A Theoretical and Experimental Analysis of Dual Halide Treatment in Lead Sulfide Quantum Dot Solar Cells

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A Theoretical and Experimental Analysis of Dual Halide Treatment in Lead Sulfide Quantum Dot Solar Cells

by

Dasol Yoon

Submitted to the Department of Physics
in partial fulfillment of the requirements for the degree of

Bachelor of Arts in Physics with Honors

at

WELLESLEY COLLEGE

May 2019

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Abstract

Lead sulfide (PbS) quantum dot (QD) solar cells are emerging thin film solar cells that are solution processible at low temperatures, potentially on lightweight and flexible substrates at a low cost. Despite this prospect, PbS QD solar cells remain far from commercialization due to their low power conversion efficiency compared to other types of solar cell. This thesis explores the development of a novel surface passivation protocol to raise the open circuit voltage of PbS QD solar cells and thereby improve the power conversion efficiency. The protocol implements a novel solution phase ligand exchange method that involves two kinds of halide salts. The impacts of these salts on PbS QD solar cell performance and optical properties are studied through a comparison of a control process—that involves only one kind of halide salt—to the proposed process—that utilizes dual halide treatment. Particularly, open circuit voltage is both experimentally measured and theoretically calculated to assess the potential of the proposed treatment. In both cases, devices made with the novel dual halide treatment show improved open circuit voltage compared to the devices made with the control process. This improvement presents the potential for multiple halide treatment in better surface passivation. Moreover, theoretical results being in good agreement with the observed results suggests the viability of theoretical performance analysis using optical measurements in surface passivation studies.

Thesis Supervisor: Rebecca Belisle
Title: Assistant Professor
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Chapter 1

Introduction

1.1 An Environmental Motivation

Many sources—including NASA, U.S. Global Change Research Program, Intergovernmental Panel on Climate Change (IPCC), and nearly 200 worldwide scientific organizations [4]— acknowledge that ongoing climate change and global warming are human driven. The IPCC, which is the United Nations’ intergovernmental body for providing an extensive and scientific view of climate change by hundreds of esteemed scientists worldwide, predicts that the global mean temperature may rise ranging from 1.7°C to 4.2°C by 2100 depending on how we regulate ourselves with regard to carbon dioxide emission [5], [6]. Such a seemingly small increase in temperature may bring catastrophic outcomes, such as more heat waves and droughts, loss of agricultural and inhabitable lands due to sea level rise and droughts, and yet more unpredicted outcomes. (Extensive risks of global warming can be found in section 19.5.1 of [7]).

One of the major causes of global warming is carbon dioxide emission. From 1990 to 2010, 45-53% of carbon dioxide emission was from an energy sector, which includes fossil fuel combustion for electricity and heat by energy, construction, and manufacturing industries. This section excludes transportation, residential, commercial, and institutional energy use [8]. In order to reduce such massive emission of carbon dioxide from using fossil fuels as energy sources, research on clean energy technology is going
Figure 1-1: Current and Future Carbon Footprints of electricity generation technologies. Coal and gas are fossil fuels. The rest are renewable energy technologies. (CCS stands for Carbon Capture and Storage, which is a process of capturing 90% of carbon dioxide emitted from the source and storing it in an underground storage site. This process may consume 10-40% of the produced energy). Figure from [1].
on. As shown in figure 1-1, the carbon emission footprints of such clean technologies are significantly lower than those of fossil fuels (e.g. coal and gas in the figure).

Solar cells are one of the popular alternative energy sources due to their lower catastrophic risk relative to the risks from nuclear energy or hydroelectricity [9] and location insensitiveness [10]; in particular, sunlight is an abundant resource worldwide relative to the resources of biomass or marine energies. Also, since solar cells can be installed for each household or more locally, loss in electricity transmission from power lines connecting power stations and households can be reduced. Moreover, households or villages without the access of electrical grids may benefit from such an accessibility of solar cells.

