textsuperscript{58}. The CdSe phase served as the electron transporting material while the P3HT shuttled the holes. The first infrared CQD cell also used a hybrid polymer architecture with PbS CQDs embedded within a poly(2-methoxy-5-(2’-ethylhexyloxy-\textit{p}-phenylenevinylene)) (MEH-PPV) conjugated polymer\textsuperscript{56}. Most work on hybrid cells has focused on the use of Cd chalcogenides; with a CdSe blend, Zhou \textit{et al.} achieved a 4.7% PCE at 1 sun\textsuperscript{59}. Despite the ubiquity of hybrid CdSe research, the best reported efficiency of 5.5% was achieved using a PbS\textsubscript{x}Se\textsubscript{1-x} blend by Liu and colleagues\textsuperscript{60}. Intriguingly,
quantum dots may hold the key to exploiting singlet fission in PV devices as the energy transfer has independently shown to be near-unity by two groups recently.\textsuperscript{61,62}

Figure 3.4: Main structures of CQD solar cells. Schematic diagrams of device structures for (a) thin-film all-CQD cells, (b) CQD-sensitized solar cells, (c) hybrid polymer-CQD solar cells. (d-f) The band diagrams showing charge extraction processes for each respective cell.

Quantum dot sensitized solar cells (QDSSCs) replace the molecular dyes in dye-sensitized (or Gratzel) cells. The quantum dots are deposited on a mesoporous scaffold, typically titania, which acts as an electron acceptor. It should be noted that this structure is often used for \textit{in situ} grown QDs as it is generally easier to attain high surface coverage of the mesoporous material.
Recently, a number of breakthroughs in colloidal QDSSCs have been reported using various materials systems. A ligand exchange using mercaptopropionic acid (MPA) enabled water soluble Cd chalcogenide quantum dots which demonstrated high loading and PCEs over 8%.

Use of ternary CuInS$_2$ CQDs enabled the first certified results for QDSSCs, first at 5.1%, and then at 6.7%.

### 3.5.2 CQD Solar Cells with p-i-n Structure

Solar cells in which a thick CQD layer acts both as absorber and charge transporter are the focus of this thesis. These cells have thus far shown the highest efficiencies for CQD photovoltaics, with lead chalcogenides as the most commonly used materials. The following section will review progress up to approximately 2011, prior to the work contained in this thesis.

Simple Schottky junction solar cells were among the first developed, with a low work function back contact forming a rectifying junction with p-type CQDs. Development of a depleted heterojunction structure, with p-type quantum dots on an n-type metal oxide such as ZnO or TiO$_2$, first brought the efficiency beyond 5%. This architecture relies on drift transport within the depletion region to effectively collect photogenerated carriers. This structure was further enhanced with a “quantum funnel” consisting of layers of various bandgap quantum dots appropriately graded to sweep electrons towards the TiO$_2$ electrode. A record certified efficiency of 6% was reached in 2011 using an atomic ligand approach: the organic surface ligands were replaced with bromide ions, allowing for a high degree of surface passivation.

The relatively short diffusion lengths of current quantum dot films constrain the thickness of the absorber layers to ensure mostly complete depletion and therefore efficient charge collection. However, this thickness is often not enough to enable complete absorption, particularly of long wavelength photons. To address this issue, cues have been taken from the bulk heterojunction approach of organic solar cells, in which donor and acceptor layers are intermixed in order to
efficiently separate electrons and holes. Barkhouse et al. used a porous electrode of TiO$_2$ crystals hundreds of nanometers in diameter that was fully infiltrated with PbS quantum dots.\textsuperscript{69} The quantum dots within this porous structure were always within a depletion width of an electron extracting interface, allowing construction of a thicker layer with greater absorption. This resulted in an enhancement of short circuit current approaching 30% compared with a planar approach.

Other strategies for improving the efficiencies of quantum dot solar cells have focused on the charge collecting electrodes and their interfaces.\textsuperscript{71} Modification of the n-type electrode has been explored to fine tune band alignment, reduce interfacial recombination, and increase the depletion width within the quantum dot absorber.\textsuperscript{72-74} Improved hole-extraction has been achieved using metal oxides as selective transport layers between the quantum dot film and the back metal contact.\textsuperscript{75-77}

While heterojunction solar cells have achieved increased efficiencies in recent years, there remain some limitations since proper band alignment to the n-type electrode is required. Thus, even though the quantum dots may be tuned to a smaller bandgap, the change in band alignment may result in a large barrier to charge extraction without reoptimization of the n-type electrode.

3.5.3 Multijunction CQD Solar Cells

A multijunction approach is a method that can be used to exceed the single junction Shockley-Queisser limit. A cascading interconnected stack of solar cells with progressively smaller bandgaps is used to reduce losses due to thermalization of carriers. The size tunability of quantum dots allows for precise optimization of constituent cell bandgaps and provides a path for a multijunction cell made from a single absorber material. Notably, PbS quantum dots can be tuned to the ideal bandgaps for a triple junction cell: 0.71 eV, 1.16 eV and 1.83 eV.\textsuperscript{2}
Two reports of tandem quantum dot solar cells were published in 2011. Choi et al. reported a tandem cell using an interconnecting layer of ZnO/Au/PEDOT:PSS between the 1 eV and 1.6 eV PbS QD cells. The thin gold layer was found to be crucial for minimization of series resistance from the interlayer. Wang, Koleilat and colleagues reported a depleted heterojunction tandem using a graded recombination layer consisting of a stack of metal oxides with a progression of work functions. This layer allowed efficient recombination of electrons from the back cell with holes from the front cell and led to cells with PCE of 4.2% and open circuit voltages of 1.06 V. Besides the design of the interconnecting recombination layer, optimization of the individual subcells was also important for realization of the tandem cell.

Extending methods used in recent efficiency advances in single junction cells will allow for further progress in tandem or multijunction quantum dot solar cells. The precise bandgap tunability and infrared absorption of quantum dots also provide a unique opportunity towards design of a back cell in a multijunction approach with other materials systems that are unable to harvest long wavelength photons.

3.6 Limiting Factors in CQD Performance

While many advances in CQD photovoltaics have been through the development and optimization of new device structures, improvements in the CQD materials themselves hold the most potential for performance enhancement. These improvements tend to focus on the surfaces of CQDs. The same feature that affords CQD their unique properties— their small size—also results in an extremely high surface to volume ratio. While other PV semiconductors certainly require careful consideration of grain boundaries, the situation is magnified for CQD devices. Surface trap states act as non-radiative recombination centres that reduce the efficiency of PV cells.
The existence of traps on CQD surfaces is a function of the composition of the nanocrystals and the interplay with its capping ligands.\textsuperscript{82,83} As synthesized, the nanocrystals tend to be non-stoichiometric, with an excess of metal atoms at the surface.\textsuperscript{84,85} This excess leads to an imbalance of charge which must be passivated by anionic ligands to prevent trap formation, though a poor ligand choice can itself produce midgap states. An alternative method for reducing surface recombination is the use of wide bandgap shells around the absorber core material.\textsuperscript{34,86,87} These can significantly reduce non-radiative recombination, but improper implementation can result in sub-optimal electronic coupling.

Trap states in CQDs are widely considered to be the limiting factor in photovoltaic performance. Improvements in charge carrier mobility would not have an appreciable effect unless trap states were significantly reduced\textsuperscript{88}. These sub-bandgap states are likely the cause of the large deficit seen between the material bandgap and the observed open-circuit voltage.\textsuperscript{89} Thus, proper management of CQD surface states, through rational ligand engineering, holds the key to continued progress in CQD solar cells.

In light of this, the research included in this thesis has focused on the identification and elimination of surface traps in CQD solids for the development of high performance solar cells. In the following chapters, an approach to trap reduction in CQD solids is presented and characterized. A combined ligand scheme, utilizing organic and inorganic passivants, will be shown to greatly improve the efficiency through better surface state management.


3.7 References


This chapter contains work from “Hybrid Passivated Colloidal Quantum Dot Solids”, published in *Nature Nanotechnology*, 7, 577-582 (2012) and reprinted with permission from Nature Publishing Group. I was first author on this publication and contributed to all experimental design, interpretation and manuscript preparation. Density functional theory calculations were performed by O. Voznyy, CQD synthesis was performed by L. Levina, grazing incidence small-angle X-ray measurements were performed by L. R. Rollny and K.W. Chou, and time-of-flight measurements were performed by G. Carey.

### 4.1 Introduction

As discussed in the previous chapter, CQD solids exhibit a high surface to volume ratio. Imperfectly passivated surfaces are thus prone to produce a high density of trap states which promote undesirable recombination of charge carriers\(^1\). These traps are the limiting factor in device performance and thus improvements in passivation are required to build efficient devices. In this chapter, a hybrid passivation approach is presented which leads to suppression of surface traps in high performance CQD solar cells.

Recent advances in CQD devices have used solid-state ligand exchanges to replace the long insulating ligands that enable colloidal stability following synthesis with shorter organic linkers or halide anions\(^2-6\). However, performing passivation in solution should provide increased control over the balance of charges on the surface of the dot, which is essential to eliminate midgap trapping states\(^7,8\), and also allow researchers to take advantage of recent progress in metal:chalcogen chemistry in the liquid phase\(^9-13\). Here, we quantify the density of midgap trapping states\(^14-16\) and show that the performance of CQD solids is now limited by electron-hole recombination due to these states.
We sought first to quantify using transient photovoltage spectroscopy\textsuperscript{17,18} the trap state density of the best previously-published CQD photovoltaic materials: organic crosslinked solids\textsuperscript{19} and all-inorganic-passivated solids\textsuperscript{6}. Upon illumination of a trap-free p-type semiconductor, the promotion of photoelectrons to the conduction band is followed by rapid thermalization to the bandedge, resulting in an excess free carrier density sustained over the band-to-band lifetime of the charge carriers. This can be pictured as establishment of two distinct quasi-Fermi levels, one for electrons and the other for holes: this separation produces an open-circuit voltage $V_{OC}$.

However, when a semiconductor with trapping states in its bandgap is illuminated, much of the photogenerated charge is instead consumed in filling midgap levels, producing a smaller $V_{OC}$ for the same photogeneration rate. The photovoltage transient method directly probes these processes. Each film that we studied exhibited a high density of trap states ($\sim$10$^{17}$ cm$^{-3}$ eV$^{-1}$) near the middle of the bandgap.

Next, we used density functional theory (DFT) to explore why such conventional passivation approaches fail to remove midgap traps more completely. First, we confirmed that charge-balance in the as-synthesized lead-rich surface\textsuperscript{20} determines the overall degree of trap passivation (Figure 4.1a-b). DFT calculations show that even a slight imbalance between the number of ligands and the excess Pb atoms results in trap states that severely degrade the cleanliness of the bandgap of the quantum solid. Over an entire film, the device performance will suffer dramatically if even a small fraction of dots have just a small number of midgap centres. It is therefore imperative that the end-to-end film processing flow ensures the best possible surface passivation.
Figure 4.1: (a) DFT calculation of the density of states for a charge-balanced quantum dot with a clean bandgap. A 2.4 nm PbS quantum dot with the amount of ligands adjusted to provide an ideal electronic balance and close to maximally sterically allowed surface coverage was modeled for the calculation. Note that the obtainable $V_{oc}$ under illumination is limited by the bandgap in the case of a film made from these dots. (b) DFT calculation of the density of states for a non-charge-balanced quantum dot (containing half the number of ligands as the dot in (a)) showing a drastic increase in the midgap density of states associated with trap levels (trap states are plotted in light pink). In the case of a film with a significant density of midgap traps, the quasi-Fermi level separation (and therefore $V_{oc}$) under the same illumination is limited by the filling of midgap states. (c), Schematic illustration of a cross-section of a PbS colloidal quantum dot with organic passivation (left) based on mercaptopropionic acid (MPA), an alkanethiol, and the hybrid passivation scheme (right) in which both MPA and halides are present after solution-phase treatment and solid-state exchange. In the organic case, the MPA molecules are unable to fill all of the inter-atom trenches on the lead-rich surface due to steric considerations (top) or lack of proper coordination number (bottom). In the hybrid case, halogen atoms are small enough to easily fill the trenches and can be easily by multiply coordinated.
We next studied, also using DFT, whether such complete passivation is feasible using organics alone. We found that steric considerations prevent organic ligands from penetrating the intercation trenches on the surface of the quantum dots. They are thus prone to leave unpassivated metal surface sites, as illustrated in Figure 4.1c. In contrast, halide atoms are compact enough to infiltrate these difficult-to-access sites. In addition, halides can easily be multiply-coordinated, in contrast with the covalent thiol ligands typically used in organic passivation.

In light of these findings, we devised a hybrid passivation scheme aimed at achieving a dramatic improvement in the combination of surface passivation and film density. We would present halide anions in the solution phase to bind hard-to-access sites. We would at the same time introduce optimally-chosen metal cations to bind unpassivated surface chalcogens, targeting removal of valence-band-associated trap states. Finally, during the solid-state film-forming process, we would use bidentate organic linkers to maximize packing. Specifically, we introduced a metal-halide salt (optimally CdCl$_2$ dissolved in a mixture of tetradecylphosphonic acid (TDPA) and oleylamine) during synthesis immediately following nucleation and growth of PbS quantum dots. The halides bind excess surface atoms while displacing a fraction of the oleic acid ligands.
We used photoluminescence (PL) spectroscopy to investigate the impact of halide exposure. Both untreated and metal-halide-treated dots start out with approximately the same solution-phase PL quantum yield directly after synthesis. However, after the solution-phase washing steps, the PL quantum efficiency is significantly degraded for conventionally-processed nanoparticles due to loss of some oleic acid ligands, but minimally for the more robust hybrid-passivated dots. This suggests a picture in which only the oleic acid passivants that were presumably in sterically non-ideal locations on the surface are removed. These are replaced with halide passivants having superior effectiveness – in particular, their small size allows them to tie up hard-to-access surface sites.

**Figure 4.2:** (a) Schematic of the depleted heterojunction CQD device used in this study and (b) cross sectional SEM image of the same. Scale bar represents 500nm.

