CONTROLLING THE PHOTOPHYSICAL PROPERTIES OF SEMICONDUCTOR QUANTUM DOT ARRAYS BY STRATIGICALLY ALTERING THEIR SURFACE CHEMISTRY

by

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A thesis submitted to the Faculty of the Graduate School of the University of Colorado in partial fulfillment of the requirement for the degree of Doctor of Philosophy Department of Chemistry and Biochemistry 2017 This thesis entitled:

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Strategic Alteration of Their Surface Chemistry

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Controlling the Photophysical Properties of Quantum Dot Arrays by Strategically Altering

Their Surface Chemistry

Thesis directed by Professor Arthur J. Nozik

Semiconductor quantum dots (QDs) are interesting materials that, after less than 40 years of research, are used in commercial products. QDs are now found in displays, such as Samsung televisions and the Kindle Fire, and have applications in lighting, bio-imaging, quantum computing, and photovoltaics. They offer a large range of desirable properties: a controllable band gap, solution processability, controlled energy levels, and are currently the best materials for multiple exciton generation. The tunable optoelectronic properties of QDs can be controlled using size, shape, composition, and surface treatments—as shown here. Due to the quasi-spherical shape of QDs the surface to volume ratio is high, *i.e.* many of the constituent atoms are found on the QD surface. This makes QDs highly sensitive to surface chemistry modifications. This thesis encompasses the effects of surface treatments for QDs of two semiconducting materials: lead chalcogenides and CsPbI₃.

Our group developed a new synthetic technique for lead chalcogenide QDs via the cation exchange of cadmium chalcogenides. An in-depth chemical analysis is paired with optical and electrical studies and we find that metal halide residue contributes to the oxidative stability and decreased trap state density in cation-exchanged PbS QDs. We exploit these properties to make air-stable QD photovoltaic devices from both PbS and PbSe QD materials.

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Beyond the effects of residual atoms left from the synthetic technique, I investigated how to controllably add atoms onto the surface of QDs. I found that by introducing metal halides as a post-treatment in an electronically coupled array I am able to control the performance parameters in QD photovoltaic devices. These treatments fully infiltrate the assembled film, even under short exposure times and allow me to add controlled quantities of surface atoms to study their effects on film properties and photovoltaic device performance.

Finally, I sought to apply the knowledge of the lead chalcogenide QD surfaces to produce QD photovoltaics from a new material: CsPbI₃. I fabricated the first perovskite QD photovoltaic devices and using similar treatment methods as the lead chalcogenide QD arrays, I am able to influence the photophysical properties of CsPbI₃ QD arrays.

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Chapter 1: Introduction

1.I Nanomaterials

Nanomaterials have features on the scale of 1-100 nm causing them to display unique properties compared to bulk materials of the same composition and therefore producing interesting and important macro-scale effects. For example, the beautiful, rainbow reflections of opals are due to 100-300 nm silica spheres, which pack in ordered arrays altering the optical properties of silica. Nanostructured surfaces can be superhydrophobic, self-cleaning, or "sticky" (such as the bottom of gecko's feet) depending on the material and structure. Nanomaterials also have very high surface areas, which can be useful for catalysis and energy storage. Because of these features, nanomaterials are widely researched in a variety of disciplines from drug delivery to television screens, and provide new, high-tech routes to advance many technologies.

Semiconductor nanomaterials in particular have unique photophysical properties when the extent of the semiconductor crystal is smaller than the Bohr radius of an exciton in the material. This causes quantum confinement of electrons or holes, and alters the optical and electrical properties of the material. When semiconductor nanocrystals are confined in all three dimensions, they are called quantum dots (QDs) and the quantum confinement imparts advantageous photophysical properties that are the foundation of this thesis work. QDs are found in many modern-day technologies and research is ongoing to use them in energy applications, lighting systems, televisions, quantum computing, and bioimaging. In this thesis I focus on the photophysical properties which make QDs an attractive material for photovoltaic devices. Specifically appealing is the control over band gap, transport properties, and energy level structure afforded by tuning the size, shape, and surface chemistry.

1.II Motivation

Global energy consumption has been steadily increasing and energy needs are expected to continue to rise. In 2012, the world consumed about 18 TW of energy and this is projected to increase to almost 30 TW by 2040. In Figure 1.1b, energy production by fuel type shows that we burn fossil fuels to produce the majority of our energy, which has been the driving force of climate change since the industrial revolution. As global energy demand rises, it is important that clean energy technologies are implemented to meet these higher demands and replace fossil fuels as the dominant source of energy. In Figure 1.1b the energy consumption by sector is also included. Photovoltaics are best suited to replace the burning of fossil fuels for electricity generation. Burning coal and natural gas produced 63% of U.S. electricity in 2015, Figure 1.1b, releasing dangerous pollutants such as SO₂, mercury, NO_x, and the green-house gas CO₂. By replacing coal and natural gas with solar and wind technologies, we can reduce environmental pollution and help curb global climate change. It is important to note that transportation makes up over 25% of our energy consumption. This sector will require the proliferation of electric cars and renewable fuels (solar fuel production or biomass), which are active areas of research as well, but are not the focus of the studies presented here. Although, with the adoption of electric vehicles, the transportation and electricity sectors will overlap and demands for electricity will increase at an even faster rate.

2



U.S. primary energy consumption by source and sector, 2015 Total = 97.7 quadrillion British thermal units (Btu)



Figure 1.1: Energy usage by source in the world and in the U.S. (a) This bar graph from the U.S. Energy Information Administration shows the global energy usage with colored segments representing the percentage of total energy consumed from each source listed in the key. This graph has data from 1990 through 2013 and projected usage for 2014 through 2038. Source: Adapted from EIA International Energy Outlook 2016 (May 2016) (b) For 2015, this graph shows how much of each energy source was used for each sector. The numbers associated with the arrows on the left are the percentage of the resource going to a specific sector and numbers on the right show the percentage of the sector supplied by a specific source. For example, nuclear electric power is only used for the electric power (100% on the left), but accounts for just under a quarter of the electric power sector (22% on the right). Sources: U.S. Energy Information Administration, Monthly Energy Review (April 2016), Tables 1.3, 2.1-2.6.