1.2 Fundamentals of Solar Cells

A solar cell is a semiconductor device that generates electricity from sunlight through the photovoltaic effect. When a photon with energy equal to or greater than the bandgap of a semiconductor gets absorbed into a material, it excites an electron to the conduction band. This excited electron leaves a positively charged ”hole” in the valence band. Such an electron-hole pair is crucial to the photovoltaic effect [11].

In a p-n junction solar cell, p-type (with excess positively charged ”holes”) and n-type (with excess negatively charged electrons) materials are combined together, forming a joint called a p-n junction. Due to an inherent electric field present in this junction, the electrons and holes generated through light absorption can move to p- and n- type regions respectively. In a connected circuit, this overall photovoltaic process generates voltage and current [12]. (The current and voltage behavior will be discussed more in section 2.3).

There are a number of parameters that are frequently used to examine the performance of solar cells:

- Open circuit voltage ($V_{oc}$): Maximum possible voltage one can get when there is no net current (dark current $J_o =$ short circuit current $J_{sc}$) in the cell. As there is no net current, excited electrons and ”holes” reunite through a process
Figure 1-2: A generic J-V curve of a solar cell. MPP stands for maximum power point, which indicates a point on the J-V curve that makes the maximum product of voltage and current density.) Figure from [2].

called recombination. Hence, $V_{oc}$ is a measure of recombination, which can be thought of as two categories:

- radiative recombination: An unavoidable loss due to spontaneous emissions. Any object not at absolute zero temperature emits electromagnetic radiation (black-body radiation). Photons are generated as a result, decreasing the current in the cell.

- non-radiative recombination: an avoidable process, primarily due to imperfect material. An excited electron may relax to a sub-bandgap/trap state that exists within the bandgap of the material.

- Short circuit current density ($J_{sc}$): Maximum possible current per area for a solar cell when the voltage is 0V. It depends on the semiconductor’s ability of absorbing light, absorption, as solar cells convert the incident light to electricity.

- Power conversion efficiency (PCE): The percentage of energy of incoming sunlight that can be converted to electricity. It denotes the performance of a solar
cell, which is calculated as following:

$$PCE = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P},$$ (1.1)

where FF is a fill factor (visualized in figure 1-2), and P is an incident light density [13].

### 1.3 Motivations for PbS QDSC

Although commercial solar cells emit less carbon dioxide than fossil fuels, they still have nonzero carbon footprints [1]. In order to reach the carbon dioxide emission goal, we need to reduce the emission further. Currently, most commercial solar cells are silicon solar cells [11]. Significant amounts of carbon emission of silicon solar cells are a consequence of high temperatures (around 1200 – 1420°C) required in making pure silicon and processing the material [14][15]. By making the manufacture process available at room temperature, we could avoid such carbon dioxide emissions from heating and save energy [16].

Also, single junction silicon solar cells have a low theoretical (Shockley-Queisser) limit efficiency of about 33% [17], [18]. Using multiple materials with different band gaps to implement multiple junctions can improve the theoretical limit up to 68 % (under unconcentrated sunlight) [19]. However, multi-junction solar cells are more expensive and require careful engineering due to the types of materials and their fabrication method used currently [20].

Another weakness of crystalline silicon solar cells is that they are too rigid and heavy. These properties require more trained people for installation, increasing the cost and limiting the installation sites. For instance, more and more rural areas in India may heavily rely on using solar cells for electricity generation. However, because the panels are heavy and bulky, specific training is required for installation, and thus there is a limit on number of panels that can be transported and installed at a time [21]. Flexible and lightweight solar cells could ease the installation process.
and broaden installation sites.

Lead Sulfide (PbS) Quantum Dot Solar Cells (QDSCs) could solve the problems described above through utilization of bandgap tunability and solution processibility.

1.4 Basics of PbS QDSCs

A quantum dot solar cell is one of the emerging thin film photovoltaics that uses several nanometer sized nanocrystals of semiconducting materials (e.g., CdS, CdSe, PbS, PbSe, InAs, etc.) to absorb light [22].