### 4.2 Device Performance

We deployed our hybrid passivation strategy to build a series of devices in the depleted heterojunction (DH) architecture\(^2\) (Figure 4.2). We employed a solution-processed n-type electrode that used a ZnO nanoparticle film as a template for producing TiO\(_2\) through a TiCl\(_4\) treatment\(^21,22\). We measured the current-voltage characteristics of our hybrid passivated cell in an inert nitrogen environment under 100 mW cm\(^{-2}\) AM1.5 illumination (Figure 4.3). The typical cell area was 0.049 cm\(^2\) defined by aperturing during cell measurement. We produced
devices with a power conversion efficiency (PCE) of 7% or greater on over 40 separate substrates. The average performance of these devices is shown in Table 4.1, demonstrating a significant performance advance over previously-reported organic\textsuperscript{19} and inorganic\textsuperscript{6} passivated CQD devices. Using capacitance-voltage measurements, we found the free carrier densities of all devices shown in Figure 4.3 to be between $1 \times 10^{15}$ and $1 \times 10^{16}$ cm\textsuperscript{-3}; thus, the $V_{oc}$ enhancement cannot be attributed to a difference in doping density alone. The external quantum efficiency spectrum (Figure 4.3, inset), when integrated, predicts 22 mA cm\textsuperscript{-2} current density, consistent with our AM1.5G measurements.

**Figure 4.3:** Measured current-voltage characteristics under AM1.5 simulated solar illumination for representative devices employing organic (red), inorganic (green), and hybrid (blue) passivation schemes. The black diamonds are the IV curve for a hybrid passivated device as measured by an internationally accredited PV calibration laboratory (Newport Technology and Application Center – PV Lab). Inset is an external quantum efficiency curve for a hybrid passivated device. The integrated current value is also shown.
One of our devices measured by an internationally accredited photovoltaics laboratory (Newport Technology and Application Center - PV Lab) was found to display the following figures of merit: an open circuit voltage, $V_{oc}$, of 0.605 V; a short circuit current, $J_{sc}$, of 20.1 mA cm$^{-2}$; a fill factor of 58%; and a power conversion efficiency (PCE) of 7.0%. This was, at the time, the highest certified PCE reported for a colloidal quantum dot solar cell. Our devices also exhibited relatively good performance stability (less than 15% total PCE degradation over a period of two weeks) when stored in a nitrogen environment, which suggests that encapsulated devices will also display promising performance stability.

**Table 4.1**: Figures of merit for previous champion CQD photovoltaic devices compared with the hybrid passivated devices. Statistics for the hybrid case are based on a total of 47 devices prepared on separate substrates.

<table>
<thead>
<tr>
<th>Type</th>
<th>Organic [Ref. 19]</th>
<th>Inorganic [Ref. 6]</th>
<th>Hybrid (N=47)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{oc}$ [V]</td>
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<td>0.48</td>
<td>0.59±0.01</td>
</tr>
<tr>
<td>$J_{sc}$ [mA/cm$^2$]</td>
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<td>20.2</td>
<td>21.8±0.8</td>
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<tr>
<td>FF [%]</td>
<td>59</td>
<td>62</td>
<td>58±2</td>
</tr>
<tr>
<td>PCE [%]</td>
<td>5.6</td>
<td>6.0</td>
<td>7.4±0.3</td>
</tr>
</tbody>
</table>

### 4.3 Characterization

We used transient photovoltage spectroscopy to obtain the midgap trap state density inside the hybrid-passivated film, as shown in Figure 4.4. The density was $2 \times 10^{16}$ cm$^{-3}$ eV$^{-1}$, fully fivefold lower than in the conventional organic-crosslinked and inorganic-only films. The improvements in both current and voltage are explainable through our considerably cleaner midgap.
To clarify the role of the metal cation vs. the halide anion, we also characterized the midgap of films treated with PbCl$_2$ using the same synthesis-phase protocol. These measurements reported a density of trap states in the gap comparable to that of the CdCl$_2$-treated films and device performance of above 6% PCE. We conclude that the halide plays the primary role in midgap trap removal.

**Figure 4.4:** The DOS in the bandgap calculated from transient photovoltage measurements for organic (red), inorganic (green) hybrid (blue) passivation of PbS CQD films.

We further elucidated the role of each individual constituent in the hybrid approach by using different treatment materials in synthesis, as shown in Figure 4.5. The oleylamine serves to dissolve the metal-halide salt and also helps remove synthesis ligands to facilitate the attachment of the halide passivants$^9$. The TDPA facilitates binding of the metal cations to the sulphur-rich dot facets while preventing full cation exchange$^{23}$. Adding a reactive cation complex such as cadmium oleate or cadmium acetate results in the formation of a core-shell structure with associated increase in open circuit voltage and large decrease in short circuit
current. Adding tetrabutylammonium chloride, which should contribute only halogens to the dot surface, results in an increase in device performance, and further adding a metal binding complex achieves device performance nearly equivalent to that of the optimum metal-halide salt treated devices.

![Graph showing current density vs. voltage for different treatments.](image)

**Figure 4.5:** Devices fabricated from dot batches with different synthesis treatment constituents: no treatment, oleylamine (OLA) treatment, OLA and tetradecylphosphonic acid (TDPA) treatment, tetrabutylammonium chloride (TBAC) treatment, TBAC and cadmium oleate (CdOl) treatment, CdOl treatment, PbCl$_2$ treatment and CdCl$_2$ treatment.

We also compared our hybrid approach with an all-inorganic solid-state approach recently reported which achieved approximately 6% power conversion efficiency$^6$. We performed synchrotron grazing-incidence small-angle X-ray scattering (GISAXS) measurements to elucidate the role of the organic ligands,$^{24-26}$ as shown in Figure 4.6. Though the nanoparticles are ~ 3.1 nm in diameter as seen via transmission electron microscopy, GISAXS shows the average centre-to-centre nanocrystal spacing is 4.4 nm, consistent with the approximately nanometer-scale spacing attributable to the bulk oleic acid. When the short bidentate crosslinker
MPA was used, the dot spacing was reduced to 3.4 nm. Though their organic content was removed, the all-inorganic films retained a 4.4 nm spacing, their average centre-to-centre distance unchanged in the solid-state exchange. These findings confirm the important role for the bidentate organic crosslinker in achieving densification at the time of volume-contraction during solid-state treatment.

**Figure 4.6:** By integrating the GISAXS intensity plots azimuthally, the average interparticle spacing can be found. Inorganic passivation (green curve), in spite of minimally sized atomic ligands, does not increase the film density compared with initially cast dot films (red curve). An exchange using short bidentate organic thiols (blue curve) results in a significant reduction in average interparticle spacing.

The final aspect of the hybrid scheme is valence band passivation for improved hole mobility. This was pursued through solution-phase metal-cation-based passivation of exposed surface sulphur anions. To study its impact on hole mobility, we performed time of flight (TOF) measurements\(^4\)\(^2\)\(^7\) on five different types of films. With no metal halide treatment, the organic-crosslinked films achieve hole mobility \(\mu_p = 1.0 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\). The hybrid film based on PbCl\(_2\) exhibited modestly improved hole mobility \(\mu_p = 2.6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\). The optimal hybrid
film based on CdCl$_2$ exhibited the highest hole mobility $\mu_p = 4.2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. We conclude that while the halide played the determinative role in midgap state passivation, the choice of cation was important in improving transport associated with the valence-band.

The PL spectra of both the as-synthesized quantum dot solutions and the quantum dot solids reported herein further confirm the effectiveness of the hybrid passivation method. As mentioned above, the solution-phase PL quantum yield (Figure 4.7a) after the washing steps was improved approximately twofold when the metal-halide treatment had been employed. The measured PL efficiencies after methanol washing for the CdCl$_2$-treated PbS, the PbCl$_2$-treated PbS and the untreated PbS were 42%, 31%, and 21%, respectively, whereas the efficiencies before exchange were all between 45% and 50%. MPA-exchanged films made from all three types of dots exhibited bandedge PL (Figure 4.7b) shifted approximately 150 nm from the excitonic absorption peak. A significant additional feature exists 300-400 nm further to the red in the case of the organic and hybrid PbCl$_2$ which can be associated with trap-to-band transitions$^{28}$. The optimized hybrid CdCl$_2$ consistently showed bandedge-only PL, consistent with its clear gap both below and above the equilibrium Fermi level.

![Figure 4.7](image.png)

**Figure 4.7:** (a) Solution-phase photoluminescence (PL) intensity of untreated (red), PbCl$_2$ hybrid (pink) and CdCl$_2$ hybrid (blue) passivated solutions. Full PL quantum efficiency measurements indicate a two-fold increase in the PL efficiency of CdCl$_2$-treated dots compared
to untreated dots (see text for details). (b) PL of organic (red), PbCl$_2$ hybrid (pink) and CdCl$_2$ hybrid (blue) passivated films. All films show band-edge PL, but a marked decrease in trap-associated long wavelength PL is observed from the organic to the hybrid case, with the CdCl$_2$ sample showing negligible signal at longer wavelengths.

Our results affirm that, given the diversity of atomic sites present on a quantum dot surface arising as a function of stoichiometry, faceting, and initial ligand coverage, a multiple-liganding strategy can be more effective than one based on a single ligand class. Moreover, developing methods to ensure that the bandgap is substantially free of electronic trap states will further enhance voltage via reduced recombination, and increase current by improving the transport of chargers through the CQD array. The next two chapters will explore this liganding approach more deeply to elucidate the roles of the passivating components.
4.4 References


Chapter 5
Photoelectron Spectroscopy of Hybrid Passivated CQDs

This chapter contains work found in “Complete in-gap electronic structure of colloidal quantum dot solids and correlation with electronic transport and photovoltaic performance”, published in Advanced Materials, 26, 937-942, (2014) and reprinted with permission from John Wiley & Sons. I wrote about 80% of the manuscript, fabricated and tested device samples, and contributed to all experimental design and data interpretation. Photoelectron spectroscopy measurements were performed by K. Katsiev, density functional theory calculations were performed by O. Voznyy, and GISAXS measurements were performed by L. Rollny.

5.1 Introduction

In the previous chapter, CQD solar cells using metal halide passivation were reported that achieved a certified power conversion efficiency of 7.0%, at the time a record for this class of materials.\(^1\) The nanometer-diameter CQDs exhibit a high surface-to-volume ratio, making proper management of surface states very important, since trap states associated with surface defects are the key factor limiting CQD photovoltaic device performance today\(^2\): unpassivated sites give rise to surface defect-related electronic trap states within the band gap that create fast non-radiative de-excitation channels for photo-generated charge carriers. The geometric structure and dimensions of organic ligands were found to prevent the ligands from fully complexing to all surface cation sites in need of passivation, particularly hard-to-access sites such as inter-cation trenches. In contrast, atomic ligands such as halides are sufficiently compact to infiltrate and passivate otherwise inaccessible sites.
Thorough investigation of the electronic character of CQD solids is of great importance to achieving further improvements in performance through identification and elimination of detrimental trap states within the band gap. Much progress has been made in this direction,\textsuperscript{2–7} including the use of photovoltage transient measurements to explore the midgap density of states in CQD solids as a function of metal halide passivation schemes employed. However, this technique probes only the portion of the band gap between the two quasi-Fermi levels. In fact, electronic transport is influenced instead by those traps lying beneath the hole quasi-Fermi level, and lying above the electron quasi-Fermi level. Furthermore, optical techniques have been used to measure midgap states,\textsuperscript{8,9} however, parity selection rules may complicate interpretation of optical measurements and therefore may not provide a complete picture. For these reasons, a direct measurement of the entire band structure of PbS quantum dot solids – one that would resolve in detail the entire region from the conduction band to the valence band, elucidating the impact of surface passivation on both deep and shallow states within the gap is of interest.

Direct techniques for probing electronic structure, principally photoelectron spectroscopies (PES) and scanning tunneling spectroscopy (STS), have greatly aided in understanding of the fundamental properties of various materials systems including in heterogeneous catalysts,\textsuperscript{10} solid oxide fuel cells,\textsuperscript{11} and nanocrystals and nanocrystal films.\textsuperscript{12–15} Previous photovoltaics-relevant work includes studies on prototypical polymer/fullerene hybrid solar cells,\textsuperscript{16} organic photovoltaic materials,\textsuperscript{17} thin film solar cell interfaces,\textsuperscript{18} and metal oxides used for charge extraction.\textsuperscript{19,20} PES techniques provide a statistically robust picture of the electronic structure as it relates to macroscopic device performance, since they deliberately probe over macroscopic areas, whereas STS is a local probe technique allowing to probe the electronic structure on the nanometer scale. Spectroscopies can be combined to obtain a picture of the entire electronic structure, where PES will offer valence band associated states,\textsuperscript{21} and inverse photoelectron spectroscopy (IPES) can report on largely unfilled states such as those in the conduction band.

Here we combine synchrotron-based PES and inverse photoemission spectroscopy (IPES) to measure directly the electronic structure of the entire valence and the conduction band of PbS.
CQD films. We also deploy density functional calculations that both validate and help to explain the observed features in the electronic spectra. Specifically, we report the structure of the valence and the conduction band of PbS CQD films formed using mercaptopropionic acid (MPA) as a ligand that is utilized to build photovoltaic devices. We examine the effect of metal halide passivation on the PbS CQD occupied and unoccupied electronic structure by additionally studying films of CQDs that have been passivated with CdCl₂ or PbCl₂ during synthesis. We find that trap states are indeed affected by the passivation scheme used, as suggested by recent computational and charge transport studies. We find that halide ligands reduce deep trap states, and we find from IPES that the nature of the metal cation at the CQD surface determines the shallow trap state density near the conduction band edge. We relate these findings to devices by measuring the electron mobility in the various samples: we observe improved electron mobility when the density of shallow conduction-band associated traps states is decreased with the aid of the best cation. Finally, we show that the PES-measured reductions in midgap and shallow trap states due to metal halide passivation ultimately result in improved photovoltaic device efficiency.

5.2 Spectroscopy results

Complete electronic structures of MPA- and hybrid-passivated PbS CQD films obtained by a combination of PES and IPES are shown in Figure 5.1, accompanied by schematic representations of the corresponding quantum dots (Figure 5.1a). As seen in Figure 5.1b, a broad feature exists deep in the valence band of the PbS-MPA-only sample. In contrast, both halide-passivated samples show significant changes in the structure, with spectral features at 1.8, 3.8, 6.4 and 8.5 eV becoming more pronounced with narrowed energy width, closely resembling the detailed valence band structure of single crystal samples. The broad feature of the PbS-MPA-only sample, between approximately -9 and -5 eV, may be due to excess carbon from organic ligands, as previously measured by XPS, and in agreement with literature reports. During the metal halide passivation step, a fraction of long-chain oleic acid ligands are displaced which results in the suppression of carbon signals seen here. To validate further these assignments, we calculated the density of states (DOS) obtained using density functional theory.
for a PbS CQD capped with MPA and Cl (Figure 5.1b). The broad feature is aligned with carbon and oxygen related peaks of the MPA ligands. Chlorine is found to have a large contribution in the valence band, explaining the prominence of the 3.8 eV feature in the halide-passivated samples.