1.III Next-Generation Photovoltaics

The Shockley-Queisser limit has been the cornerstone of photovoltaic research since they published the detailed-balance limit in 1961.¹ Shockley and Queisser calculated the detailed-balance limit based on the hypothesis below.

There is an ultimate efficiency for any device employing a photoelectric process which has a single cut-off frequency v_g ... According to the ultimate efficiency hypothesis: Each photon with energy greater than hv_g produces [only] one electric charge q at a voltage of $V_g = hv_g/q$.¹

Where hv_g is the band gap energy of the semiconductor. This hypothesis is generally thought of in two parts: 1) photons with energy above the bandgap will be absorbed while photons without sufficient energy to excite an electron into the conduction band will be transmitted and 2) electrons and holes excited with photons at a higher energy than the band gap (hot carriers) will cool to the band edge through electron-phonon scattering before being extracted as current.

The Shockley-Queisser limit is widely accepted as the thermodynamic limit for single-junction solar cells and in order to surpass this limit one must subvert the assumptions discussed in the previous paragraph. Two ways researchers are working to recoup the energy lost from hot carriers cooling to the band edge are: hot carrier extraction and multiple exciton generation. It has been proposed that if contacts with varying work functions are used in a device, hot carriers could be extracted before they cool to the band edge. Extracting carriers before they are allowed to cool results in a higher photovoltage and the maximum theoretical efficiency of a device with hot carrier extraction is 66 %.²⁻⁷ Utilization of hot carrier extraction has been difficult to achieve in photovoltaic devices.

Multiple exciton generation (MEG) has been demonstrated in photovoltaic devices and this process can increase the theoretical maximum power conversion efficiency to 42%.⁸⁻¹¹ In MEG a single photon that has energy at least twice the band gap is used to produce two electron-hole pairs. Instead of hot carriers cooling to the band edge and losing the excess energy as heat, the energy is used to create additional electron-hole pairs, which are then extracted as excess current from the solar cell. If a material is able to produce extra carriers efficiently (i.e. two excitons at energies twice the bad gap, three excitons at energies three times the band gap, and so on), the theoretical maximum power conversion efficiency of a photovoltaic device increases to 42% (Figure 1.2).⁹ Another important consideration is that the ideal band gap of a semiconductor with MEG enhancement is 0.7 eV⁹ while a standard, single-junction device has an ideal band gap of 1.3 eV (Figure 1.2).¹



Figure 1.2: Photovoltaic efficiency in MEG enhanced devices. (a) The theoretical maximum power conversion efficiency (PCE) as a function of band gap is shown for a range of MEG efficiencies. The ideal band gap without utilizing MEG is ~1.3 eV, while a device with MEG has an ideal bandgap of ~0.7 eV. Reprinted with permission from Beard, *et al., Acc. Chem. Res.,* **2013**, *46* (6), pp 1252–1260. Copyright 2013 American Chemical Society.¹² (b) The theoretical maximum efficiency is also dependent on the threshold energy in addition to the MEG efficiency. Here, L(*n*) is the number of band gaps of energy required for the MEG threshold and the slope is the MEG efficiency above the threshold energy. Reprinted with permission from Nozik, *Nano Lett.,* **2010**, *10* (8), pp 2735–2741. Copyright 2010 American Chemical Society.²

In Figure 1.2 the theoretical maximum power conversion efficiency (PCE) is shown as a function of band gap and MEG efficiency. In Figure 1.2a, the MEG efficiency is denoted by *P* which is the ratio of the rate of MEG (k_{MEG}) to the rate of cooling (k_{cool}); k_{MEG}/k_{cool} . The value *P* describes the competition between MEG and cooling processes.¹² The maximum efficiency of >40 % is only achieved when MEG out-competes cooling by a substantial amount (P = 10,000). In Figure 1.2b, the threshold energy is also taken into account. The threshold energy is the energy at which MEG is first observed in a material. Ideally, this threshold energy is two times the band gap, so that each photon at exactly twice the band gap energy creates two excitons. The threshold energy is denoted as L(n) in Figure 1.2b where *n* is the number of bad gaps of energy required to reach the threshold energy. The MEG efficiency is still included in the calculation of maximum PCE and the slope in this figure is the MEG efficiency above the threshold energy. Figure 1.2b reveals the importance of the threshold energy and the MEG efficiency on PCE improvement. Having a threshold energy of exactly two times the band gap is significantly better than even n = 2.5, and when the MEG efficiency follows the staircase function (100 % MEG efficiency) the device performance is maximized.

QD materials are attractive candidates for photovoltaic devices that can surpass the Shockley-Quiesser limit because of their inexpensive production and the ability to finelytune the photophysical properties. Beard and Nozik, *et al.* showed that QD materials are very efficient at the MEG process because of the relaxation of the requirement for momentum conservation, ability to influence the carrier relaxation time, and the strong Coulomb coupling between excitons, which drives MEG.⁹ QDs are therefore good

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candidates to be materials with a threshold energy of two times the band gap and a high MEG efficiency. For a thorough review of the MEG process in QDs see reference 13.

In addition to gaining desirable photophysical properties, making a material nanosized can influence the strucutral properties as well. Due to the large surface energy of nanocrystals, colloidal QDs can exist in crystal phases that are typically only observed at high temperatures in bulk samples of the same material. These high-temperature crystallographic phases can maintain stability at room temperature when the material is in the form of QDs. This property will be discussed in detail in Chapter 7.