Such a small size enables the quantum confinement effect to vary the band gap of QDs from that of the bulk material. Since the size of QDs is comparable to the Bohr radius, they are in the realm of so called particle in a box or infinite potential well. The size of the dots determines the size of the box or well, and hence the energy difference between the conduction and valence bands (band gap). For example, the band gap of bulk PbS is about 0.4 eV. Decreasing the size of the PbS particles increases the bandgap range from 0.6 eV to 1.6 eV. Such band gap tunability (from simply varying the size of the dots) gives an advantage to QDs for application in multi-junction (or tandem) solar cells to achieve a higher theoretical limit of efficiency [23].

QDs can be colloidally (evenly dispersed throughout a solution without being dissolved) synthesized in solutions. Such solution processibility allows the use of lightweight and flexible substrates and mass production technology like roll-to-roll coating [22], [24].

Moreover, PbS QDs can be synthesized below 150 °C, and PbS QDSC devices can be fabricated at room temperature [24], unlike monocrystalline silicon solar cells which require fabrication temperatures around 1000°C. Again, this reduction in manufacture temperature could save energy and cost spent in heating. Furthermore, as PbS is an earth abundant material, it could achieve a low cost of manufacture [22].
Figure 1-3: A model of atomic structure of a PbS quantum dot (of size 5 nm in diameter) passivated with oleic acid (OA$^-$) and hydroxyl (OH$^-$) ligands. The color scheme of the model: Pb, gray; S, yellow; O, red; H, blue; C, brown. Figure from [3].

1.5 Research Question

PbS QD solar cells are solution processible at low temperatures, potentially on lightweight and flexible substrates at a low cost. Despite this prospect, PbS QD solar cells remain far from commercialization due to their low power conversion efficiency (PCE) of around 10% [25], [26] compared to other types of single junction solar cell of PCE over 25%. One of the factors that hampers the improvement of PbS QDSC PCE is considered to be incomplete surface passivation (stabilization/inactivation through covering the surface) [27].

For stable long term storage, PbS QDs are capped (passivated) with oleic acid ligands as shown in figure 1-3 in order to protect QDs from moisture and oxidation. Yet, these long ligands are not ideal for electron transport in device application. Hence, a process called ligand exchange—replacing these long ligands with shorter ligands—can be done on QDs to improve device performance. Iodide salts like lead iodide (PbI$_2$) are popularly used to passivate the surface of QD. However, current ligand exchange methods with iodide salts leave behind un-passivated surface states which
reduce the open circuit voltage and hence the power conversion efficiencies of QD photovoltaics. For industry-scale low-cost module manufacturing, further improvements in performance and device fabrication are necessary [24].

Using a novel solution phase ligand exchange protocol, we aim to improve surface passivation and understand the influence of halide salts on device performance of QD photovoltaic films. The new protocol involves additional treatment of bromide, which is smaller than the conventionally used material, iodide. We compare performance and optical properties of devices made with two different types of QDs; (1) QDs treated with iodide only; (2) QDs treated with both iodide and bromide. Particularly, open circuit voltage is both experimentally measured and theoretically calculated to assess the potential of the proposed treatment. Consequently, this project will let us better understand the relationship between the surface chemistry and the optoelectronic properties of QDs.
Chapter 2

Methods and Experiment

Colloidally stable PbS QDs are synthesized and capped with long ligands [24]. When such QDs are used in devices, these long ligands left on the surface of the QDs act as insulating barriers that significantly limit the charge transport, and thereby reduce $J_{sc}$. For better conduction, long ligands are exchanged with shorter ligands [28].

In this chapter, two types of PbS QD ink production protocol with a different number of halides used are presented. Experiment details—such as device fabrication and performance measurement methods—and related theories that we use to assess the effect of proposed protocol on PbS QDs are also introduced.

2.1 Device Fabrication

Syntheses of PbS QDs and ZnO nanoparticles

PbS QDs and ZnO nanoparticles are synthesized via methods described in the literature [24].