**Figure 5.1:** a) Combined PES (left, showing valence band structures) and IPES (right, showing conduction band structures) spectra of PbS CQD films with different passivation schemes. b) DFT calculated density of states for a 2.4 nm PbS CQD passivated with MPA and Cl ligands. The colors show the contribution from each element.
The relevant region of interest for the operation of photovoltaic devices comprises the band gap and the band edges where charge transport and trapping occur. Therefore, in Figure 5.2 we focused on the changes in the valence band edge (Figure 5.2a) and the conduction band edge (Figure 5.2b) caused by different passivation schemes.

**Figure 5.2:** a) Magnified view of the valence band edge as measured by PES. Halide passivation reduces the density of band edge and midgap states, but there is no significant difference between the PbCl$_2$ and CdCl$_2$ treated samples. b) Magnified view of the conduction band edge as measured by IPES with the spectra offset for clarity. The density of states in the band edge tail is reduced by halide passivation and further reduced upon cadmium incorporation. c) Integrated intensity of tail states in (b), in area bounded by curve and dotted lines.

Investigation of the PES derived spectra (Figure 5.2a) shows a significant change associated with the halide passivation. The density of states at the Fermi level is appreciably reduced compared with the PbS-MPA-only film, demonstrating the role of surface halides in reducing
deep traps states. Notably, the valence band edge states do not change appreciably between PbCl$_2$ and CdCl$_2$ treated CQDs. We have also observed changes in the absorption spectra of the CQDs following metal halide passivation (Figure 5.3), with an improved excitonic peak sharpness. The cause of this is unclear at the moment, but we speculate it is passivation related rather than due to improved monodispersity.

As seen in Figure 5.2b, there is a slight shift of the conduction band edge towards the Fermi level for both the halide passivated samples compared to MPA-only passivation. This is consistent with the view that chloride can protect the surface from oxidation,\textsuperscript{27} with oxygen acting as a p-type dopant.\textsuperscript{28,29} Previously, it was shown that there are not substantial enough changes in doping to explain the improvement in device performance.\textsuperscript{1} More striking is the marked difference in the tail states at the conduction band edge, measured by integrating the measured PES signal beyond the band edge (Figure 5.2c). In the PbS-MPA-only sample, a large tail persists past the band edge, which prevents efficient splitting of quasi-Fermi levels, for photo-generated charges are consumed in filling of these states, leading to sub-optimal open circuit voltage ($V_{OC}$). In comparison, the relative density of states for the CdCl$_2$ passivated sample is dramatically reduced to just 40% compared to the PbS-MPA-only sample; however, this effect is less prominent with the PbCl$_2$ treatment, with a reduction to 70% relative to the PbS sample.
Figure 5.3: Solution phase absorption spectra of CQDs before and after cadmium chloride passivation treatment. A modest sharpening of the excitonic peak is observed with a small red shift.

This finding suggests that while the halide ligands are efficient at passivating deep traps, the nature of the cations on the quantum dot surface is crucial for the reduction of shallow traps. However, a direct experimental probe of conduction band edge states has not been presented. Here, the IPES spectra clearly show that Cd prevents formation of shallow, surface-associated trap states that arise from Pb termination of the CQDs. We note that these measurements probe ensemble characteristics of the CQD film and therefore, states with much lower populations may not be visible. These may include localized small bandgap inclusions – due to larger diameter quantum dots – that could also act as efficient recombination centres. However, the ensemble characteristics are useful for examining the effect of passivation on similarly monodisperse populations of CQDs.
5.3 Correlation with device performance

To relate these fundamental measurements of the electronic structure of CQD solids with device performance, we built depleted-heterojunction solar cells\textsuperscript{1,22} employing the three different classes of CQDs studied above. The device structure consists of a fluorine-doped tin oxide bottom electrode, a TiO$_2$ n-type electron extracting layer, a CQD film approximately 300 nm in thickness, and a top electrode of MoO$_3$/Au/Ag.

We studied electronic transport in these devices using the photocurrent transient method.\textsuperscript{30} By measuring the transit time – the time for photocurrent to decay to $1/e$ of its maximum value - across a range of applied biases, we were able to probe the mobility of the limiting charge carrier.

Figure 5.4 shows the fit of transit time as a function of bias for each sample. As expected, the mobilities for the halide passivated samples are both improved over the solely MPA passivated sample. The PbS-MPA-only sample exhibited a mobility of $7.2 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, while the addition of chloride through PbCl$_2$ resulted in a doubling of the mobility to $1.4 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. The CdCl$_2$ treated film also shows a modest improvement over the PbCl$_2$ film, with a measured mobility of $1.9 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$. This trend in mobility would be expected to arise from a reduction in transport inhibiting shallow trap states, as was seen in the IPES results. This implies that minority carrier mobility is indeed the limiting mobility in this type of device and that electrons are the probed carriers in photocurrent transient measurements on the films measured herein.
Mobility in CQD films is also affected by interparticle spacing.\textsuperscript{31} We therefore investigated whether nanoparticle spacing could be playing a role in the findings on transport. Synchrotron-based grazing incidence small angle X-ray scattering (GISAXS) has been used to determine the average centre-to-centre distance of nanocrystal films.\textsuperscript{1,32,33} We measured a representative film for each passivation method and found, as shown in Figure 5.5, that the average spacing was approximately the same for all MPA treated films, regardless of chloride or cadmium incorporation. Both halide treated films were found to have a spacing of 3.2±0.2 nm, while the PbS-MPA-only sample had a spacing of 3.0±0.1 nm, equal within error from these measurements. Even though the average interparticle distance in Figure 5.5 appears slightly smaller for the PbS-MPA-only sample, this would be expected to improve coupling and boost the measured mobility. However, the metal halide samples still show much improved transport. From this we conclude that the differences in mobility among the different samples are attributable principally to differences in electronic structure resulted from the different surface passivation and not the interparticle spacing.

**Figure 5.4:** The square of film thickness, d, divided by photocurrent transient derived transit times as a function of bias. The linear fit is used to calculate the limiting mobility of each film as shown in the legend.
Figure 5.5: Azimuthally integrated GISAXS intensities give the average particle spacing; the average spacings are found to be the same for all passivation schemes in this study. The spectra are offset for clarity; differences in peak definition are due to slight differences in sample alignment.

The performance of solar cells using these films was also evaluated and the resulting current density vs. voltage curves are shown in Figure 5.6. The halide passivated films showed a significant improvement in performance relative to the purely organic-passivated device. In particular, the reduction in subgap states results in an improved $V_{OC}$, with the CdCl$_2$ passivated sample demonstrating the largest voltage at open circuit conditions. Transport is improved due to enhanced mobility and increased lifetime as a result of better passivation. The improvements in charge transport are also manifested in the improved current extraction from the halide passivated devices.
In summary, we used photoelectron spectroscopy to map the full electronic structure of PbS CQD films and observe the effects of different passivation strategies on device relevant states in the vicinity of the band gap. We find that halide passivated films have a drastic reduction in states in the midgap as measured both by PES and IPES, which contributes to the improvements in device performance. Interestingly, a reduction is also seen in conduction band tail states when using CdCl$_2$ instead of PbCl$_2$, confirming the role of surface cations in preventing shallow trap formation. Short circuit current transient spectroscopy confirms that charge transport is improved in halide passivated films and device studies demonstrate the benefits to photovoltaic performance. This study provides a platform for investigating the electronic structure of CQD films, including direct evidence for the formation of detrimental deep and shallow trap states, as well as motivation for reducing their density. Further progress in advancing CQD photovoltaic performance will involve careful surface management to avoid these trap states, potentially through identification of better ligand materials or even passivating shells which have helped in light emission applications but have thus far limited carrier transport in photovoltaic applications. The effect of the metal cation in altering the electronic structure is an interesting finding, and the mechanism is explored in depth in the next chapter.

**Figure 5.6:** Experimental J-V curves of devices under simulated AM1.5G illumination.
5.4 References


Chapter 6
Bond Adaptability of Surface Cations

This chapter contains work reproduced in part with permission from “The role of bond adaptability in the passivation of colloidal quantum dot solids”, published in *ACS Nano*, 7, 7680-7688, (2013). Copyright 2013 American Chemical Society. I was co-first author and contributed to all experimental design, data interpretation and writing. Density functional theory calculations were performed by O. Voznyy, and CQD synthesis was performed by L. Levina.

6.1 Introduction

In the previous chapters, a new surface passivation approach for CQDs was presented and the effect on the electronic structure was explored. Ligand choice has long been known, as expected, to influence electronic transport through the CQD solid,\(^1\)–\(^3\) both for reasons of passivation and internanoparticle spacing. For instance, mobilities well over 1 cm\(^2\)/Vs have been demonstrated in nanocrystal films.\(^4\)–\(^7\) Additionally, the doping of quantum dots has attracted significant interest recently for development of novel devices such as those leveraging inherently-matched quantum junctions, and improved potential gradient profiles favoring charge extraction.\(^8\)–\(^11\) These new devices have been enabled by an enhanced understanding of how overall stoichiometry in the quantum dot solid, taking into account both ligand and nanocrystal material, determines the net doping and electronic properties of the final film.\(^12,13\)

Inorganic strategies based on a complete semiconductor shell surrounding the nanoparticle core have long been pursued.\(^14\)–\(^16\) Growth of an appropriate shell material has been used to improve luminescence properties\(^17\) and suppress blinking and Auger recombination.\(^18\)–\(^20\) Unfortunately, when the goal is excellent passivation combined with superior charge transport, the strategy of employing a thick shell achieves the first, but militates against the second priority.
It was found that a full shell is not, in fact, necessary to achieve beneficial influence on quantum dot passivation. Early hints of this possibility came in the form of pioneering solution-phase ligand exchanges involving halide adjustment\textsuperscript{21,22} as well as investigations of stoichiometry adjustment\textsuperscript{23,24} due to the enhanced surface availability and flexibility afforded by solution-phase approaches.

The relevance of inorganic halide passivation to devices and performance came when all-inorganic colloidal quantum dot solids, and solar cells based thereon, were reported in 2011.\textsuperscript{25} The joint role of organic bidentate linkers in forming densely-packed films, and both cationic and halide inorganic passivants, in achieving lowered trap state densities and improved transport, was demonstrated in Chapter 4.

Metal cations on the surface have been shown to have an effect on net nanocrystal surface charge and photoluminescence efficiency.\textsuperscript{26} Mechanistically, the role of a submonolayer of inorganics at the surface has been explained \textit{via} its capacity to prevent, or reform, deep electronic trap states.\textsuperscript{27} Interestingly, initial experiment\textsuperscript{28} and theory\textsuperscript{27} both indicate a role for both the halide, and also for the metal cation, in passivation and thus performance. The previous chapter revealed that, while the halide served to reduce deep traps, a change in metal cation resulted in suppression of shallow trap states.

In this chapter, we sought to build a more thorough understanding of the role of metal cations introduced to the surface of colloidal quantum dots and investigate their impacts on the performance of photovoltaic devices. The work includes a suite of experimental studies in which we vary the identity of the cation and investigate its impact on electronic materials parameters, such as mobility and trap state density, and ultimately on device performance. We finish with a
density functional theory-based exploration of reasons why the identity of the cation has such a large impact on trap state passivation and consequent device performance.

6.2 Outline of Passivation Scheme

We focused on inorganic passivation implemented in the solution phase, prior to film formation. We took this approach since this process architecture had led to the highest solar cell efficiencies reported to date based on CQDs. Carrying out the treatments in the solution phase offers a high degree of accessibility to the surface by prospective inorganic passivants, maximizing the opportunity to remedy surface trap states.

The approach is depicted in Figure 6.1. The first portion of the synthesis is standard: a solution of PbO, oleic acid and octadecene (ODE) is heated to 130°C (Figure 5.1i). Rapid injection of bis(trimethylsilyl) sulfide (TMS) in ODE into the flask causes nucleation of PbS quantum dots capped with oleate ligands (Figure 5.1ii). The solution is then allowed to cool while the CQDs grow to the desired size (Figure 5.1iii).

Next is implemented the metal-halide treatment that is the subject of this study. During the growth phase, a small volume of a metal chloride (MClₙ) dissolved in oleylamine is rapidly introduced. It has been proposed that chloride ions are able to passivate sites that organic ligands are unable to reach in light of steric hindrance or unfavorable surface topology, thereby reducing surface-associated electronic trap states. This results in CQDs which are capped with both chloride and oleate ligands and which retain colloidal stability.
Figure 6.1: The CQD synthesis procedure including the metal halide passivation process. (i) A solution of PbO, oleic acid (OA) and ODE is heated to 130°C. The magnification box depicts lead oleate in solution. (ii) Bis(trimethylsilyl) sulfide (TMS) in ODE is added, causing nucleation of PbS quantum dots capped with oleic acid ligands. The magnification box shows a schematic of a CQD with surface Pb atoms capped with OA. (iii) As the solution cools, 1.0 mL of a solution of MCl\textsubscript{x} (where M is a metal cation) in oleylamine is added quickly, typically once the CQD solution reaches a temperature of 80°C. This results in a partial exchange of oleate for chloride ligands and the incorporation of M cations into the quantum dot surface as seen in the magnification box.

Metal cations have been reported to incorporate by binding to exposed sulfur atoms on the CQD surface in sub-monolayer amounts (1-20% relative to Pb). The high Pb:S ratio in the as-synthesized CQDs suggests that the surfaces are, by and large, predominantly cation-rich. Thus, the new metal cation is likely replacing the original surface Pb by adsorbing to the surface during growth in lattice sites typically occupied by Pb.
6.3 Development of Passivation Strategy

We now describe the development of the metal halide passivation strategy using the prototypical cadmium-based method as an example. In particular, we were interested in learning how the true extent of surface passivation, measured through both luminescence and device performance, was influenced by the incorporation of halide atoms and metal cations. In the suite of treatments explored, we systematically adjusted the concentration of the halide salt in the precursor solution up to the solubility limit (0.86 M) while keeping the volume ratio of the added precursor constant.