1.IV Lead Chalcogenide QDs

Materials that have strong quantum confinement and a low initial band gap are ideal systems for studying MEG. Strong quantum confinement enhances MEG in semiconductors and the low bulk band gap provides a large range of feasible band gaps when the material is quantum confined. Lead chalcogenides meet both of these material requirements, offering an ideal system for the study of MEG. The bulk band gaps are 0.37 eV PbS and 0.28 eV PbSe and the Bohr exciton radii for PbS and PbSe are 18 and 46 nm, respectively.^{14–17} When QDs are produced the band gap is adjustable from the bulk band gap up to ~2 eV, allowing the band gap to be tuned for single-junction solar cells (1.3 eV), MEG-enhanced solar cells (0.7 eV), or any band gap value desired for a particular layer in a multijunction device or light emitting diode. Lead chalcogenide QDs have been shown to be efficient at MEG, with a low threshold energy and high k_{MEG} to k_{cool} ratio,^{13,18–23} and are therefore an ideal system to study MEG enhancement in photovoltaic devices.

In order to show the large effect of QD size on the band gap we turn to quantum mechanical mathematics. Lead chalcogenide QDs are in the strong-confinement regime and so the energy levels follow the same pattern as the simple particle-in-a-box analysis:²⁴

$$E_{confinement} = \frac{h^2}{8mR^2}$$

Where *h* is Planck's constant, *m* is the reduced mass of the electron and hole, and *R* is the radius. This confinement energy is added to the band gap energy (E_g) of the bulk material and the Coulomb interaction energy in order to determine the size-dependent band gap (the lowest energy transition) of the QD:^{24,25}

$$E \simeq E_g + \frac{h^2}{8mR^2} - \frac{1.8e^2}{\epsilon R}$$

Where e is the charge of an electron and ϵ is the dielectric constant of the semiconductor material.

1.IV.a Synthesis

The size-dependent band gap has been harnessed by having precise control over the QD size. In 2003, Hines and Scholes published the Pb-oleate and bis(trimethylsilyl)sufide (TMS) synthesis of PbS QDs that has been the standard in the field for the past decade due to the good size distribution and easily tunable band gap.²⁶ The final QD size is responsive to reaction temperature, oleic acid concentration, and reaction time.^{26,27} Researchers have similar control over the synthesis of PbSe QD using trioctylphosphine selenide by adjusting the same three reaction conditions.²⁸⁻³⁰

Another route to synthesize QDs of a particular composition and shape is through a multi step process of ion substitution or ion exchange. This allows independent control of the shape and composition that may not be possible through direct synthesis, as well as the ability to synthesize core-shell and Janus particles (nanocrystals composed of two or more distinct materials) with desirable optical properties.^{31–37} Our group also recently found that performing a complete cation exchange of cadmium chalcogenide QDs produces high quality and air-stable lead chalcogenide QDs.^{38,39} Using PbCl₂ as the cation source, the CdS or CdSe QDs are injected at elevated temperature and rapidly convert to PbS and PbSe QDs, respectively. The increased air-stability and enhanced optical properties are attributed to the *in situ* halide passivation and the residual cadmium that is most likely residing on the QD surface. In a previous synthetic report my group showed that using PbCl₂ as a precursor in place of PbO increases the air-stability of the lead chalcogenide QDs and the cation exchange synthesis improves on this technique.⁴⁰ The synthesis and characterization of the cation exchanged QDs is described in detail in Chapter 2. The QDs produced from the cation exchange procedure will be discussed in depth in Chapters 3, 4, and 5.

In the past few years, researchers have been exploring halide passivation for lead chalcogenide QDs, as well as increasing the monodispersity of the products. Having airstable QDs is preferred for manufacturing processes and increasing the monodispersity lowers the energy dispersion in a QD array, which can increase the conductivity of coupled QD-arrays.⁴¹ In addition to the PbCl₂ synthesis published by our group,⁴⁰ the Sargent group regularly uses a CdCl₂ treatment as the final step in the synthesis of PbS QDs, which are then used to fabricate high efficiency photovoltaics,^{42–45} and Pietryga, *et al.* used molecular chorine to passivate PbSe QD surfaces and increase the air-stability of the final product.⁴⁶ It is hypothesized that halides can bind in-between the oleate ligands, providing better surface passivation than oelate alone and protecting the QD surface from oxidation. QDs with halide passivation can be processed, stored, and deposited as films in ambient conditions, as opposed to using air-free techniques from beginning to end.

In order to increase the monodispersity of lead chalcogenide QDs, Tisdale, *et al.* used a large molar excess of PbCl₂, which slowed down the Ostwald ripening process.⁴⁷ In pioneering work done by the Owen group, thiourea and selenourea precursors are used to control the reaction kinetics and produce QDs with extremely narrow size distributions.^{48,49} In Figure 1.3 the absorption spectra for three different QD syntheses are presented for comparison. Figure 1.3a is the PbSe QDs synthesized from the cation exchange reaction and Figure 1.3b and c are PbS QDs synthesized by the Tisdale PbCl₂ technique and the Owen thiourea technique, respectively. These new synthesis techniques provide greater control over the size of the QD product, but each new synthesis also changes the resulting QD surface chemistry, which will be discussed in the next paragraph.



Figure 1.3: Absorption spectra of new lead chalcogenide QD syntheses. (a) Absorption spectra of cation exchanged PbSe QDs. The text next to each spectrum notes the position of the first exciton peak for the CdSe QDs used as the precursor for the PbSe QDs. The largest sizes are synthesized using the CdSe with a first exciton peak at 601 nm and the temperature of the reaction was increased to result in larger PbSe QDs.³⁸ Reprinted from Zhang, *et al. Nano Lett.* **2014**, *14* (10), 6010–6015. **(b)** These absorption spectra show the

PbS QDs synthesized using a large molar excess of PbCl₂ to reduce Ostwald ripening. The QDs 5.1 nm and larger were all synthesized at 120C with various reaction times.⁴⁷ Reprinted from Weidman, *et al. ACS Nano* **2014**, *8* (6), 6363–6371. **(c)** PbS QDs synthesized using thiourea precursors to control the reaction kinetics. By changing the chemical moiety attached to the thiourea, the reactivity of the precursor can be tuned to produce a wide range of PbS QD sizes.⁴⁸ Reprinted with permission from Hendricks, *et al. Science* **2015**, *348* (6240), 1226–1230. Copyright 2015, American Association for the Advancement of Science.