Ligand Exchange

We adapted the ligand exchange method from the literature [29]. To make one device for each method, 35.175 mg of tetrabutylammonium iodide (TBAI) is dissolved in 0.175 ml of ethanol. This solution is added to a vial containing 0.1 ml of the oleic-
acid-capped PbS QDs (60 mg ml\(^{-1}\) in octane). The vial is mixed for 30 s using a vortexer and then centrifuged at 5000 rpm for 2 min. The resulting supernatant is discarded, and the QD pellet is resuspended in 0.2 ml dimethylformamide (DMF). This solution is halved into two vials, which go through different processes:

- **Control ink (TBAI only):** 0.3 ml of ethanol is added to one of the vials for re-precipitation.

- **Bromine treated ink (additional TBABr treatment):** 0.3 ml of tetra-butylammonium bromide (TBABr) in ethanol (–mg ml\(^{-1}\)) is added to the other vial.

Then, both of the vials are centrifuged at 5000 rpm for 2 min. After the supernatants are discarded, the pellets are dried under nitrogen air flow for 30 s. Each pellet of the QDs is resuspended in 30 µl of DMF. The resulting inks are purified via centrifugal filtration.

**Substrate preparation**

Pre-patterned Indium-doped Tin Oxide (ITO) glass substrates are used as the bottom electrode of the full device stack shown in Figure 2.1. These substrates are cleaned through sequential sonication in 2% Micro-90 in deionized (DI) water, acetone, and isopropanol. The substrates are then dried under nitrogen flow, and oxygen plasma cleaned.
ZnO and PbS QD ink deposition

ZnO is spin coated onto the clean substrate following the procedure described in the literature [24]. To prepare a device, 30 µl of one of the QD inks prepared through the ligand exchange process is dropped on the middle of the substrate, on top of the ZnO layer, as shown in figure 2.1. Then, the substrate is immediately spun at 1000 rpm for a minute and at 3000 rpm for 30 seconds in a fume hood under an ambient atmosphere at room temperature.

Electrode

To complete the device, Au electrodes are deposited on top of the QD layer by thermal evaporation. A shadow mask is used to allocate six separate areas where Au electrodes are deposited. Each of the resulting devices has six cells. The active area — which is the overlapping area of the Au electrodes and the layer below — of a cell prepared through this setup is 5.44 mm².

2.2 Experimental Performance of PbS QDSCs

J-V testing

Current density (J) and voltage (V) measurements are done via the method used in the literature [24]. A device was placed under AM 1.5 simulated solar illumination of 1 sun at 100 mWcm⁻². Its J-V characteristics were tested using a Keithley 2636A sourcemeter by sweeping through short circuit - forward bias - short circuit - reverse bias points with a voltage step size of 0.02 V.

2.3 Theoretical Performance Limit of PbS QDSCs

In order to analyze whether radiative or non-radiative loss mechanisms get affected by Br treatment, we implement a theoretical analysis. In this section, equations and film characterization methods used in calculation of theoretical limits for open circuit
voltage are introduced. The limits are examined for both — (1) the control and (2) Br treated— device groups to study the effect of additional halide ion (Br\(^-\)) treatment on QDs.

Since the well known Shockley-Queisser (SQ) theory assumes the use of ideal semiconductors [17], we use the approach of Rau et al. that incorporates a generalized version of SQ limit in order to take non ideal effects into account [30].

From the Shockley diode equation at open-circuit conditions

\[
J_{sc} = J_0 \left( \exp \left( \frac{qV_{oc}}{k_B T_c} \right) - 1 \right),
\]

(2.1)

where \(J_{sc}\) is short circuit current density, \(J_0\) the saturation current of the solar cell, \(q\) the elementary charge, \(V_{oc}\) open circuit voltage, \(k_B\) the Boltzmann constant, and \(T_c\) the absolute temperature of the solar cell, we can solve for the open circuit voltage

\[
V_{oc} = \frac{k_B T_c}{q} \ln \left( \frac{J_{sc}}{J_0} + 1 \right) \approx \frac{k_B T_c}{q} \ln \left( \frac{J_{sc}}{J_0} \right).
\]

(2.2)

The estimation made in the latter part of equation 2.2 is based on the fact that the ratio of \(J_{sc}\) to \(J_0\) typically ranges from \(10^{14}\) to \(10^{18}\).