The passivation extent in the solution-phase was monitored using photoluminescence quantum efficiency (PLQE) measurements. PLQE measured in the solution-phase serves as a proxy for the extent of passivation extent since, in the colloid, the quantum dots are kept well-separated; in contrast, in the film-phase, the PLQE is very strongly affected by transport. As seen in Figure 6.2, a low concentration of CdCl₂ precursor results in a PLQE of approximately 20%. At cation precursor concentrations of 0.3 M or above, the PLQE is increased to above 30%, indicating a significant enhancement in surface passivation. The PLQE approximately saturates at these precursor concentrations, indicating that in this treatment protocol, there is no further benefit from a surface-passivation perspective in introducing greater amounts of metal-halide precursor. We hypothesize that this is due to a saturation of the surface binding sites available to chlorine anions as the ions are not able to efficiently lead to the removal of bound oleate ligands. Some oleate ligands are likely replaced by chloride ions due to an equilibrium process as the ligands bind and unbind. We note that the specifics of the concentration and surface coverage at which this point of diminishing returns is reached are very likely tied to the details of the strategy, in which a finite quantity of surface sites are accessible to balance passivation and colloidal stability.

We carried out a series of electronic, materials, and photovoltaic device studies using films processed from the same suite of solution-treated samples described above. We used these
devices to monitor several film-phase performance metrics as a function of metal-halide precursor concentration, including the limiting (minority) carrier mobility, midgap density of states, and photovoltaic power conversion efficiency. All measurements were performed on photovoltaic devices utilizing the depleted heterojunction architecture.³⁰

![Graph showing PLQE vs. CdCl₂ concentration](image)

**Figure 6.2:** PLQE vs. CdCl₂ precursor concentration showing some saturation with increasing concentration.

With the goal of measuring the photocarrier mobility, we obtained photocurrent transients for devices made from several batches of CQDs employing different metal-halide passivation. A 640 nm pulsed diode laser with an illumination density set to approximately 1 sun in intensity (100 mW/cm²) was used to excite photocarriers in the device. Effective transit times (the time for current to decay to 1/e of the peak value) were obtained as a function of net bias. With knowledge of film thickness, we used transit time vs. average field to extract the limiting carrier mobility for films based on different solution-phase precursor concentrations.
The mobility, calculated using photocurrent transient measurements and plotted in Figure 6.3, shows an upward trend relative to increased CdCl₂ precursor concentration. This suggests an improvement of transport within the CQD film. Notably, the power conversion efficiency saturates at CdCl₂ concentrations above 0.3 M in spite of the increased mobility as shown in Figure 6.4. This suggests that the mobility must exceed ~ 1x10⁻³ cm²/Vs in order for maximum device performance to be obtained, but that, once this mobility threshold is cleared, another performance-determining mechanism then begins to dominate.

**Figure 6.3:** Mobility vs. precursor concentration.
Figure 6.4: PCE vs. precursor concentration shows saturation with concentration, indicating that trap density (as quantified by PLQE and photovoltage transient measurements) plays a more determinative role in device performance than carrier mobility.

With this in mind, we also characterized the midgap density of states (DOS) in devices fabricated with CQDs utilizing various CdCl\textsubscript{2} precursor concentrations (Figure 6.5). The DOS was obtained using the photovoltage transient method.\textsuperscript{28,31,32} An 830 nm diode laser provides a constant light bias and a pulsed 640 nm diode laser modulates the open circuit voltage (V\textsubscript{OC}). By measuring the change in V\textsubscript{OC} and the total generated charge for each perturbation across a wide range of light-bias intensities, we are able to extract the DOS as a function of energetic depth within the bandgap of the quantum dot solid.
Figure 6.5: Density of states for different precursor concentrations determined by photovoltage transient measurements, showing saturation with increasing concentration.

The results show that the DOS for devices using CQDs with 0.3 M or higher CdCl₂ precursor concentration are all very similar, while lower concentrations clearly show greater DOS deep within the gap. This correlates well with the current density vs. voltage curves shown in Figure 6.6 and the PCE saturation behavior seen in Figure 6.4. We conclude that further progress in deep trap passivation is the performance-limiting mechanism once the mobility exceeds the 1x10⁻³ cm²/Vs threshold.
Figure 6.6: Current density-Voltage curves for devices made using CQDs with different precursor concentrations of CdCl₂.

6.4 Effect of Cation Species

Focusing on a single metal chloride, and varying its concentration, we were able to establish the importance of the passivation of deep traps in CQD solids. We sought then to explore how the identity of the metal cation influences passivation and performance.

We screened a wide range of cations with an eye towards maximizing photovoltaic device performance. All of our studies used chlorine as the anionic passivant for consistency and to exclude the effects of varying the anion type on photovoltaic device metrics. We followed the general synthesis optimization procedure described for cadmium above for each of the different metal cations tested. Each cation passivation type was tested with various synthesis conditions. Each of the characterization metrics described in Figure 6.7 was correlated with device performance for the specific batch, and therefore some PCE values are different for the same cation in each panel.
Figure 6.7 shows the correlation of device performance with solution-phase photoluminescence quantum yield, film mobility and film density of states for the different cation passivation types. As seen in Figure 6.7a, the device power conversion efficiency is correlated with solution-phase photoluminescence quantum yield, suggestive that the benefits of passivation during solution-phase treatment are at least partially transferred to the final films following the solid-state ligand exchange. Points for slightly different CQD batches utilizing the same metal-cation passivant show variation in both PLQE and PCE, and the correlation of PCE with PLQE remains consistent across cation types, and is well-correlated for a given cation species as well, indicating the strong predictive value of this metric.

In contrast, the mobility of charge carriers in films, as measured using the photocurrent transient method, shows a saturation of power conversion efficiency with increasing mobility for the different cation types, as can be seen in Figure 6.7b. Cation type has a relatively strong effect on mobility which does not necessarily correlate with photovoltaic device performance. Cation type also has a strong effect on the midgap density of states measured through the photovoltage transient method: in Figure 6.7c, we plot power conversion efficiency as a function of the open-circuit voltage at which a $5 \times 10^{16}$ cm$^{-3}$/eV threshold has been reached.

From these studies, it is clear that the midgap density of states is the strong determinant of device performance, and that mobility must simply satisfy a similar threshold to that reported in the CdCl$_2$ study above.
Figure 6.7: (a) Correlation of PLQE (determined by passivation extent) with device performance. Different batches of CQDs employing the same metal cation passivant under different synthesis conditions show a positive correlation of device performance with PL
quantum yield. (b) Mobility for different cation processes determined by photocurrent transient measurements. PCE shows saturation behavior with increasing mobility. (c) Midgap density of states for different cation processes determined by photovoltage transient measurements (inset) and correlation of PCE with DOS threshold edge.

In general, most metal chloride passivation variants produced an increase in device performance compared to CQDs that utilized a solid-state ligand exchange only. The identity of the cation was an important factor, with certain cations – notably Cd, Ca, and Zn – leading to the best device performance. We next sought to understand the origin of this variance to determine the mechanistic source of the improved passivation and performance.

We performed X-ray photoelectron spectroscopy (XPS) measurements to quantify both the amount of chlorine and amount of metal cation incorporated into our quantum dots in the film phase. The variation of power conversion efficiency with anion incorporation extent (measured relative to the amount of lead) for the different processes is presented in Figure 6.8. Although the amount of chlorine varied over a relatively large range, the power conversion efficiency saturated with increased chlorine film incorporation. Clearly, some chlorine incorporation is beneficial for device performance, but it does not fully account for the observed variation in efficiency as a function of cation type. The amount of cation incorporation also varies over a wide range for different metal types but displayed no predictive effect on device performance.
This observation suggests that the cation *type* plays an important role in surface passivation; and that even a relatively low concentration of the most desired cations can have a significant beneficial impact. We sought to investigate the role of cation type in surface passivation, for which we turned to density functional theory (DFT) simulations.

Using DFT, we calculated the electron affinity of each type of cation that we had tested experimentally. Shallower cation electron affinity is expected to shift the undercoordinated cation dangling bonds deeper into the conduction band, providing better passivation. Simulations of cations adsorbed on the CQD surface were performed but, because of interaction with PbS orbitals, each cation’s contribution was observed to spread to a wide range of energies, and could not provide a single numerical value to be used as a metric.
Figure 6.9: PCE vs. the electron affinity of the metal chloride molecule calculated via Density Functional Theory. There is a weak correlation of PCE with chloride electron affinity. The dotted lines are guides to illustrate the trend.

We therefore calculated the electron affinities of the corresponding metal chlorides, which we chose to mimic the likely binding configurations of the cations on the CQD surface. The results of the calculations are plotted in Figure 6.9. The experimental power conversion efficiency shows a weak correlation with chloride electron affinity. This correlation is maintained even when XPS shows minimal incorporation of the cation itself on the CQD surfaces.

Molecular dynamics simulations on quantum dots with cations bound in several different starting geometries to help explicate this trend further. In particular, the effect of coordination on the electron wave functions and density of states was studied. The results of calculations for surface cadmium atoms are shown in Figure 6.10a, and the corresponding results for lead are shown in Figure 6.10b. Due to the lower ionicity of Cd and the more covalent nature of Cd-S bonds, tetrahedral coordination is preferred over the rocksalt structure. Cadmium is stable on the
surface for binding geometries involving 4, 3, (Figure 6.10a, left) and even 2 neighbors, adopting $sp^3$, $sp^2$ and sp orbital hybridizations, respectively. Conversely, the rocksalt structure of PbS requires Pb to have a total of six bonds to be fully coordinated (Figure 6.10b, left). Therefore, neither Cd-3 (three-fold coordinated) nor Cd-4 (four-fold coordinated) contributes significantly to the conduction bandedge, as can be seen in the density of states plotted in Figure 6.10c, right, while undercoordinated Pb-4 and Pb-3 contribute significant amplitude to the conduction bandedge, and this contribution is in the form of increased surface-like states.

The contribution of certain metal cations to the conduction band edge explains the moderate dependence of device performance on the metal chloride electron affinity. Surface metal chlorides with shallow electron affinities, such as Cd and Ca, contribute states that fall deep within the conduction band (Figure 6.10a, middle), whereas surface metal chlorides with deep electron affinities such as Pb and Sn can contribute states that fall much closer to the conduction band edge. These states associated with undercoordinated atoms display a partial surface-like character (Figure 6.10b, middle). Such surface contributions shift the band edge energy, shrinking the bandgap. On a CQD film scale, quantum dots with strong surface contributions are responsible for Urbach tails,\textsuperscript{33,45} also contributing to broadening of the first absorption peak in solution. If surrounded by well-passivated dots, a dot with undercoordinated surface atoms would act like a shallow trap and inhibit transport.

We propose the following term to describe this behavior: bond adaptability. Cd can adapt to passivate a wide variety of surface geometries. It can do so without creating partially-filled dangling bonds. Cd therefore outperforms Ca, which in spite of having a shallower electron affinity is in fact more ionic, thus requiring six-fold coordination and still contributes to the bandedge when it has only 3 neighbors.
Figure 6.10: (a) Left to right: binding configuration of Cd on the surface of a PbS CQD with 4 neighbors (top) and 3 neighbors (bottom); the surface of a CQD with Cd incorporated showing that neither Cd-3 nor Cd-4 contribute to conduction band edge-associated surface states (red); electron density map showing the core-like nature of the conduction band edge states; a density of states plot showing that Cd-associated states are well within the conduction band. (b) Left to right: binding configuration of Pb on the surface of a PbS CQD with 4 neighbors (top) and 3 neighbors (bottom) having more dangling bonds than Cd; the surface of a CQD showing the significant contribution of Pb-3 to the conduction band edge-associated surface states; electron density map showing the partial surface-like nature of the conduction band edge states; a density of states plot showing the contribution of Pb-associated states to the conduction band edge.

This picture may explain superior photoluminescence quantum yield in solution, where Cd can find and then occupy sites most in need of passivation. Its role is likely of considerably greater importance during the formation of CQD films. The widely employed solid-state ligand exchange is a disruptive process, involving as it does protic attack on the oleate bound to the nanoparticle surface, followed by replacement with the more strongly-bound bidentate linker. One can readily envision that some sites of oleate removal could remain unpassivated in the sudden (completed in a matter of a few seconds) MPA treatment; or, worse still, that Pb-oleate could be removed, leaving unpassivated a previously-Pb-terminated chalcogen site. An
abundance of adaptable Cd in the film may aid in repairing those sites, facets, and geometries most urgently in need of repassivation. These findings illustrate the importance of a multi-pronged materials approach towards increasing the efficiency of CQD-based optoelectronic devices.

Having now developed and studied a passivation scheme for optimal single-junction bandgap CQDs, the next chapters aim towards optimal spectral usage for efficient solar harvesting.
6.5 References


Chapter 7
Visible Spectrum Absorbing Perovskite Solar Cells

This chapter contains work found in “A two-step route to planar perovskite cells exhibiting reduced hysteresis”, published in Applied Physics Letters, 106, 143902 (2015), reproduced with permission from AIP Publishing. I was first author and contributed to all experimental design, data interpretation and writing.

7.1 Introduction

In the previous three chapters, the passivation of CQDs was studied for the case of single-junction photovoltaic applications. During the course of those studies, a new materials system emerged that achieved very high efficiencies through strong absorption in the visible spectrum.

This material, organolead halide perovskite, has garnered significant interest in light of the rapid rise in photovoltaic (PV) power conversion efficiency (PCE). Building on early reports of promising device performance,\(^1\)–\(^4\) the certified efficiency has now reached over 20%.\(^5\)–\(^6\) This is comparable to vacuum deposited thin film solar cells (such as CdTe), but, remarkably for such efficiencies, perovskites are amenable to low-temperature solution processing.\(^7\)–\(^9\)

Efficient perovskite devices have been developed in many configurations, including both as planar films\(^10\) and with perovskite infiltrated into mesoporous scaffolds of titania,\(^11\) alumina,\(^12\) nickel oxide\(^13\) or zirconia.\(^14\) These structures have been used with conventional materials stacks on TiO\(_2\) and with organic photovoltaic (OPV) style inverted structures.\(^15\) While the most efficient devices are currently mesoscopic in nature, planar films are of interest due to their relative processing simplicity as well as their potential in other non-PV applications such as photodetection and photoemission. However, one-step processing of uniform and pinhole-free planar films has been found to require stringent processing conditions.\(^16\) A two-step
interdiffusion approach has recently been shown to result in high quality films in an OPV-style structure.\textsuperscript{17}

Unfortunately, planar devices have also been shown to be more susceptible to hysteretic effects\textsuperscript{18,19} which have been attributed to the migration of ions within the perovskite film.\textsuperscript{20,21} The ionic current can arise due to unpassivated trap states that are found at perovskite grain boundaries due to non-ideal formation conditions.\textsuperscript{22} Various schemes have been developed to reduce the effect of these dangling bonds by application of passivants at the film interfaces\textsuperscript{23,24} and within the film.\textsuperscript{20} Indeed, fullerenes have been found to passivate these trap states efficiently and reduce hysteresis in perovskite devices.\textsuperscript{20,25,26} Intriguingly, inverted (or OPV style architecture) perovskite cells typically use PCBM as an electron extracting layer and tend to have low hysteresis.\textsuperscript{27,28} Here we aimed to build efficient planar conventional architecture perovskite solar cells through a two-step interdiffusion route using a phenyl-C\textsubscript{61}-butyric acid methyl ester (PCBM, a fullerene derivative) interfacial layer to reduce hysteresis.