1.IV.b Surface Chemistry

The surface chemistry and composition of metal chalcogenide QDs has been widely studied and is generally well understood in terms of ligands and binding motifs. QD ligands are classified in a similar way to organometallic complexes, summarized in Figure 1.4. This naming convention was first proposed by Owen, *et al.* and has become pervasive in the field.^{50,51} Using this convention a ligand is classified as L-type if it is a Lewis base, Z-type if it is a Lewis acid, and X-type if it contributes one electron to the bond. X-type ligands can either be part of an ion pair or terminate the QD lattice. This ligand binding notation is helpful when categorizing new ligands, calculating charge balance in a QD, and understanding ligand exchange schemes.



Figure 1.4: Types of ligands on metal chalcogenide QDs. The various types of ligands are shown in this schematic, along with examples of each ligand type in the bottom left corner. This schematic is drawn assuming that the QD core is stoichiometric and the only atoms drawn explicitly are metal (M) and chalcogenide (E) atoms that are part of or interacting with the ligand shell.⁵⁰ Reprinted with permission from Anderson, *et al. J. Am. Chem. Soc.* **2013**, *135* (49), 18536–18548. Copyright 2013 American Chemical Society.

Lead chalcogenide QDs are modeled as a stoichiometric core surrounded by an excess of lead, which is bound as Pb(OA)₂ to satisfy charge balance. The oleate ligand is best described as an X-type ligand bound to excess surface Pb or as an L-type ligand binding as Pb(OA)₂ associated with the surface. Many elemental analysis techniques along with NMR studies have corroborated this structure^{52–57} and researchers have shown that in CdSe, the metal in the outer shell does not contribute strongly to the electronic structure of the QD,⁵⁰ suggesting the L-type binding of metal-oleates is a more accurate binding picture. When other anions are introduced into the QD synthesis, such as halides, the number of bound ligands or excess Pb will be modified to keep the QDs charge balanced.⁵⁴ This is an important concept to keep in mind when analyzing XPS, ICP, and NMR measurements: the QDs will always be charge neutral. Using FTIR, Weiss *et al.* determined the binding motif of

oleate on the QD surface. The oleate molecules bind in both chelating and bridging fashions to the Pb²⁺ on the QD surface.⁵⁵ Because the ligands can bridge between multiple Pb²⁺, the oleate molecules are most likely spread over the surface of the QD, not bound strictly as Pb(OA)₂ clusters.

1.IV.c QD Arrays

Many constructions of QD solar cells are possible, but the method that has become most popular is connecting the individual QDs into a conductive array. In this structure, the QD array has the macroscopic properties of bulk semiconductor on the macroscopic level, but retains quantum confinement and the desirable properties of QD materials. In order to make conductive films for optoelectronic devices the long, organic ligands (usually oleate) must be removed. This is accomplished by a ligand exchange procedure, which replaces the native ligands with short molecules or inorganic compounds. This ligand exchange can be done in solution or in the solid state (after a film has been cast). There are many recent reports of solution-phase ligand exchange which have great potential for single-layer depositions of optoelectronic devices and the reader should refer to the following references to learn more about that technique.^{58–63} Here, I focus on the layer-by-layer deposition approach that is described in detail in Chapter 2. Overall, this technique proceeds as follows: a layer of QDs is deposited on the substrate and it is subsequently exposed to a solution containing the desired ligand. For short organic ligands such as ethanedithiol, an acid-base reaction occurs at the QD surface, protonating the oleate, which is able to leave and the remaining thiolate binds to the QD surface. For inorganic ligands, a solvent that is able to strip ligands from the QD surface—in our case dimethylformamideis employed to remove Pb(OA)₂, and the inorganic compound then passivates the QD surface.

Ligands influence the optical and electronic properties of the QDs; shifting QD energy levels and enhancing optical absorption.^{64,65} Certain surface modifications can influence MEG as well. For example, hydrazine treated PbSe QDs show MEG, while EDT treated PbSe QD arrays do not,⁶⁶ and both published MEG PbSe QD solar cells employed hydrazine as one of the treatment layers.^{10,19} Therefore, the control over QD surfaces is vital for researchers to tune the properties of QDs in order to optimize these materials for a variety of applications. In this thesis I will discuss tuning the surface chemistry using the synthesis, ligand exchange, and post-treatments of assembled QD arrays. Through these controls I show increased air-stability of lead chalcogenide QDs, improved transport properties, and improved power conversion efficiencies of QD photovoltaic devices.

1.V Perovskite Materials

Researchers first started having success with perovskite materials in photovoltaic devices just as I began my PhD program (2012),^{67,68} with the first perovskite based solar cell certified in 2013. In just 4 years since that first certification the record efficiency has climbed to an impressive 22.1%,⁶⁹ making perovskites competitive with CdTe and CIGS, which are two of the first solar cell efficiencies ever recorded on the best efficiency chart (1976).^{70,71} Generally, perovskites are of the formulation ABX₃, where A and B are cations with B having twice the charge of A (for example Cs⁺ and Pb²⁺ or Ca²⁺ and Ti⁺⁴ as A and B, respectively) and X is an anion (for example a halide or oxygen). Perovskite solar cell research has focused on organic-lead-halide formulations that keep the crystal structure in the cubic phase. The perovskite crystal structure is shown in Figure 1.5a, where the cubic

phase shown on the left has superior absorption properties and the orthorhombic phase shown on the right is undesirable. The relative ionic radii of the constituent atoms determine the crystal structure, so only certain perovskite formulations are relevant for solar cell applications. The Goldschmidt tolerance factor (*t*, shown below) uses the ionic radii to determine which combinations of ions will form stable cubic structures.