Rau et al. derive an equation that incorporates a nonradiative loss mechanism in equation 2.2 by introducing external quantum efficiency (EQE),

\[
\text{EQE} = \frac{J_{rad}^{\text{rad}}}{J_0^{\text{rad}} + J_0^{\text{nrad}}} = \frac{J_{rad}^{\text{rad}}}{J_0},
\]

(2.3)

where \(J_0^{\text{rad}}\) denotes the saturation current that induces one emitted photon per injected electron, and \(J_0^{\text{nrad}}\) the saturation current that does not induce photon emission. Writing \(J_0\) in terms of EQE, equation 2.2 can be rewritten as

\[
V_{oc} = \frac{k_B T_c}{q} \ln \left( \frac{J_{sc}}{J_0^{\text{rad}} / \text{EQE}} \right) = \frac{k_B T_c}{q} \left[ \ln \left( \frac{J_{sc}}{J_0^{\text{rad}}} \right) + \ln(\text{EQE}) \right].
\]

(2.4)

Using the principle of detailed balance, we can find that emission is closely related to absorption [30]. Applying this principle to equation 2.4, we can get
\[ V_{oc} = \frac{k_B T_c}{q} \ln \left( \frac{\epsilon_{\text{in}} \int A(E) \Phi_{\text{sun}}(E) dE}{\epsilon_{\text{out}} \int A(E) \Phi_{\text{bb}}(E) dE} \right) + \frac{k_B T_c}{q} \ln(\text{PLQY}), \tag{2.5} \]

where \( \epsilon \) is a measure of how spread out the light is, \( \Phi_{\text{sun}}(E) \) photon flux of sun, and \( \Phi_{\text{bb}}(E) \) black body radiation flux at the cell temperature. The numerator measures how well the material absorbs sunlight at the given photon energy. The denominator evaluates how much light the cell emits based on its absorption quality with the principle of detailed balance.

For clarity, I will explicitly separate equation 2.5 into two terms:

\[ V_{oc}^{\text{rad}} = \frac{k_B T_c}{q} \ln \left( \frac{\epsilon_{\text{in}} \int A(E) \Phi_{\text{sun}}(E) dE}{\epsilon_{\text{out}} \int A(E) \Phi_{\text{bb}}(E) dE} \right) \tag{2.6} \]

\[ V_{oc}^{\text{nrad}} \approx \frac{k_B T_c}{q} \ln(\text{PLQY}) \tag{2.7} \]

Equation 2.6 is governed by radiative recombination losses. For example, if photon emission was the only source of loss, we would only need this term in the equation. That being said, there is another loss mechanism, non-radiative loss, present in the system. For example, electrons excited by photon absorption could recombine via traps and lose their energy as heat. Equation 2.7, which is the second term of equation 2.5, takes this entropic loss mechanism into account [30].

\subsection{2.3.1 Radiative Limit}

\textbf{Film Characterization - Absorbance}

Absorbance, \( A \), gives some measure of the light absorbing capacity of a substance at a specific wavelength of light. It is often called optical density, and is given by

\[ A = -\log_{10} \left( \frac{I_t}{I_0} \right) = -\log_{10} T, \tag{2.8} \]

where \( I_t \) is transmitted radiation, \( I_0 \) is incident radiation, and \( T (= I_t/I_0) \) is transmittance. Note that it does not necessarily mean that all of the non-transmitted
radiation is absorbed by the substance. There could be some portion of radiation that is reflected and thus not absorbed.