![Fabrication process used in this work.](image)

Figure 7.1: Fabrication process used in this work. (a) PbI\textsubscript{2} is deposited on the TiO\textsubscript{2} substrate followed by casting of a methylammonium halide solution. Perovskite is formed at the interface between the two layers. Upon annealing, the precursors interdiffuse and the complete perovskite
film is formed. (b) Electronic band structure of the device. Electrons are extracted through the TiO$_2$ while holes are extracted through the Spiro-OMeTAD layer.

The process used is depicted in Figure 7.1(a). Fluorine-doped tin oxide (FTO) substrates were coated with a 50 nm TiO$_2$ compact layer deposited by sputtering in an Angstrom Engineering Åmod deposition system and followed by a TiCl$_4$ treatment described previously. For devices using PCBM interfacial layers, a 10 mg/mL solution of PCBM dissolved in chlorobenzene was cast on top of the TiO$_2$ at 4000 rpm. PbI$_2$ was dissolved in dimethylformamide (DMF) to a 0.8 mol/mL concentration and methylammonium iodide (MAI) was dissolved in isopropanol (IPA) at 0.25 mol/mL. Both the substrates and the PbI$_2$ solution were heated to 65°C. 80 µL of the PbI$_2$ precursor was spin-cast onto the hot substrate at 6000 rpm and the film was left to dry at 65°C for 5 minutes. The substrate was cooled to room temperature, after which 100 µL of the MAI solution was cast while the substrate was spinning at 3000 rpm. This led immediately to a darkening of the film as perovskite was formed at the interface of the two precursors. To form the perovskite fully, the film was dried at 70°C for 10 minutes, then ramped to 90°C for 15 minutes and finally at 125°C for 12 minutes to encourage crystal growth. Spiro-OMeTAD was dissolved in chlorobenzene at 63 mg/mL and doped using 20 µL/mL of tert-butylpyridine and 70 µL/mL of an acetonitrile solution containing 170 mg/mL bis(trifluoromethane)sulfonimide lithium salt. This solution was filtered and spin-cast at 4000 rpm after the films had cooled. To form the top contacts, 100 nm of gold was deposited through a shadow mask by e-beam evaporation. The electronic structure of the device is displayed in Figure 7.1(b), with the TiO$_2$/PCBM serving as the electron-extracting electrode and the Spiro-OMeTAD serving the same purpose for holes.

### 7.2 Perovskite Film Formation

Though perovskite was formed, the films were visibly hazy and in our initial tests the devices were often short-circuited. This suggested that poor morphology was preventing full coverage of each device layer and resulting in non-selective charge carrier extraction.
We used scanning electron microscopy (SEM) to verify this hypothesis. Since the haziness occurred as the MAI solution was deposited, we first inspected a sample immediately prior to the annealing step. Surprisingly, the film did not consist of a flat MAI layer on top of PbI$_2$, as shown in Figure 7.2(a); instead, large micron-scale protrusions from the surface of the film were observed. These dramatic features are much larger than the combined thickness of the device layers. As seen in the 45° view of Figure 7.2 (c), many of these features are distributed over the film, resulting in large nonuniformity. Rapid reaction of the precursors may lead to perovskite growth over droplets of MAI solution as the IPA is evaporating. In some cases the solution is pushed upwards as the perovskite grows, leading to the structures seen in Figure 7.2 (a). Following the annealing process, the structures are not as apparent but result in large morphological variations throughout the film, as shown in Figure 7.2 (e).

**Figure 7.2:** Scanning electron micrographs of the perovskite films formed with and without chlorine inclusion. (a,b) Cross sectional view of the films of PbI$_2$ and either (a) MAI or (b) MAI and MACl, both prior to annealing. (c) 45° view of the iodide only film prior to annealing. (d)
45° view of the film with chlorine inclusion prior to annealing. (e) 45° view of the iodide only film after annealing. (f) 45° view of the film with chlorine inclusion after annealing. Inset: close-up view to show grains.

Since these poor morphologies showed poor performance, we sought to control the crystallization of the film by adding chlorine into the process. The addition of chlorine as a precursor has been shown to improve electronic properties of perovskites, even though it is not detected in the final product.\textsuperscript{22,31,32} Chloride is also known to aid formation of high quality perovskite films by controlling crystallization.\textsuperscript{33,34} We took the view that this would be particularly helpful for the two-step interdiffusion method to maintain uniform growth from the interface between the precursors. We introduced Cl in the form of methylammonium chloride (MACl, prepared according to literature methods).\textsuperscript{32} A 0.25 mol/mL solution of MACl in IPA was produced and mixed with the MAI solution at a ratio of 2:1 (MAI:MACl). The mixture was then used in place of the MAI solution in the film preparation.

Notably, the film formed following deposition of the precursors was specularly reflective, in contrast to the diffuse reflectance of the films prepared using iodine only. SEM of the chloride prepared film, shown in Figure 7.2 (b), showed flat films with no apparent protrusions caused by rapid reaction. The unreacted precursors are apparent and evenly distributed. As seen from the 45° micrograph in Figure 7.2 (d), the film has long range uniformity. Finally, upon annealing, a dense perovskite film is formed, with crystallites in the range of hundreds of nanometers (Figure 7.2 (f)). In sum, through simple addition of a chlorine precursor, the morphology was drastically improved. Absorption and photoluminescence (PL) measurements confirmed that, for both precursor sets, MAPbI\textsubscript{3} perovskite was formed. As seen in Figure 7.3, the absorption onsets for both films are the same, and sharp PL peaks were observed. Notably, the film with MAI precursor had better absorption beyond 550 nm, likely due to the difference in morphology.
7.3 Device Performance

The improved dense and uniform perovskite films allowed us to build devices with a high yield. We proceeded to build solar cells and observe the effect of a PCBM interlayer. A Keithley 2400 source-meter was used to measure the current density-voltage scans of the devices under AM1.5G simulated solar illumination. Scans were recorded both for increasing and decreasing voltage to observe any hysteretic effects. The stability at the maximum power point (MPP) was determined by measuring the current density while the voltage was held at MPP as determined by the open-circuit to short-circuit scan. The source intensity was measured using a Melles-Griot broadband power meter and spectral mismatch was corrected for using a calibrated reference Si solar cell.
A J-V scan for a device with no PCBM layer is shown in Figure 7.4(a). It can be seen that there is a large discrepancy between the two scans in different directions due to the lack of passivation. While the open-circuit to short-circuit scan displays good short circuit current ($J_{SC}$), open circuit voltage ($V_{OC}$) and fill factor (FF), the reverse scan shows significant losses in all of these parameters. In contrast, the device with a PCBM interfacial layer (Figure 7.4(b)) demonstrates greatly reduced hysteresis.

The operation of a solar cell must be judged not be through J-V scans, but rather through constant power output at MPP conditions. Thus the efficiency of the cells in Figure 7.4 (a) and (b) were measured over time in order to approximate the expected efficiency of an operating device and eliminate the complications of hysteretic J-V curves. The device with no PCBM layer dropped nearly 50% from its initial value before settling at 6.2% PCE. In contrast, the addition of a PCBM interlayer resulted in a very stable PCE output at 11.1% PCE. The PCBM interlayer significantly reduces the hysteresis and leads to high efficiency devices due to improved passivation of the TiO$_2$/perovskite interface. It is likely that PCBM infiltrates somewhat into the relatively thin (250 nm) perovskite film and thus reduces internal traps while improving electronic extraction$^{20}$. The distribution of device performance can be seen in Figure 7.4 (d). Here we show the PCE of each device based on a static MPP scan to most fairly compare the performance. The use of the passivating PCBM layer increases the mean PCE from 4.4% up to 9.0% over approximately 30 devices.
Figure 7.4: Device performance of chloride derived perovskite films with and without PCBM layer. (a) J-V scans of a device with no PCBM interfacial layer. The arrows correspond to the scan direction. (b) J-V scans for a device with a PCBM interfacial layer demonstrating reduced hysteresis. (c) Static PCE scan with the voltage held at the MPP voltage. Open blue squares represent device with no PCBM, while closed red circles indicate the device with PCBM layer. (d) Distribution of device performance. For each box plot, the horizontal line represents the mean of the data set while the shaded box shows the standard error of the mean. The whiskers represent the standard deviation and each point is a different device.
To better understand the effect that the PCBM layer had on the device performance, we measured time-resolved photoluminescence decay curves (Figure 7.5(a) and (b)) of perovskite films on TiO$_2$ with and without a PCBM interfacial layer. Measurements were carried out on a Horiba FluoroLog-3 spectrofluorometer using a 504 nm pulsed laser diode excitation source and the emission was monitored at 770 nm. Without PCBM, the decay exhibits single exponential character with a decay time of 43.5 ns. Inclusion of the PCBM layer changes the decay to bi-exponential, with a fast component of 2.1 ns and a slow component of 74.5 ns. The addition of PCBM results in a remarkable increase in PL quenching, indicating very fast electron transfer to the PCBM. This improved extraction can prevent the accumulation of excess capacitive charge that leads to hysteresis.\textsuperscript{19} This explanation is supported by the observation of an increased hysteresis appearing at very fast scan rates when settling time is insufficient to eliminate the effect of stored charge, as shown in Figure 7.6. PCBM may also be passivating interface states that trap charge carriers, both at the junction\textsuperscript{26} and at grain boundaries.\textsuperscript{20} This result also serves to emphasize the importance of reporting the steady state power output, as in Figure 7.4(d), in order to avoid transient effects that can obscure actual device performance.

**Figure 7.5:** (a) Transient photoluminescence curves at 770 nm emission for perovskite films on TiO$_2$ with (red circles) and without (open blue squares) PCBM. (b) Semilog plot of transient PL measurements at short time scales to show fast decay behavior.
Figure 7.6: J-V curves of perovskite on TiO$_2$/PCBM with delay times of (a) 500 ms, (b) 100 ms, (c) 10 ms and (d) 1 ms. Each data point is taken at intervals of approximately 30 mV. The solid curves are measured from open circuit to short circuit conditions, and vice versa for the dashed curves.

In summary, we have demonstrated a method of producing efficient planar perovskite solar cells with high yield through morphological and interfacial improvements. Addition of a chloride precursor to the film fabrication results in a significantly more uniform film that prevents device short-circuiting. A PCBM passivation layer serves to significantly reduce the hysteresis that plagues many planar perovskite devices and results in a high, stable PCE. Furthermore, the technique should be extendable to other perovskite stochiometries, including those containing bromide or alternative organic compounds. This work provides a simple route to development of various planar perovskite solar cells which operate efficiently using visible wavelength photons. Such cells are prime candidates for use with infrared-absorbing CQDs.
7.4 References


Chapter 8
Broad Spectrum Solar Harvesting

This chapter contains work found in “Infrared Colloidal Quantum Dot Photovoltaics via Coupling Enhancement and Agglomeration Suppression”, under review at ACS Nano. I was first author and contributed to all experimental design, data interpretation and writing. Density functional theory calculations were performed by O. Voznyy, detailed balance calculations were performed by I. J. Kramer, conductivity measurements were performed by A. Kiani, and CQD synthesis was performed by L. Levina.

8.1 Introduction

In the previous chapter, a method of fabricating high efficiency perovskite solar cells was demonstrated. These cells have very high absorption in the visible region, but are unable to be tuned to absorb infrared. Like other technologies, this makes them a prime candidate for integration with infrared-sensitive quantum dots.

Silicon solar cells dominate solar photovoltaics (PV),\textsuperscript{1} with laboratory power conversion efficiencies (PCEs) that reach 25%\textsuperscript{2}. Thin film CdTe\textsuperscript{3} and CuInGaSe (CIGS)\textsuperscript{4} cells have also demonstrated high efficiencies and are commercially available. Emerging solution-processed PV materials such as polymers\textsuperscript{5} and dyes\textsuperscript{6} have been developed as lower cost alternatives. Most recently, solution-processed perovskite solar cells have gained significant attention as their certified efficiencies have rapidly increased to over 20%\textsuperscript{7–10}.

Each of these cells leave a large portion of the available solar spectrum untapped. Half of available photons reside in the infrared (IR), presenting a large opportunity to improve spectral utilization\textsuperscript{11}. High-efficiency III-V multi-junction cells absorb this region\textsuperscript{12} but require costly
wafer growth techniques and complex concentrator and tracking systems. Many low-cost solution-processed materials are transparent in this region, as even the narrowest-bandgap polymers and dyes have absorption onsets near 960 nm and 800 nm, respectively.\textsuperscript{[13,14]} Highly efficient perovskite cells have absorption onsets that are shorter than 850 nm.\textsuperscript{[15,16]}

Colloidal quantum dots (CQDs) are a solution-processed material that can potentially overcome these limitations. CQDs have a bandgap that is tunable via the quantum size effect. The absorption onset can be simply and precisely tuned across the solar spectrum.\textsuperscript{[17]}

Because CQDs are synthesized in solution, they are amenable to rapid, large-area fabrication on lightweight, flexible substrates.\textsuperscript{[18,19]} Performance advances have focused on the passivation of trap states\textsuperscript{[20–23]} as well as development of device structures for optical absorption enhancement.\textsuperscript{[24–26]} The efficiency of CQD cells has thereby been advanced to certified efficiencies approaching 10\%.\textsuperscript{[10,27]} In addition to their promise as single junction devices, CQD solar cells are attractive as a low-cost, IR-absorbing material that could be combined with other PV materials that lack infrared spectral response.