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}$$

Figure 1.5b shows the calculated Goldschmidt tolerance factor for two A-site cations (formamadimium and Cs) and the mixed cation compositions in APbI₃. From this graph it is apparent that mixtures of the A-site cations result in a stable cubic phase, while the pure CsPbI₃ and FAPbI₃ do not.



Figure 1.5: Perovskite crystal structure and tolerance factor. (a) Diagram of the perovskite crystal structure. The schematic on the left shows the desirable cubic phase and the schematic on the right shows the orthorhombic phase.⁷² Reprinted with permission from Green, *et al. J. Phys. Chem. Lett.* **2015**, *6* (23), 4774–4785. Copyright 2015 American

Chemical Society. **(b)** The Goldschmidt tolerance factor is shown for the A-site cations cesium and formamidinium. Each cation is outside of the range for the cubic phase to be thermodynamically stable, but by alloying the A-site these cations can be used to make stable, cubic phase lead-halide perovskite films.⁷³ Reprinted with permission from Li, *et al. Chem. Mater.* **2016**, *28* (1), 284–292. Copyright 2016 American Chemical Society.

1.V.a Perovskite QDs

Nanocrystals of methylammonium (MA)-lead-halide perovskites were first synthesized in 2014.⁷⁴ In 2015 all-inorganic nanocrystals were synthesized from CsPbX₃⁷⁵ and were met with enthusiasm because of their impressive photoluminescence quantum yields (PLQY) and possible lasing applications.^{76–81} Notably, even though the Goldschmidt tolerance factor shows that CsPbI₃ is orthorhombic at room temperature, QDs of CsPbI₃ stay in the cubic phase. Thin films of cubic CsPbI₃ have been fabricated, but they readily convert to the orthorhombic phase when exposed to ambient conditions.^{82,83} High-temperature phase stabilization is a known effect in nanocrystalline materials (such as cadmium chalcogenides and titania^{84,85}) and exploiting this ability for CsPbI₃ has the potential to help with the stability challenges of MAPbI₃, where loss of the organic cation causes decomposition.^{86,87} Switching to an all-inorganic perovskite material is therefore preferred for long-term stability and the nano-scale phase stabilization of CsPbI₃ provides a promising avenue to produce all-inorganic perovskite photovoltaics.

CsPbX₃ QDs are synthesized using a hot-injection method that is procedurally similar to the metal chalcogenide QD syntheses. In contrast to the metal chalcogenides, the CsPbX₃ QDs are formed by a salt metathesis reaction, which proceeds very quickly and is complete within a few seconds of injection.⁷⁵ The size of the QDs is therefore very sensitive to the reaction temperature and 4-15 nm cubes can be synthesized by tuning the reaction temperature from 140 to 200°C.^{75,77} In general the overall reaction is shown in Figure 1.6a.

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The true reaction is more complicated because PbX₂ does not dissolve in octadecene (ODE), which is the reaction solvent. Shown in Figure 1.6b, oleic acid (OA) and oleylamine (OLAm) are both used to dissolve the PbX₂, the OA and OLAm form a salt pair (oleylammonium oleate), which can form a lead-oleate compound and an oleylammonium (OLAm⁺) halide. The potential ligands for CsPbX₃ QDs include OA, OLAm, OLAm⁺ halide, cesium and lead oleates, and the OLAm⁺ oleate ion pair.



Figure 1.6: CsPbI₃ **QD reaction scheme. (a)** This schematic shows the general reaction that occurs when the Cs-oleate is injected into the PbI₂ solution. **(b)** PbI₂ does not dissolve in neat octadecene (ODE) so oleic acid and oleylamine are used to dissolve the PbI₂ in the ODE. This schematic shows the likely mechanism for PbI₂ dissolution using oleic acid and oleylamine. This scheme was proposed for PbBr₂⁸⁸ and here we consider PbI₂ to be similar enough in chemical nature to undergo similar reactions. There is some evidence to the contrary as PbBr₂ forms a colorless solution when dissolved in OA, OLAm, and ODE, while PbI₂ is a transparent yellow solution.

1.V.b Surface Chemistry

Initial reports on the surface chemistry and composition of the CsPbX₃ QDs have been contradictory and focused on CsPbBr₃ QDs. In a report from Kovalenko and Hens, *et al.* NOESY NMR is used to determine which ligands are interacting with the CsPbBr₃ QD surface.⁸⁸ In the 1D NMR ODE, OA, and OLAm⁺ are all present, suggesting that there is excess precursor in the sample even after the QD purification process. The 2D NOESY spectrum shows that only the OLAm⁺ interacts with the CsPbBr₃ QD surface and that the oleic acid and ODE are free in the solvent. This report hypothesizes that the OLAm⁺ interacts with the QD surface as a bound ion pair with a halide anion. Although, when excess OLAm is present, the OA is deprotonated and the OLAm⁺ oleate ion pair can also bind to the surface of the QD. Overall, the most interesting conclusion of this report is that the common ligand for metal chalcogenides—metal oleates—do not bind to the surface of the SPbX₃ QDs, instead ion pairs and neutral L-type ligands stabilize the QD surface. They also conclude that adding excess ligand during the purification process is vital to maintaining high PLQY and colloidal stability; in the same line of thought, maintaining the acid-base equilibrium with the correct amounts of amine and acid is crucial to keep ligands strongly bound to the CsPbBr₃ surface.⁸⁸