A more accurate measure of light absorbing capacity is given by absorptance, which is given by

\[ A_p = 1 - T - R, \quad (2.9) \]

where \( R \) is reflectance. When the reflectance of the film is negligible, absorptance can be approximated as

\[ A_p \approx 1 - T = 1 - 10^{-A}. \quad (2.10) \]

For solar cell application, due to a reflective electrode (e.g., \( \text{Au} \) or \( \text{Al} \)) at the back of device, we can assume that the incident light reflects from the back surface and thus passes through the solar cell twice [31]. Therefore, for characterization of the film, this assumption makes the final equation to be

\[ A_p \approx 1 - 10^{-2A}. \quad (2.11) \]

For calculation of radiative limits, we will use experimentally measured absorbance \((A)\) of films after an interpolation process for the region with photon energy below bandgap. As described in the definition of the photovoltaic effect, the film does not absorb a photon with energy lower than the bandgap. Yet, actual measurement may involve some noise or offset. Neglecting this process may yield a theoretical dark current orders of magnitude higher than the actual value and hence reduce the \( V_{oc} \) significantly. To prevent this issue, we will use published values [32] for interpolation in this tail part. (Figure 3-3 may be helpful for visualization).

Then, the corrected absorbance spectra are plugged into equation 2.11 to approximate absorptance \((A_p)\). Through such a calculation, we can examine whether there is a difference in radiative recombinations of the two types of devices—(1) the control and (2) \( \text{Br} \) treated—and if so, how influential the difference is to device performance.
Absorbance spectra are obtained using a Cary 5000 UV-Vis-NIR spectrophotometer, by measuring film samples (PbS QD ink deposited on glass substrates). Figure 2-2 shows the overall scheme of the measurement.

2.3.2 Non-radiative Loss

Film Characterization - Photoluminescence Quantum Yield (PLQY)

Quantum yield is defined as a ratio of the number of photons emitted to the number of photons absorbed [33]. In PLQY measurement, the ratio of photons emitted through photoluminescence to the number of photons absorbed is calculated. This in effect gives us the percentage of radiative recombination occurring in our device. Again, we apply the principle of detailed balance to use PLQY measurement in the theoretical calculation; collected carriers are balanced with emitted photons. Hence we can use PLQY instead of EQE to calculate the upper limit of the non-radiative loss.

Measurement Method - PLQY

The measurement setup and method are described in the literature [34]. A film sample was placed in an integrating sphere as shown in figure 2-3. The data was collected by an 818-IR germanium photodetector.
Figure 2-3: Schematic diagram of photoluminescence quantum yield measurement setup. A film sample is placed in the integrating sphere for the measurement. Insets in the callout are sequential diagrams of an electron in the sample changing its state in response to the light source (a) Initial state of the electron in sample. (b) The electron (blue, filled circle) is promoted to an excited state in conduction band due to absorption of the incident light. The unfilled circle shows where the electron was before. (c) Relaxation of the electron and consequential light emission.
Chapter 3

Results and Discussion

In this chapter, in order to compare the performance of the (1) control and (2) Br treated devices, we compare three kinds of open circuit voltages:

- experimental open circuit voltage $V_{oc}^{\text{exp}}$, measured with the J-V testing setup

- theoretical radiative limit of open circuit voltage $V_{oc}^{\text{rad}}$, calculated by plugging absorptance into the first term of equation 2.6

- theoretical non-radiative limit of open circuit voltage $V_{oc}^{\text{nrad}}$, calculated by plugging photoluminescence quantum yield into the second term of equation 2.7

3.1 Experimentally Measured Parameters

Key parameters of the devices measured through J-V testing setup are shown in figure 3-1 and table 3.1. On average, there were about a 40 mV increase in open circuit voltage and 0.9 % increase in power conversion efficiency (PCE) of Br treated devices.
Figure 3-1: J-V curve of the control and Br treated devices. Data courtesy of Nicole Moody.