### 8.2 Bandgap selection

We begin using a detailed balance approach to select a CQD bandgap that will combine well with a variety of systems. Specifically, we considered crystalline silicon and methylammonium lead halide perovskite front absorbers due to their commercial ubiquity and rapid rise in efficiency, respectively. In Figure 8.1a bromide perovskite refers to CH\textsubscript{3}NH\textsubscript{3}PbBr\textsubscript{3}, while iodide perovskite refers to CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}. Figure 8.1b shows the available short circuit photocurrent density (\(J_{\text{SC}}\)) for CQD cells as a function of CQD bandgap for different front cells. Notably, there is sufficient light available to current-match to perovskites in a series-connected tandem, while the same is not true of the smaller-bandgap silicon cell. There is also enough subgap photocurrent available to current-match with the best polymer triple junction cells (10
mA cm$^{-2}$, not shown).\textsuperscript{28,29} The best-case open-circuit voltages (\(V_{OC}\)) are shown in Figure 8.1c, and the theoretically achievable PCE is shown in Figure 8.1d. The bandgap used for CQD solar cells with the best AM1.5 performance, 1.3 eV, is marked as \(E_g1\). The bromide perovskite allows a maximal additive CQD PCE with a bandgap in the range of 900 to 1300 nm, with a peak of 22 additive points at 1100 nm. The iodide perovskite peaks with approximately 12 power points for 1300 nm bandgap, noted in Figure 8.1d as \(E_g2\), with shoulders that extend from 1100 to 1800 nm. The silicon case also shows a local maximum at about 1300 nm (6 additive power point), though the peak PCE is achieved at 1770 nm, marked as \(E_g3\). The broad maxima in these curves arise due to the dips in the AM1.5G spectrum caused by atmospheric water absorption of sunlight. Decreasing the bandgap in these regions results in potential \(V_{OC}\) loss with insufficient benefit to \(J_{SC}\).
Figure 8.1: (a) Solar spectrum (black curve) with portions accessible to labeled material: orange is a lead-bromide perovskite, orange + brown is a lead-iodide perovskite and orange + brown + grey is crystalline silicon. Everything to the right of each absorption edge represents the available solar spectrum for any subsequent cells. (b-d) Detailed balance simulations for solar cells accessing the solar spectrum transparent to the front cells identified in (a) according to the same color scheme including (b) short-circuit current density ($J_{SC}$), (c) open-circuit voltage ($V_{OC}$) and (d) power conversion efficiency (PCE). Bandgaps of interest are marked here. $E_g^1$ corresponds to ~950 nm, the optimized single junction bandgap. $E_g^2$ corresponds to 1300 nm, the edge of a broad peak for the lead-bromide perovskite case, an absolute maximum for the lead-iodide perovskite case and a local maximum with little compromise to total efficiency in
the crystalline silicon case. $E_g^3$ represents 1770 nm, the optimal bandgap for integration with silicon.

### 8.3 Device Design

In light of these findings, we focused on developing the 1.3 μm bandgap ($E_g^2$) CQD solid. We built our devices based on the fully-developed depleted heterojunction structure. At first, a very thin layer of the polyethylenimine ethoxylated (PEIE) was spin-coated over the pre-etched indium-tin oxide (ITO) coated glass substrate, after which we apply a 50 nm-thick layer of TiO$_2$ nanoparticles (NPs). The PEIE/TiO$_2$ stack forms a low-temperature electron acceptor layer. We have found that PEIE not only makes the charge collection at the electrode more efficient through lowering the barrier between ITO and TiO$_2$ NPs, but also improves the adhesion of the TiO$_2$ and CQD layers substantially and hence yields a better quality film. A lead sulfide CQD film with a thickness of over 500 nm was used as the absorber. The thickness was optimized to maximize the absorption while allowing efficient charge collection.

Mercaptopropionic acid (MPA) was used to replace the poorly conductive, as-synthesized oleic acid (OA) ligands in a solid-state ligand exchange process. A thin layer of molybdenum oxide (MoO$_3$) was used as the hole collector. Gold and silver (140 nm combined) were used to form the top electrode. Figure 8.2 shows schematically the conduction bandedge density of states of the PbS CQD as a function of its absorption onset and compares it to the electron affinity of TiO$_2$ for the bandgaps of interest from Figure 8.1d. For the optimal CQD single junction bandgap ($E_g^1$), a favorable offset allows electron injection into the TiO$_2$ even for a broad distribution of bandedge states, while at $E_g^3$ a large barrier between the CQD conduction band and that of TiO$_2$ prevents electron transfer. The conduction bandedge of optimal $E_g^2$ or ~1300 nm PbS CQDs lies at the threshold of efficient electron injection: carriers in tail states would not be extracted.
Figure 8.2: Comparing TiO$_2$ and PbS CQD conduction band DOS with respect to CQD electron affinity/absorption onset at bandgaps of interest. Positive values for the offset (towards yellow) indicate a favorable injection of electrons from CQD conduction band into the TiO$_2$ acceptor. Negative values for the offset (towards blue) means there is a barrier for the electrons injecting into the TiO$_2$.

8.4 Ligand Scheme Design and Characterization

We were therefore particularly attentive to possible agglomeration of CQDs as these particles would have a narrower bandgap and their conduction band would lie below that of the electron acceptor. As shown schematically in Figure 8.3a (top), exposing the surface of adjacent CQDs during solid state ligand exchange can lead to fusing, creating larger nanoparticles with smaller bandgaps. We sought to prevent this following a recently reported strategy involving short thiol ligands introduced in solution.$^{23}$ Since these thiols remain tightly bound on the surface during solid state exchange, agglomeration can be prevented (Figure 8.3a, bottom).

Through density functional theory (DFT) modeling, we investigated how the liganding strategy affected the electronic landscape for carriers. The calculated density of states (DOS) for a PbS
quantum dot is shown in Figure 8.3b (i). The states introduced by mercaptopropionic acid (MPA) are shown in panel (ii), and their peak is near the valence bandedge of the CQDs, thereby providing a reduced barrier to hole transport. On the other hand, propane-thiol ligands only introduce states deep within the valence band and therefore militate against hole transport (panel (iii)). Thus, while they are able to prevent unwanted agglomeration, these ligands are expected to lead to poor interparticle conduction of carriers.

Figure 8.3: (a) Top: CQDs can fuse during solid state exchange as surfaces are left temporarily uncovered. Bottom: The bromothiol ligands sterically prevent the necking of adjacent nanocrystals during solid state ligand exchange. (b) The DFT calculated density of states for a ligand-covered CQD, separated into contributions from (i) the bare PbS quantum dot, (ii) MPA ligands, (iii) alkane thiol ligands, (iv) bromothiol ligands.

Interestingly, DFT also shows that the addition of a halide end group to the thiol ligand should prevent this problem. As shown in panel (iv), bromine-functionalized thiols introduce a large
DOS near the valance bandedge. Importantly, no detrimental midgap states arise from addition of these ligands to the quantum dot surface. DFT indicates that this bromothiol exchange should allow close proximity among CQDs while providing enough steric hindrance to prevent agglomeration, as shown in Figure 8.3a (bottom), and simultaneously reduce the interparticle barrier to hole transport by introducing of a large density of states near the bandedge.

Guided by these indications from theory, we made films of CQDs using different surface passivation schemes and investigated their effects through optical and electrical studies. All films were crosslinked using an MPA solid-state exchange. Due to the strong binding of the short thiols, it is not expected that MPA can displace them. The various ligand approaches used are shown schematically in Figure 8.4.

We first investigated the steady-state photoluminescence (PL) spectrum of each film (Figure 8.5a). One film had no solution phase ligand treatment, one involved a hybrid passivation approach using CdCl$_2$ solution-phase treatment, and the final film combined the CdCl$_2$ treatment with a solution-phase bromothiol exchange.

All films exhibited a PL peak at approximately 1375 nm. However, both the untreated and CdCl$_2$-only films displayed a broadened peak with a tail on the long-wavelength side. This is consistent with the existence of agglomerated CQDs that have a narrower bandgap than the parent population. These agglomerates are optically active and thus are apparent in the PL spectra. The PL spectrum of the film with bromothiol ligands is comparatively narrower, indicating that the ligands were able to prevent the fusion of CQDs into larger nanoparticles.
Figure 8.4: Schematic of CQD ligand schemes used for characterization.
Figure 8.5: (a) Solid state PL comparing films with only MPA ligands (Untreated), hybrid passivation with added CdCl$_2$ (CdCl$_2$), and combined hybrid approach with bromothiol added in solution (Br-thiol). The absence of thiol ligands results in agglomeration, leading to optically active large nanocrystals exhibiting long wavelength emission. (b) Transient photoluminescence decay spectroscopy of the same films, monitored at 1375 nm emission. Improved surface passivation through solution phase CdCl$_2$ addition leads to a reduction in surface trap associated decay dynamics.

Transient PL decay measurements were then carried out on each film, with emission monitored at the PL maximum. The decay dynamics are plotted in Figure 8.5b and all traces are fit using a biexponential function. The results are summarized in Table 8.1. The fast decay component of each film has a time constant of approximately 1 ns and is attributable to the efficient dissociation of excitons in coupled CQD films. The longer decay component, $\tau_2$, combines the effects of radiative recombination ($\sim$ 1 µs) and surface trapping processes which accelerate the decay.$^{34}$ Notably, $\tau_2$ for the MPA-only film (untreated) is 35 ns, while the inclusion of CdCl$_2$ (both with and without Br-thiol) increases this value to about 100 ns. This confirms the surface passivation effect of added CdCl$_2$ in reducing non-radiative recombination of CQD films.
These PL studies reveal the benefits of a combined ligand strategy incorporating bromothiols with a hybrid passivation approach. The MPA-CdCl₂ treatment provides effective passivation of surface trap sites but is unable to prevent CQD fusion. Adding thiol ligands in solution prevents the formation of quantum traps and, combined with CdCl₂ and MPA, produces the best available passivation.

**Table 8.1**: Summary of transient PL results

<table>
<thead>
<tr>
<th>Sample</th>
<th>A₁ (ns)</th>
<th>τ₁ (ns)</th>
<th>A₂</th>
<th>τ₂ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>0.765</td>
<td>0.72</td>
<td>0.267</td>
<td>7.3</td>
</tr>
<tr>
<td>CdCl₂</td>
<td>0.872</td>
<td>1.45</td>
<td>0.088</td>
<td>95.9</td>
</tr>
<tr>
<td>Br-thiol</td>
<td>0.913</td>
<td>1.38</td>
<td>0.065</td>
<td>96.4</td>
</tr>
</tbody>
</table>

We probed the electronic transport properties of our films using conductivity measurements on films. We developed test structures with symmetric hole-extracting contacts (i.e. Au and PEDOT:PSS/ITO). Hybrid CdCl₂ films showed a high conductivity of $8.4 \times 10^{-3} \Omega^{-1} cm^{-1}$ due to strong coupling from MPA ligands, and potentially reduced interparticle barriers due to CQD fusion. Using propane-thiol reduced the conductivity fourfold to $2.2 \times 10^{-3} \Omega^{-1} cm^{-1}$. We propose that the replacement of MPA surface sites by the insulating alkane chains leads to a reduction in their DOS near the valence bandedge and a greater barrier to hole transfer between CQDs. Notably, the use of Br-thiol ligands – with the added valence band associated states – allowed the film to match the conductivity of the hybrid passivated film at $9.0 \times 10^{-3} \Omega^{-1} cm^{-1}$ while simultaneously preventing fusing of dots as indicated by the narrower, bluer PL seen in Figure 8.5a.
8.5 Device Performance

The PV performance of our CQD films was assessed under AM1.5 simulated solar illumination. The current density-voltage (J-V) curves for devices made using different ligand strategies are shown in Figure 8.6. While the hybrid CdCl$_2$ device displayed high short circuit current ($J_{SC}$), the open circuit voltage ($V_{OC}$) was quite low, as expected from the PL-proven existence of agglomerated nanoparticles. The fill factor was also low, likely due to poor extraction of carriers that are trapped in these small-bandgap inclusions. Addition of propane-thiol ligands to prevent agglomeration increased the $V_{OC}$, but with a slight reduction in $J_{SC}$ and a fill factor below 0.5. The use of Br-thiol ligands instead resulted in an increase in the fill factor to over 0.6, as well as a further increase in $V_{OC}$ without any reduction of $J_{SC}$. This led to a power conversion efficiency (PCE) exceeding 7%. Thus, the combined ligand strategy enabled us to produce high efficiency solar cells using small-bandgap CQD absorbers.

![Figure 8.6: J-V curves of devices with different ligand treatments.](image)

We applied the optimized approach to devices illuminated using filtered AM1.5, thereby mimicking the effect of absorption by a front wide bandgap solar cell. We used long wave pass (LWP) filters to emulate either a perovskite (750 nm LWP) or silicon (1100 nm LWP) front cell and calculated a mismatch factor to account for differences between our lamp and AM1.5
spectra. Figure 8.7 shows the J-V characteristics of the device under unfiltered (Figure 8.7a), perovskite-filtered (Figure 8.7b), and silicon-filtered (Figure 8.7c) AM1.5 light. The device employed the full ligand strategy using bromothiols and CdCl$_2$ treated 1300 nm PbS CQDs as the absorber. The representative $V_{OC}$, $J_{SC}$, fill factor (FF) and PCE results are shown in Table 1. The reported 7.3% PCE for the unfiltered case is the best AM1.5 performance reported for any solution-processed material with a bandgap narrower than 1 eV. Interestingly, the loss of $V_{OC}$, referenced to the CQDs bandgap, decreases as the bandgap of the nanocrystal decreases (i.e. $E_g - qV_{OC} \approx 0.5$ eV, compared with $\approx 0.7$ eV for 1.3 eV CQDs). We attribute this improvement to the reduced conduction band offset. An external quantum efficiency curve is shown as the inset for Figure 8.7 that demonstrates a broad spectral response and an integrated current density of 30.3 mA cm$^{-2}$, which matches well with the value reported under AM1.5 solar simulator.

Filtering the device leads to 2.8% PCE after 750 nm long-wave pass (LWP) filter (perovskite PV) and 0.8% PCE after 1100 nm LWP filter (silicon PV), with the results shown in Table 8.2.

**Table 8.2:** Open circuit voltage ($V_{OC}$), short circuit current density ($J_{SC}$), fill factor (FF) and power conversion efficiency (PCE) results for unfiltered, perovskite-filtered and silicon-filtered devices.