The next report on CsPbBr₃ QD surface chemistry points out the difficulty of interpreting NMR spectra when the QDs are not fully purified due to the overlapping alkyl and alkene peaks of ODE, OA, and OLAm. In the process of exploring the effect of different carboxylic acids and primary amine precursors on the shape of the final nanocrystals, Liu *et al.* found that the ligand composition is highly dependent on the purification process;⁸⁹ similar to the conclusions from Hens, *et al.*⁸⁸ First, by purifying with hexane only, OLAm⁺ and oleate peaks were present in the NMR spectrum. On the other hand, when hexane and acetone were both used during the purification process, the OLAm⁺ was removed and only oleate remains, as seen in the FTIR spectra.⁸⁹ The authors propose that both oleate and OLAm⁺ bind to the CsPbBr₃ QD surface, but that the OLAm⁺ is bound much less strongly and is removed when polar solvents are used for purification. These highly labile ligands are removed, leaving the more-strongly bound oleate ligands on the QD surface. This contradicts the idea from Hens, *et al.* that excess OLAm is required to keep the oleate

species bound to the QD surface. Liu, *et al.* cite the strong binding motif of oleate to surface metal atoms as compared to the surface OLAm⁺, which binds through a hydrogen bridge to the surface halide, as the reason for oleate retention on the QD surface after purification with polar solvents.⁸⁹ The proposed binding motifs for the various ligands are shown in Figure 1.7.



Figure 1.7: Binding motif for ligands on CsPbBr₃ **QDs.** OLAm can interact with a stoichiometric QD core as an L-type ligand. The ion pairs of OLAm⁺ with halide or oleate are also potential ligands. Oleate ligands can also interact with surface metal species.⁸⁸ Reprinted with permission from De Roo, *et al. ACS Nano* **2016**, *10* (2), 2071–2081. Copyright 2016 American Chemical Society.

While these two studies on the surface composition of CsPbBr₃ may disagree on the role of oleate on the QD surface, they agree that the OLAm is bound as OLAm⁺ in an ion pair and is a highly labile ligand. They also both report that the purification of the QDs from the reaction solution plays a large role in determining the bound ligands. The presence of OLAm⁺ halide ligands is also supported by the fast ion exchange that is observed for CsPbX₃ QDs. The halide in CsPbX₃ QDs can be exchanged quickly and easily by adding the preferred halide in almost any form or by simply by mixing solutions of QDs containing different halides.⁹⁰⁻⁹⁴ For example, mixing CsPbBr₃ and CsPbI₃ QDs in solution will form CsPbBr_{3-x}I_x where *x* depends on the mixing ratio.^{91,92} In order to better understand the surface

composition, detailed elemental analysis through ICP and XPS should be used to determine the absolute ratios of the constituent atoms. Using Rutherford Back Scattering, the CsPbX₃ QDs were determined to be approximately stoichiometric,⁷⁵ but more detailed and careful analysis will determine if excess metal or halide is part of the ligand shell. Understanding the ligand binding on the CsPbX₃ QDs will be vital to using this material in applications. The first experiments removing surface ligands and making coupled QD perovskite films are presented in Chapter 7.

1.VI Quantum Dot Solar Cells

The simplest way to construct a solar cell is to sandwich a semiconductor between two contacts. This type of device is called a Schottky-junction solar cell and usually uses a transparent contact that forms a space-charge layer in the semiconductor at the contact interface at the front, and a reflective, ohmic metal contact on the back. Light is able to penetrate the semiconductor material, and then any transmitted light is reflected off the back metal contact and travels through the semiconductor material a second time. Figure 1.8a shows the operation of a simplified solar cell. Incident light is absorbed in the semiconductor material (the absorber layer) creating an electron-hole pair, or exciton, and then the carriers are separated by the electric field in the space-charge layer, extracted and sent to an external load. The most common transparent layer is indium-doped tin oxide (ITO, or fluorine-doped, FTO) and common metal ohmic contacts are gold, silver, and aluminum. In a Schottky-junction solar cell the separation of the electron-hole pair is assisted by band-bending that is induced in the space-charge layer at the semiconductormetal interface (Figure 1.8b).⁹⁵

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Figure 1.8: Schematic of photovoltaic device operation. (a) This diagram is a simplified model of how a photovoltaic device operates. The sun excites an electron-hole pair, then the electron and hole are separated and each is extracted at either the front or back contact. The extracted carriers are sent to an external load, in this diagram represented using a charging cell phone. (b) An example of band bending in a Schottky junction solar cell. This simple solar cell structure has a V_{OC} that is determined in part by the Fermi energy of the back metal contact. The band bending is induced by the metal contact as the Fermi energies of the semiconductor (in this diagram the PbSe NCs) and metal equilibrate. Reprinted with permission from Luther, *et al. Nano Lett.* **2008**, *8* (10), 3488–3492. Copyright 2008 American Chemical Society.

While a Schottky junction causes band bending at the contact interface, a p-n junction can be used to create an energy landscape that induces electrons and holes to flow toward their respective contacts. The n-type layer used in Figure 1.9a (TiO₂) extracts and transports electrons effectively from the CQD Film (colloidal quantum dot film) in this solar cell. The band bending at this interface also shows how electrons can flow "downhill" on the energy landscape to transfer into the TiO₂, while holes would need extra energy to pass through the TiO₂-CQD interface. The holes are instead extracted at the back metal contact (Au) because the Fermi level of the contact is at a more favorable energetic position for the holes in the valence band (E_v). The majority of the band bending in the QD layers occurs close to the TiO₂-QD interface, which means the carriers mainly travel by diffusion instead of drift. In silicon solar cells both halves of the p-n junction can be made from Si by varying the dopant levels. In this case, the band bending induced by the Fermi level equilibration
can be more pronounced and extends farther into each layer, depending upon the p and ntype doping levels and sweep carriers apart by the electric field. QD solar cells mimic this behavior using the band energy shifting properties of different ligand treatments instead of the electronic doping used in Si, discussed in the next paragraph.