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>Br Treated</th>
<th>Difference (Br - control)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{oc}$ [V]</td>
<td>0.51 ± 0.01</td>
<td>0.555 ± 0.004</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>$J_{sc}$ [mA/cm$^2$]</td>
<td>21.7 ± 0.2</td>
<td>21.8 ± 0.5</td>
<td>0.1 ± 0.5</td>
</tr>
<tr>
<td>FF</td>
<td>0.56 ± 0.03</td>
<td>0.58 ± 0.03</td>
<td>0.02 ± 0.04</td>
</tr>
<tr>
<td>PCE [%]</td>
<td>6.2 ± 0.6</td>
<td>7.1 ± 0.5</td>
<td>0.9 ± 0.8</td>
</tr>
</tbody>
</table>

Table 3.1: Average of key parameters of the two types of devices studied. About six cells are measured for each type of devices. The values given after ± symbols are standard deviation of the mean.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}^{exp}$ [V]</th>
<th>$J_{sc}^{exp}$ [mA cm$^{-1}$]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>0.51 ± 0.01</td>
<td>21.7 ± 0.2</td>
<td>0.56 ± 0.03</td>
<td>6.2 ± 0.6</td>
</tr>
<tr>
<td>Br treated</td>
<td>0.555 ± 0.004</td>
<td>21.8 ± 0.5</td>
<td>0.58 ± 0.03</td>
<td>7.1 ± 0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>$V_{rad}^{rad}$ [V]</th>
<th>$J_{sc}^{cal}$ [mA cm$^{-1}$]</th>
<th>$J_{o}^{cal}$ [mA cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.97 ± 0.01</td>
<td>21 ± 8</td>
<td>$9 \times 10^{-16}$</td>
</tr>
<tr>
<td>Br treated</td>
<td>0.99 ± 0.01</td>
<td>18 ± 8</td>
<td>$3 \times 10^{-16}$</td>
</tr>
</tbody>
</table>

Table 3.2: The theoretical upper limits of key parameters calculated using the estimated absorptance spectra shown in figure 3-2. Due to multiple steps of estimations used in calculations, the uncertainties may be greater than the given values.
Figure 3-2: The estimated absorptance spectra of the control group (red dashed line) and the Br treated group (blue solid line) are depicted with the matching y-axis scale on the right. Photon flux (green dotted line) calculated from AM 1.5 solar irradiance is overlaid in the graph to visualize the integrand of the numerator in equation 2.5. Note the blueshift of the absorptance peak after the Br treatment, which is magnified in the inner plot.

### 3.2 Calculated Theoretical Limits

#### 3.2.1 Radiative limit

The estimated absorptance spectra are used to examine the effect of bromide treatment on radiative $V_{oc}$. From equation 2.6, theoretical upper limits of $V_{oc}$ and $J_{sc}$ are calculated, which are shown in table 3.2. The spectra used in this calculation are plotted in figure 3-2 to help visualization. The inner plot of figure 3-2 shows the blueshift (shift to shorter wavelength/higher energy) of the absorptance peak in Br treated device. This blueshift corresponds with an anticipated improvement in theoretical radiative open circuit voltage $\Delta V_{oc}^{rad}$ of 20 mV.

#### 3.2.2 Non-radiative limit

PLQY values are used to examine the effect of bromide treatment on non-radiative losses. Figure 3-4 shows photoluminescence of the control and Br treated films. The
blueshift, as well as an almost threefold increase in quantum yield, was observed.

When the device is ideal (EQE = 1; all the incident photons are converted to electrons without any loss), then non-radiative loss becomes zero, as ln(1) evaluates to 0. On the other hand, any EQE smaller than 1 will make ln(EQE) < 0. In other words, the less a device is ideal, the more negative the $V_{\text{oc}}^\text{nrad}$ is. Hence, it is more likely to have smaller (more negative) $V_{\text{oc}}^\exp$ for a non-ideal device.

The blueshift in exciton peak for Br treated samples may increase $\Delta V_{\text{oc}}^\text{rad}$ by 20 mV. However, this improvement does not fully explain the experimental difference $\Delta V_{\text{oc}}^\exp$ of 40 mV. Another theoretical value comparison, $\Delta V_{\text{oc}}^\text{nrad} = 30$ mV, shows an improvement comparable to the improvement seen in experimental $V_{\text{oc}}$.