<table>
<thead>
<tr>
<th>Type</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfiltered</td>
<td>0.48</td>
<td>31 ± 1</td>
<td>52</td>
<td>7.3</td>
</tr>
<tr>
<td>Perovskite filtered (750 nm)</td>
<td>0.45</td>
<td>11 ± 1</td>
<td>57</td>
<td>2.8</td>
</tr>
<tr>
<td>Silicon filtered (1100 nm)</td>
<td>0.40</td>
<td>3.0 ± 0.2</td>
<td>61</td>
<td>0.8</td>
</tr>
</tbody>
</table>

An addition of 2.8 power points to the perovskite cell power conversion efficiency that recently soared to over 20% certified PCE$^{10}$ is of potential applied interest. Silicon PV technology is
sufficiently mature that an improvement of 0.8 power points over the best Si cells is also attractive\textsuperscript{35}. If the 6 power points in principle available to crystalline Si cells could be more closely approached, this enhancement could significantly impact power generation given the ubiquity of silicon solar cells.
Figure 8.7: Measured current-voltage characteristics under AM1.5 simulated solar illumination for (a) Br-thiol/CdCl$_2$ treated PbS QD device, black curve, and after using perovskite solar cell representative filter (long-pass 750 nm filter), brown curve, and silicon solar cell representative filter (long-pass 1100 nm filter), gray curve. Inset: EQE curve for an unfiltered device. The integrated current value is also shown.
In sum, we have demonstrated the utility of CQDs as an infrared absorber that can enhance the performance of high-efficiency PV materials. Detailed balance modeling was used to select a suitable optical bandgap for use with a wide range of systems, and DFT calculations were used to develop a multiple-ligand strategy that prevented agglomeration of adjacent dots while facilitating carrier transport. Optical studies of the film confirmed that the ligand approach prevented development of two sources of electronic traps: unpassivated surface sites and small-bandgap CQD agglomerates. Conductivity measurements confirmed that the bromine-functionalized thiols are well-coupled. Depleted heterojunction devices were fabricated and achieved the highest single-junction efficiency for a <1.0 eV bandgap solution-processed solar cell. The work suggests access to significant enhancements in the solar harvesting ability of the highest-performing photovoltaic systems with the addition of low-cost, solution-processed quantum dot absorber.
8.6 References


Chapter 9
Conclusion and Future Directions

9.1 Summary and Impact

In this thesis, development of materials for broad-spectrum photovoltaic harvesting was presented, with a focus on colloidal quantum dots (CQDs). I presented the importance of surface engineering in CQDs and demonstrated a new hybrid passivation method in Chapter 4. This approach uses a combination of bifunctional organic ligands and metal halides to improve the passivation of surface states. This method resulted in a large improvement in the device performance, culminating in a solar cell certified at 7.0% efficiency, the highest achieved at the time of publication. In the ensuing two chapters, I delved deeper into the underlying mechanisms of the hybrid passivation approach. Photoelectron spectroscopy revealed the reduction in band tail states through Cd cation passivation. Further study of the cationic species on CQD surfaces identified the role of bond adaptability on the suppression of shallow traps.

Building on the foundation laid in the first chapters for single-junction CQD solar cells, I next focused on development of solution-processed materials that would utilize a wider portion of the solar spectrum. In Chapter 7, I demonstrated a simple process for fabrication of efficient, visible-absorbing perovskite cells. An interfacial fullerene layer was shown to suppress the anomalous hysteresis that has plagued planar perovskite devices.

Infrared-absorbing CQD cells were then shown in the next chapter. I used rational ligand engineering to demonstrate devices with the highest performance yet achieved for a solution-processed material with a bandgap narrower than 1.2 eV. I then showcased the potential synergy of these cells with wide-bandgap materials.
This work lays a foundation for future work on solution-processed, infrared-absorbing CQD materials. As discussed in Chapter 8, there is potential for adding upwards of 6 power points to widely-used silicon solar cells, and even more to visible-absorbing perovskite cells. Surface engineering and band alignment considerations discussed herein can also inform work on CQDs as small-bandgap thermophotovoltaic materials that can produce electricity from waste heat rather than solar irradiance.

The work contained in this thesis directly resulted in the publication of 4 peer-reviewed journal publications (plus one under review), as well as contributions to a book chapter and a number of international conference presentations. The papers resulting from this work have been cited in total over 400 times.

9.2 Parallel Progress in CQD Photovoltaics

During the course of the work reported in this thesis, there was a significant amount of progress in the field of CQD photovoltaics a number of research groups. Some of the work built on the passivation method reported in Chapter 4. An analysis of the low diffusion lengths in CQD solids confirmed that mobility is not currently limiting device performance but rather deep recombination centres. The relatively low – though still significant – number of trap states suggests inadequate surface passivation may no longer be the main cause of deep traps. Further investigation requires examination of CQD syntheses and film processing methods that may disrupt the nanocrystal structure.

To overcome the compromise between full absorption and short diffusion lengths, architectures were developed to improve extraction from a thick absorbing film. Rath et al. reported in 2012 a bulk nano-heterojunction structure using n-type Bi$_2$S$_3$ nanocrystals mixed with PbS quantum dots in solution and simultaneously cast into a film. Nanowire TiO$_2$ or ZnO structures have also been reported to allow thicker quantum dot layers while maintaining complete depletion, with
best reported efficiencies exceeding 7%.\textsuperscript{3–6} By varying the ligands used for each layer and creating a p+-p-n structure, Yuan \textit{et al.} demonstrated a heterojunction cell with improved charge extraction at maximum power point conditions.\textsuperscript{7}

Enhancing absorption in fully depleted quantum dot films has followed a few approaches. Cells incorporating a “folded-light-path” have been shown to allow multiple passes of incident light within a thin, depleted quantum dot film, leading to large enhancements in infrared quantum efficiencies.\textsuperscript{8} A periodically etched substrate was used with semi-conformal coating of the active material to produce a nanostructured back electrode which scattered light into the PbS film. This led to a broadband enhancement of the absorption.\textsuperscript{9} Most recently, micron-scale TiO\textsubscript{2} pyramid structures were conformally coated with CQDs, resulting in increased photon path length through the absorber and enhancing the performance beyond 9%.\textsuperscript{10} Absorption has also been increased using plasmonic enhancers. Gold nanoshells, specifically tuned to have a strong scattering cross section in the wavelength range most weakly absorbed by the PbS quantum dots, were used to locally increase the field strength. These plasmonic nanoshells were embedded within the quantum dot film to maximize the enhancement of absorption and photocurrent.\textsuperscript{11}

A new architecture was reported in 2012, consisting of a junction formed between n-type and p-type quantum dots, dubbed a quantum junction solar cell.\textsuperscript{12} Similar to a homojunction architecture, the same material (PbS QDs) is used on each side of the junction, but uniquely, the bandgap of each side can be tuned independently. This structure was shown to provide nearly triple the short circuit current density with 0.6 eV bandgap QDs compared with the same bandgap QDs in a heterojunction architecture. Halide ligand exchange in an inert environment was used to enable n-type quantum dot films, with the doping density determined by the halide ion used.\textsuperscript{13} Optimization of the contact to the n-type layer resulted in efficiencies over 6% and stable performance over tens of hours.\textsuperscript{14} Further tuning of the electric field within the active film was achieved through bandgap engineering\textsuperscript{15} or graded doping (using bromide and iodide ligands to form a p-n-n+ structure).\textsuperscript{16} The latter approach was used to achieve 7.4% PCE, the current record for this architecture. Recently, researchers at ICFO in Spain reported
homojunction solar cells using bismuth-doped PbS quantum dots as the n-type layer, with film fabrication occurring under ambient atmosphere.\textsuperscript{17}

Following the achievement of a record 7.0\% certified PCE as reported in Chapter 4, the record performance has continued to advance steadily. In 2014, Chuang \textit{et al.} reported 8.55\% certified PCE\textsuperscript{18} through band alignment engineering in which halide and thiol ligands were used to form a p-i-n structure for charge extraction. Most recently, the certified efficiency has reached 9.9\%.

### 9.3 Future Directions

A clear direction for the use of these small-bandgap CQDs is their integration with wide-bandgap solar cells. In the case of perovskites, this may take the form of a monolithic tandem cell, while for silicon cells a four-terminal approach would be necessary due to current-matching considerations. The tunability of CQDs also makes them attractive for use in split-spectrum solar cells which are emerging as an intriguing high-efficiency path.

The development of infrared absorbing CQDs presented here has been in parallel with further development of ~1.35 eV bandgap CQD solar cells, which have now reached nearly 10\% certified efficiency. Besides the high performance, it is very encouraging to see high stability of these devices in air. Transferring the success to smaller bandgaps is of high interest, and this thesis should provide a strong pathway towards that goal.

The use of nanostructuring for enhanced photon absorption or charge extraction is also an important pathway for improving infrared performance. As the absorption length increases with photon wavelength, it is crucial to implement these architectures for efficient small bandgap solar cells.
Looking at the CQD photovoltaics field as a whole, a number of challenges are apparent. The performance has been surpassed by organometal halide perovskites, and so CQDs still have some catching up to do for wide bandgap approaches. Current hurdles to reaching higher efficiencies revolve around limited open-circuit voltages and diffusion lengths. Solving these issues, through further development of liganding approaches and reducing film disorder, will allow CQD PV to advance beyond other solution processed technologies such as organics and dyes. CQDs have the advantage of improved stability and long wavelength absorption, so leveraging these features is important.

Transferring CQD technology to the marketplace poses some other challenges which are certainly achievable but require further development. All device demonstrations have been at small lab scales, and so demonstration of large area or module performance would be highly beneficial to the field. To this point, low temperature, roll-to-roll compatible techniques should be developed to demonstrate the manufacturability of this technology. On the materials side, this would include increasing the synthesis volume from small scale batches while maintaining high nanocrystal quality. In terms of processing, techniques beyond lab scale spin or dip coating must be used; instead, scalable processes such as spray-coating or blade-coating are preferred. Finally, demonstration of long-term device stability is necessary for commercial adoption of this technology. Initial reports of devices stable over months are highly encouraging, but well short of the many years that a device must last in the field. In all the above mentioned directions, there have been some initial reports, but certainly expanding fronts of study will positively impact the field.

In conclusion, significant progress has been achieved in CQD photovoltaics research in the past five years through deeper physical insights and improved materials development. This thesis represents a contribution to this field through improved surface engineering and development of efficient infrared sensitive materials. There remain many paths forward for continued
development of this technology, and further research will allow colloidal quantum dots to contribute to a sustainable energy future.
9.4 References


Appendix - Methods

Chapter 4

Metal halide precursor preparation: Cadmium chloride (Sigma-Aldrich, 99.98%) or lead chloride (Alfa Aesar, 99.999%) and 1-tetradecylphosphonic acid -TDPA (Alfa Aesar, 98%) were dissolved in oleylamine (technical grade, Acros, 80%) by pumping for 16 hours at 100°C. The solution was kept at 80°C to avoid solidification. In a typical procedure, precursor with 13.6:1 Cd:TDPA molar ratio was made by dissolving 0.30 g (1.64 mmol) of CdCl₂ and 0.033 g (0.12 mmol) of TDPA in 5 mL of oleylamine.

Quantum dot synthesis and metal halide treatment: PbS quantum dots were synthesized according to a previously published method.¹ For metal halide treatment, the introduction of 1.0 mL metal halide precursor into the reaction flask was made after sulphur source injection during the slow cooling process. A 6:1 Pb:Cd molar ratio was kept for the synthesis. When the reaction temperature reached 30-35°C the nanocrystals were isolated by the addition of 60 mL of acetone and centrifugation. In the next step the nanocrystals were purified by dispersion in toluene and re-precipitation with acetone/methanol (1:1 volume ratio), and re-dissolved in anhydrous toluene. The solution was washed with methanol two or three more times before final dispersal in octane (50 mg mL⁻¹).

Photovoltaic device fabrication: PbS CQD films were deposited in a layer-by-layer spin coating process under ambient atmosphere. For each layer, the CQD solution (50 mg mL⁻¹ in octane) was deposited on the ZnO/TiO₂ substrate and spin-cast at 2500 rpm. In the hybrid and organic approaches, solid state ligand exchange was performed by flooding the surface with 1% v/v MPA in methanol for 3 seconds before spin-coating dry at 2500 rpm. Two washes with methanol were used to remove unbound ligands. Each device consisted of 8-12 layers. Inorganic-passivated devices were fabricated following the procedure described in Reference 12. Top electrodes were deposited using an Angstrom Engineering âmod deposition system in
an Innovative Technology glovebox. The contacts typically consisted of 10 nm thermally evaporated molybdenum trioxide deposited at a rate of 0.2 Å/s, followed by electron beam deposition of 50 nm of gold deposited at 0.4 Å/s, and finally 120 nm of thermally evaporated silver deposited at 1.0 Å/s.

**AM1.5 photovoltaic performance characterization:** Current-voltage data was measured using a Keithley 2400 source-meter. The solar spectrum at AM1.5 was simulated to within class A specifications (less than 25% spectral mismatch) with a Xe lamp and filters (ScienceTech) with measured intensity of 100 mW cm$^{-2}$. The source intensity was measured with a Melles-Griot broadband powermeter through a circular 0.049 cm$^2$ aperture at the position of the sample and confirmed with a calibrated reference solar cell (Newport, Inc.). The accuracy of the current-voltage measurements was estimated to be ±7%.

**External quantum efficiency measurements:** The EQE spectrum was obtained by passing the output of a 400 W Xe lamp through a monochromator and using appropriate order-sorting filters. The collimated output of the monochromator was measured through a 1 mm aperture with calibrated Newport 818-UV and Newport 818-IR power meters as needed. The beam was optically chopped and cofocused on the pixel with a solar simulator at 1-sun intensity. The measurement bandwidth was ∼40 nm and the intensity varied with the spectrum of the Xe lamp. The current response was measured with a Stanford Research Systems lock-in amplifier across an appropriately small resistor (25 Ω) to approximate short-circuit conditions. The accuracy of the EQE measurements was estimated to be ±8%.

**Photovoltage Transient Measurements:** In the photovoltage transient method, a Melles-Griot 56RCS009 /HS 630 nm diode laser is used to modulate the $V_{OC}$ on top of a constant light bias. The pulse duration is set to 1 μs and the repetition rate to 50 Hz. For the constant light bias, a continuous wave 830 nm fibre-coupled diode laser is collimated on the active area of the solar
cell under study, and photovoltage transients are measured over an equivalent intensity range of 0.0001 - 5 suns, ensuring coverage of the full range of $V_{OC}$’s. A Keithley 2400 source meter is used to measure the current and voltage as required. The samples are identical in architecture to the photovoltaic devices and the measurements are performed at room temperature.