Figure 1.9: Band diagram for a QD solar cell. (a) This band diagram shows how researchers envision the band alignment in QD solar cells, here using TiO_2 and gold as the contacts. The quasi-Fermi level splitting of the electron and hole Fermi levels determines the V_{OC} in the final device.⁹⁶ Reprinted with permission from Pattantyus-Abraham, *et al. ACS Nano* **2010**, *4* (6), 3374–3380. Copyright 2010 American Chemical Society. **(b)** This band diagram shows how a bilayer structure can help separate carriers in the QD array. By pairing ligands that correctly move the energy levels in QD arrays, electron or hole blocking layers can assist in carrier separation. Here, PbS QDs treated with EDT are used as an electron-blocking layer on the back of a TBAI treated QD array.⁹⁷ Adapted with permission from Chuang, *et al. Nature Mater.* **2014**, *13* (8), 796–801. Copyright 2014 Nature Publishing Group.

In order to reduce recombination at the back contact and create more band bending in the QD layer, a secondary ligand treatment can be used. As shown in Figure 1.9b, by choosing the correct combination of ligand treatments an electron blocking layer can be deposited at the back of the solar cell. Interestingly, this bilayer QD array is almost always composed of an inorganic treatment—usually an iodide ligand—followed by an organic ligand treatment—3-mercaptopropionic acid (MPA) or 1,2-ethanedithiol (EDT).^{39,61,97-103} The reason for this treatment scheme may be two-fold. First, halide passivation can increase the air-stability of lead chalcogenide QDs, as will be discussed in Chapter 3, and the films tend to be slightly n-type even after air-exposure.^{39,40,60,104,105} Second, excess chalcogenide and air-exposure causes lead chalcogenide QD films to become p-type.^{64,106,107} With the organic ligand treatments there is no oxidative stability from halide ligands and the organic ligands bind a sulfide moiety to the QD surface. The excess chalcogenide and possible oxidation of the QD surface causes this layer to be p-type. The TiO₂ used for the transparent contact is heavily n-type and, when paired with the QD layers of different doping levels, creates a band structure that sweeps n- and p-type carriers to opposite ends of the device for extraction.

1.VII Scope of this work

This work focuses on the surface chemistry of QD materials. Using surface treatments to change the properties of QD arrays, we show enhanced photophysical properties and control over solar cell performance parameters. First, lead chalcogenide QD materials are addressed. The air-stability of lead chalcogenide materials is improved through new synthetic techniques and metal halide surface treatments. Along with air-stability improvements, we show data that suggests the new synthetic technique produces QDs with fewer trap states. Ligand exchanges and film treatments are used to keep the trap density low and produce moderate-efficiency QD solar cells.

Finally, in a project drawing from two areas of expertise in our group, I report the first perovskite QD solar cell. Similar surface chemistry manipulation can be used on the perovskite QD surface, although the chemistry is not as well understood compared to lead chalcogenide materials. There is still much work to be done on the perovskite QDs, and the research presented here represents some exciting first steps.

Chapter 2: Quantum Dot Solar Cell Fabrication Protocols

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2.I Overview

My group was invited to write a protocols paper for *Chemistry of Materials*. The journal has a vision to publish these protocol papers, similar to what is found in the field of biology, in order to help the field of materials research progress more quickly. The goal of these articles is to reduce the learning curve for producing a new material or doing a new procedure in the lab. The following chapter is the result of that effort. On the website the article contains links to videos, which I produced along with my co-author G. F. Pach and the following chapter contains an in-depth explanation of how to perform QD syntheses, layer-by-layer fabrication of QD arrays, and fabrication and testing of QD solar cells. This chapter will be referenced heavily in the methods sections of the remainder of this thesis and serves as a starting guide for working with QD materials.

2.II Abstract

Colloidally synthesized quantum-confined semiconducting spherical nanocrystals, often referred to as quantum dots (QDs), offer a high degree of chemical, optical, and electronic tunability. As a result, there is an increasing interest in employing colloidal QDs

for electronic and optical applications that is reflected in a growing number of publications. In this protocol we provide detailed procedures for the fabrication of QD solar cells specifically employing PbSe and PbS QDs. We include details that are learned through experience, beyond those in typical methodology sections, and include example pictures to aid researchers new to fabricating QD solar cells. While successful solar cell fabrication is ultimately learned through experience, this protocol is intended to accelerate that process. The protocol developed here is intended to be a general starting point for developing PbS and PbSe QD test bed solar cells. We include steps for forming conductive QD films via dip coating as well as spin coating. Finally, we provide protocols that detail the synthesis of PbS and PbSe QDs through a unique cation exchange reaction and discuss how different QD synthetic routes could impact the resulting solar cell performance.

2.III Introduction

Colloidal semiconductor quantum dots (QDs) provide a unique platform for designing a wide array of optoelectronic applications due to quantum confinement and enhanced surface-to-volume ratios. These unique size-dependent properties allow for emergent electrical and optical phenomenon derived from QD-QD, and QD-ligand electronic coupling. Benefits and advantages of QDs include: strong optical transitions (light absorption and emission), a large range of tunable bandgap onset energies, control over band edge energies¹⁰⁸ and workfunction,¹⁰⁹ facile synthesis, facile incorporation into matrices¹¹⁰ or deposition as thin films, and desirable excited state properties such as enhanced multiple exciton generation (MEG),¹¹¹ long carrier lifetimes,^{112,113} and charge and energy transfer phenomenon with surface adsorbates.¹¹⁴ Thus, QDs are being explored and commercialized as active components in displays (computer monitors, televisions, etc.),¹¹⁵

optical detector applications,¹¹⁶ bioimaging,¹¹⁷ and green energy applications such as photovoltaics,¹¹⁸ thermoelectrics,¹¹⁹ and solid-state lighting.^{120,121}

Solar cells fabricated from QDs have the potential to exhibit higher power conversion efficiencies through enhanced MEG,^{122–125} but have not yet reached their full potential. While MEG is enhanced in typical quasi-spherical QDs over bulk and conventional thin film semiconductors, the threshold and efficiency of the MEG process can be improved through shape control,¹²⁶ internal QD heterojunction interfaces,¹¹³ and further material exploration.¹²⁷ Research towards increasing the MEG efficiency is an ongoing effort. However, in order to take advantage of these unique properties, researchers must also develop prototype energy conversion architectures that can serve as a test bed for advanced nanoscale phenomena. In solar cells, the active layer typically employs electronically coupled QD arrays,¹¹⁸ however, QD sensitized architectures have shown promise as well.¹²⁸ The final solar cell performance will depend upon a myriad of correlated factors: the QD synthesis, degree of QD-QD and QD-ligand electronic coupling, QD film morphology, QD surface passivation and other defect related carrier recombination centers, and appropriate contact layers.