The theoretical open circuit voltages $V_{\text{oc}}^\text{rad}$ and $V_{\text{oc}}^\text{nrad}$ provide theoretical upper limit of $V_{\text{oc}}$. The discrepancies in the experimentally measured and calculated theoretical limit of $V_{\text{oc}}$ may be due to electrode contact loss or other mechanisms that are not considered in the calculation. However, as we are comparing just the differences in $V_{\text{oc}}$ rather than taking the calculated values as absolutely correct estimates, these
Figure 3-4: Photoluminescence of control and Br treated QD ink films. Data courtesy of Nicole Moody.

<table>
<thead>
<tr>
<th></th>
<th>$V_{oc}^{exp}$</th>
<th>$V_{rad}^{oc}$</th>
<th>$V_{nrad}^{oc}$</th>
<th>$V_{rad}^{oc} + V_{nrad}^{oc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>0.51 ± 0.01</td>
<td>0.97 ± 0.01</td>
<td>-0.145 ± 0.005</td>
<td>0.83</td>
</tr>
<tr>
<td>Br treated</td>
<td>0.555 ± 0.004</td>
<td>0.99 ± 0.01</td>
<td>-0.115 ± 0.001</td>
<td>0.88</td>
</tr>
<tr>
<td>Difference (Br - control)</td>
<td>0.04 ± 0.01</td>
<td>0.02 ± 0.01</td>
<td>0.030 ± 0.005</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table 3.3: Calculated theoretical open circuit voltages of the two types of devices studied are shown in the table with the experimentally measured values for comparison. The unit is volt.
results still remain valuable.

Better estimates may be available by using directly measured absorption spectra instead of using the estimated absorption spectra from measured absorbance spectra. Also, the films used in absorbance measurement were thinner than the films used in actual devices, which might have added a constant systematic error to film measurements of both devices. Moreover, since the optical measurements were taken with the film samples without any other layers from the device stack, such as ITO, ZnO, or Au electrode, the estimates may not incorporate the effects of interaction among these layers.
Chapter 4

Conclusion and Outlook

In this thesis, we examined the performance and optical properties of two types of PbS quantum dot solar cell devices: (1) control; (2) Br treated. Through J-V testing, it was shown that Br treated devices have higher open circuit voltage with an improvement ($\Delta V_{oc}^{exp}$) of 40 mV and power conversion efficiencies with an improvement of 0.9% compared to control devices. We then tried to find the origin of such improvement in $V_{oc}$, by comparing the differences in theoretical upper limits of both radiative ($\Delta V_{oc}^{rad} = 20$ mV) and non-radiative ($\Delta V_{oc}^{nrad} = 30$ mV) open circuit voltages.

From film characterization, we acknowledged the blueshift in exciton peak for Br treated samples. Yet, its resulting influence in $\Delta V_{oc}^{rad}$ of 20 mV does not fully cover the experimental difference $\Delta V_{oc}^{exp}$ of 40 mV. This discrepancy, along with the other independent theoretical value comparison ($\Delta V_{oc}^{nrad} = 30$ mV), indicates a significant contribution of the improvement in non-radiative $V_{oc}$ to the improvement of experimental $V_{oc}$. Hence, this noteworthy difference in non-radiative $V_{oc}$ suggests the possible enhancement in surface passivation of PbS quantum dots via the proposed Br treatment.

For future research, surface chemistry may be explored to verify the effect of Br treatment on PbS QD surface, using X-ray Photoelectron Spectroscopy, X-ray Fluorescence, or X-ray Powder diffraction measurement methods. Direct measurements
of absorption and external quantum efficiency may also be helpful for retrieving more realistic theoretical limits. The smaller halide salt treatment method presented in this thesis may be applied to different types of quantum dot solar cells to improve the open circuit voltage and power conversion efficiency without damaging short circuit current density.