To calculate the capacitance and density of trap states (DOS) at each $V_{OC}$, we also measure the photocurrent transient for an identical pulse at short circuit conditions, following the procedure described by Shuttle et al.\textsuperscript{2} We measured the $V_{OC}$ perturbation transient induced by the short change in incident power at a given light bias. Subsequently we determine the change in charge density, by integrating the short circuit current transient induced by the light pulse without the light bias present. This charge corresponds to the stored charge in the bulk of the film by assuming exciton generation is independent of an applied bias and recombination at short circuit is small. The induced voltage change by the small charge addition through the short light perturbation defines the capacitance.

The differential capacitance at each $V_{OC}$ is equal to the peak of the photovoltage transient ($\Delta V_{OC}$) divided by the integral of the photocurrent transient at short circuit (the change in charge density). This charge corresponds to the stored charge in the bulk of the film by assuming exciton generation is independent of an applied bias and recombination at short circuit is small. The carrier concentration, $n$, for each open circuit voltage is then obtained by integrating the capacitance over voltage:

$$n = \frac{1}{Aed} \int_{0}^{\nu_{OC}} CdV$$

where $A$ is the device area, $e$ is the electron charge and $d$ is the film thickness. Here $n$ is the amount of excess carriers needed to separate the quasi-Fermi levels to the corresponding $V_{OC}$, or in other words, $n$ is the number mid-gap states that need to be filled. Thus, the spectrum of the density of midgap states (DOS) can be obtained by differentiating the carrier density with respect to the Fermi level separation.

**Grazing incidence small-angle X-ray scattering (GISAXS):** measurements were performed on beamline 7.3.3 of the Advanced Light source (ALS) at Lawrence Berkeley National
Laboratory. Monochromatic light was used with a wavelength of 1.23984 Å (10 keV). The Pilatus 1M detector, a CMOS hybrid-pixel CCD camera with a pixel size of 172 µm x 172 µm and a total of 981 x 1043 pixels with a 20 bit dynamical range per pixel, was used to record the scattering patterns. Typical read-out time per image was below 3.6 ms. The images were dark current corrected, distortion-corrected, and flat-field corrected by the acquisition software. Using a silver behenate powder standard, the sample to detector distance was determined to be either 1350.74 mm or 1356.84 mm. The incident angle of the X-ray beam was varied between 0.02° to 0.15°. Typical exposure times ranged from 20 to 300 s. All three films shown in Figure 4.3 were made from the same CQDs that were treated with CdCl₂ during synthesis; the only difference was in the film-forming solid-state exchange procedure. All show primarily ring-like GISAXS patterns. We plotted azimuthally integrated intensity profiles and used Gaussian fitting plus an exponential background to determine the location of the scattering rings at q ~ 0.2 Å⁻¹. Conversion to real-space coordinates gave average centre-to-centre nanocrystal spacings of 4.37 nm, 4.48 nm, and 3.36 nm, for the unexchanged, inorganic, and hybrid films, respectively.

**Time of Flight:** This method³ was used to measure hole carrier mobility. TOF experiments employed samples with a geometry identical to that of the photovoltaic device, with the exception that the total nanocrystal layer in this case was thicker (> 500 nm). These samples were excited using a diode-pumped passively Q-switched solid state laser operating at 355 nm with 1 ns pulses at a 200 Hz repetition rate. The light was incident on the sample from the transparent FTO side. The devices were biased using a Keithley 228 Voltage/Current Source, and a digital Textronix TDS5104 oscilloscope was used to measure the current transient output across a 50 Ω load.

**Chapter 5**

**Quantum dot film preparation:** For PES measurements, quantum dot films were prepared in ambient atmosphere on indium tin oxide (ITO) coated glass substrates in a layer-by-layer approach similar to those used in previous reports of CQD solar cells.⁴ ⁵ Briefly, an octane based
solution of CQDs was spin cast onto the substrate (2500 rpm, 1000rpm/s acceleration, 10s). A solution of 1% v/v MPA in methanol was used to perform the solid-state exchange, followed by rinsing with pure methanol. This process was repeated four times to build a pinhole-free film thick enough (~100nm) to eliminate any contribution from the underlying substrate.

**Photoelectron spectroscopy measurements:** The IPES spectra were obtained by using variable kinetic energy incident energy electrons while detecting the emitted photons at a fixed energy (9.7 eV) using a Geiger-Müller detector. The inverse photoemission spectroscopy resolution was limited by an instrumental linewidth of approximately 400 meV. The PES studies were carried out at the photoemission endstation of PGM beamline at Canadian Light Source Inc., equipped with a Scienta SES100 hemispherical electron energy analyzer with a total energy resolution as 50 meV. All spectra were collected at normal emission and room temperature.

**Quantum dot device fabrication:** For photocurrent transient and photovoltaic measurements, CQD films were prepared as above but on TiO₂ electrodes on fluorine-doped tin oxide (FTO) coated glass (TEC15, Hartford Glass) and to total film thickness of ~300 nm (10 layers). To form the electrodes, an aqueous solution of ZnO nanoparticles (NanoShield® ZN-2000, diluted to 20% in deionized water) was spin-cast (2500 rpm for 20 s) on the substrates and put on a 150°C for 30 minutes. The substrates were then immersed in a 120 mM TiCl₄ solution and placed for 30 minutes in an oven held at 70°C. The substrates were then dried and annealed on a hotplate at 520°C for half an hour.

**Photocurrent transient measurements:** A pulsed 640 nm diode laser was used to excite photocarriers in the device. The light intensity was set to approximately 1 sun (100 mW/cm²). Photocurrent characteristics were measured as a function of bias and the effective transit times (defined as the time required for current to decay to 1/e of the peak value) were calculated. The
mobility was extracted by comparing transit time as a function of average field. All measurements were performed under N₂ flow.

Photovoltaic device measurements: Current-voltage characteristics were measured under N₂ flow using a Keithley 2400 source meter with 100 mW/cm² simulated AM1.5 solar illumination (Sciencetech, Class A). The source intensity was measured with a Melles-Griot broadband power meter through a circular 0.049 cm² aperture. The estimated uncertainty of the measurements is ± 7%.

Chapter 6

Device Fabrication: Devices were fabricated on commercially available FTO coated glass substrates (TEC15, Hartford Glass). To form the n-type electrode, a ZnO nanoparticle solution (NanoShield® ZN-2000 diluted to 20% concentration in deionized water) was spin-cast onto the substrates (2500rpm for 20s). The substrates were heated to 150°C for 30 minutes. Following this, the substrates were immersed in a 120mM TiCl₄ solution and held in an oven at 70°C for 30 minutes. Finally, the substrates were dried and annealed on a hotplate at 520°C for an additional 30 minutes.

CQD film formation was carried out under atmospheric conditions. To form the CQD film, a 50 mg/mL solution of CQDs in octane was passed through a 0.2 µm filter onto the electrodes and spun at 2500 rpm for 10 s. A 1%v/v solution of 3-mercaptopropionic acid (MPA) in methanol was then used to exchange the oleic acid ligands. The MPA solution was allowed to sit on the CQD film for 3 s to allow exchange before spinning at 2500 rpm for 5 seconds. Two rinses with methanol followed to ensure removal of unbound organics. The above process was repeated in a layer by layer fashion until the desired thickness was reached (typically 10 layers or ~300 nm). The top electrodes were deposited using an Angstrom Engineering Åmod deposition system integrated in an Innovative Technology glovebox. These contacts consisted of 7.5 nm of
thermally evaporated molybdenum oxide, 50nm electron-beam deposited gold and 120 nm of thermally deposited silver.

**Photoluminescence Quantum Efficiency Measurements:** PLQE was measured by mounting a small amount of CQD solution in a fiber-coupled integrating sphere. A 640 nm diode laser was used to excite the sample and the photoluminescence and laser signals were collected using near infrared and visible wavelength range spectrometers, respectively. The PLQE was calculated by taking the integrated difference between the directly-excited and indirectly-excited photoluminescence photon signals divided by the integrated difference between the direct-pump and indirect-pump laser photon signals.

**AM1.5 Characterization:** The device area was properly defined by aperturing to be 0.049 cm². Using a xenon lamp and filters (Sciencetech), the solar spectrum at AM1.5 conditions was simulated to within class A specifications. The source intensity was measured using a Melles-Griot broadband power meter and confirmed using a calibrated reference solar cell (Newport). Current-voltage data was collected using a Keithley 2400 source meter with an estimated accuracy of ±7%.

**Colloidal Quantum Dot Synthesis:** The PbS nanocrystals were synthesized following a previously published process with or without the addition of a metal chloride precursor solution added during the final cooling stage of synthesis as described in the text. Acetone was used to isolate the cooled PbS nanocrystals followed by centrifugation. The CQDs were dispersed in toluene, precipitated by acetone and methanol in a 1:1 volume ratio mixture and then washed two or three times with methanol. The final redispersion was done in octane at a concentration of 50 mg mL⁻¹.
X-ray Photoelectron Spectroscopy: X-ray photoelectron spectroscopy (XPS, PHI-5500) was used to determine the concentration incorporation of the metal cations and halide anions in the final films in amounts relative to lead. A monochromated Al Kα radiation source (1486.7 eV) was used to excite photoelectrons under ultrahigh vacuum (109 Torr).

Chapter 8

Quantum dot synthesis and halide treatment: The lead precursor was prepared by dissolving and degassing 0.75 g of lead acetate trihydrate (PbAc₂·3H₂O) in the mixture of 6.0 mL of oleic acid and 27.0 mL of 1-octadecene. The mixture was then heated to 100°C to form lead oleate in situ and also to dry the solution. After the lead precursor was made, the solution was heated to 140°C under Argon, followed by the swift injection of the sulfur precursor of 0.210 mL of hexamethyldisilathiane (TMS) and 8.0 mL 1-octadecene. Bromo-propanethiol (Beyond Pharmaceutical Co.) or propane-thiol (Sigma Aldrich) was mixed with 1-octadecene to a concentration of 0.5 mmol per batch. Thiol and/or CdCl₂ treatments were performed during the cooling process following previously published methods, with precursor concentrations of 0.5 and 0.3 mmol/mL, respectively. After synthesis, the PbS dots were purified and extracted 2 times with 50 mL of distilled acetone and re-dispersed in toluene. Two washes using methanol were performed before final redispersion at 50 mg/mL in octane.

Photovoltaic device fabrication: Unpatterned and pre-patterned ITO coated glass substrates were purchased from Delta Technologies and TFD Inc., respectively. TiO₂ nanoparticles were synthesized based on a modified solvothermal method previously reported. Briefly, TiCl₄ (Sigma Aldrich) was added dropwise to ethanol to a 1:4 volumetric ratio. 2 mol% of NbCl₅ (Sigma Aldrich) was dissolved in the resulting solution. This solution was added to benzyl alcohol in a 1:8 volumetric ratio, upon which the mixture turned red. The jar was sealed and placed in an oven at 70°C overnight (18 hours). The TiO₂ NPs were precipitated and washed twice using diethyl ether. The resulting powder was redispersed in methanol at a 10 mg/mL concentration and sonicated until uniform. Polyethyleneimine ethoxylated was purchased from Sigma-Aldrich and diluted 100 times in methanol. PbS QD films were deposited using a layer-
by-layer spin-coating process under an ambient condition. Two drops of filtered CQD solution (50 mg ml\(^{-1}\) in octane) was deposited on the PEIE/TiO\(_2\) coated ITO/glass substrate and spin-cast at 2500 rpm for 10 seconds to form each layer. Solid-state ligand exchange was performed using 5% MPA solution in methanol and spinning at 2500 rpm for drying after 3 s soaking. The QD film was washed 2 times with methanol to remove excess MPA and unbound oleate ligands. Top contacts were deposited using Angstrom Engineering Åmod deposition system in an Innovative Technology glovebox. The contact consists of approximately 40 nm thermally evaporated molybdenum oxide, 50 nm electron-beam deposited gold and approximately 100 nm of thermally evaporated silver.

**Photoluminescence:** Spectral and transient photoluminescence measurements were carried out using a Horiba FluoroLog-3 spectrofluorometer at room temperature. The sample, a ~100 nm thick quantum dot film on glass, was excited using a 633 nm pulsed laser diode (<1 ns). The emission passed through a 1000 nm blaze grating monochromator and collected by an infrared photomultiplier tube (PMT).

**AM1.5 photovoltaic performance characterization:** Current-voltage characteristics were measured using a Keithley 2400 source meter. The devices were tested in N\(_2\). The solar spectrum at AM1.5 was simulated to within class A specification (less than 25% spectral mismatch) with a xenon lamp and filters (ScienceTech; measured intensity of 100 mW cm\(^{-2}\)). The source intensity was measured using Melles-Griot broadband power meter through a circular aperture of 0.049 cm\(^2\) at the position of the device and was confirmed by a calibrated reference solar cell (Newport). The accuracy of current-voltage measurements is estimated to be ± 7%. 750 nm and 1100 nm long-pass filters from Thorlabs, Inc. were used to represent perovskite solar cell and silicon solar cell respectively.

**Spectral mismatch calculation:** The spectral power within the wavelength region of interest was calibrated using the lamp spectrum supplied by the manufacturer. The absolute power of the lamp spectrum was calibrated with a calibrated power meter and a set of calibrated long pass filters. The external quantum efficiency (EQE) spectrum of the 1.3 µm colloidal quantum dot solar cell device was measured and used to calculate the mismatch factor between the lamp spectrum filtered with a 1100 nm long pass filter (1100 LPF) and the AM1.5 spectrum beyond.
1100 nm. The spectral mismatch was calculated with the ratio of the integral of the product of the lamp spectrum, the EQE spectrum and 1100 LPF spectrum, and the integral of the product of the AM1.5 spectrum, the EQE spectrum and 1100 LPF spectrum. This resulted in a mismatch factor of 1.5. The main error in the mismatch factor is estimated to be in the calibration of the lamp spectrum, estimated to be about 10%.

**EQE measurement:** External quantum efficiency measurements were obtained by applying chopped (220 Hz) monochromatic illumination, collimated and cofocused with a 0.7 Sun intensity white light source, on the device of interest. To create monochromatic illumination, 450 W xenon lamp was used, which passes through a monochromator with order-sorting filters. Calibrated Newport 818-UV and Newport 818-IR power meters were used to measure power. The response from the chopped signal was measured using a Stanford Research system current preamplifier feeding into a Stanford Research system lock-in amplifier set to voltage mode. The uncertainty in the EQE measurements was estimated to be 3%.

**References**


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