In this protocol, we provide detailed procedures for the fabrication of standard QD solar cells using PbS or PbSe QDs that can achieve 8-9% power conversion efficiency in our laboratory. We also provide a protocol for the synthesis of PbS and PbSe QDs using a cation exchange route from CdS and CdSe QDs.^{129,130} This is a new type publication for the field of nanomaterials, modeled off of protocol publications that are common in the field of biology. This chapter will provide a detailed description of the laboratory techniques used in this

thesis and was published with the intent of helping researchers who are new to QD synthesis and photovoltaic device fabrication.

2.IV QD Solar Cell Fabrication

2.IV.a Reagents

3-mercaptopropionic acid (MPA, >99%), N,N-dimetholformamide (DMF, anhydrous, 99.8%), methanol (reagent grade), 1,2-ethanedithiol (EDT, \geq 98%), acetonitrile (99.8%), titanium(IV) ethoxide (\geq 97%), Molybdenum trioxide (MoO₃, 99.99%), and hydrochloric acid (ACS reagent, 37%) are purchased from Sigma Aldrich-USA and used as received. Lead(II) iodide (PbI₂, 99.9985%) is purchased from Alfa Aesar.

2.IV.b Substrates

Polished glass substrates (25 mm x 25 mm x 1.1 mm) with pre-patterned FTO on one side are purchased from Thin Film Devices (Figure 2.1b). The FTO (product #650) is nominally 200 ± 20 nm thick, although SEM measurements show ~400 nm FTO, with a 20 ± 5 Ω/\Box sheet resistance.





2.IV.c Preparation of Ligand Exchange Solutions

The ligand-exchange solutions used to remove the long, insulating ligands on the QD

surface are: 10 mM PbI₂ in DMF, 10 vol.% MPA in methanol, and 1 mM EDT in acetonitrile.

The stock PbI₂ powder is kept in a glove box and only the needed quantity removed. The PbI₂ is mixed with DMF in air to form the ligand-exchange solution, but the dissolution may be done inside the glove box as well. The mixture is sonicated for 10-30 minutes to completely dissolve the solid. We have found variability in the PbI₂ among different vendors; certain PbI₂ products do not readily dissolve in DMF. Therefore, we advise the usage of high purity PbI₂ purchased from Alfa Aesar. For the 1 mM EDT solution, a 1 M solution of EDT in acetonitrile is prepared inside the glove box and then transferred to air for dilution to 1 mM solutions as needed. The >99 % MPA stock solution is stored in ambient and the 10 vol.% in methanol solution is prepared in air.

2.V Overview of Solar Cell Fabrication

The entire device fabrication process (summarized in Figure 2.1a) starts with a glass substrate that is pre-patterned with FTO (Figure 2.1b: transparent, gray regions are FTO). Our pattern is comprised of a rectangular box, which we call the "racetrack," in the middle and six pads on the sides. To minimize the resistivity for current extraction in the non-active FTO regions we deposit metal bus bars on top of the FTO and in between the six individual solar cell pixels, as shown in Figure 2.1c. Inclusion of metal bus bars leads to an increased fill factor, by reducing the series resistance of the transparent conductive oxide. After bus bar evaporation, the TiO₂ is deposited (Figure 2.1d), followed by the QD absorber layer. (ZnO is often used instead of TiO₂ as the n-type window layer in the literature. We have observed significant irreproducibility in device performance when making solar cells with ZnO and have almost exclusively used TiO₂ for this reason. Due to the high annealing temperature of TiO₂ (450 °C), we predominantly use FTO for its favorable temperature stability compared to ITO. The resistivity of ITO increases with annealing at temperatures

>200 °C,¹³¹ which increases the series resistance in the solar cell.) Lastly, MoO_x and metal (Au or Al) are deposited by thermal evaporation through a mask to form six "fingers," (Figure 2.1e) thereby forming six individual 0.101 cm² solar cell pixels.

2.V.a Substrate Preparation and TiO₂ Layer Deposition

(i) The substrates are cleaned vigorously with an ethanol soaked scientific tissues, sprayed with ethanol from a squirt bottle, and then dried immediately with pressurized stream of air or N_2 .

(ii) Silver bus bars, 75-100 nm thick, are deposited by thermal evaporation using a shadow mask. (The rate of evaporation is not critical; we deposit at 0.5-2 Å/second. Bus bars should be less than 100 nm to limit their impact on the TiO_2 film morphology.)

(iii) TiO₂ sol-gel precursor is prepared by mixing 5 mL ethanol, 2 drops hydrochloric acid and 125 μ L deionized water in a beaker and stir. Then 375 μ L of stock titanium(IV) ethoxide are added drop-wise. Stock titanium(IV) ethoxide solution is stored in a glove box and only the necessary amount is removed to air. The result is a clear liquid, free of any particulates. The solution is then capped and stirred for a minimum of one hour before storing in the freezer. The sol-gel is removed from the freezer 10 min before use and stirred while it equilibrates to room temperature.¹³² (The sol-gel mixture should be discarded if particulates are visible or if the solution is obviously cloudy or yellow.)

(iv) The TiO₂ layer is fabricated by spin coating 70 μL of the sol-gel at 1400 RPM for 30 sec. The TiO₂ sol-gel layer is removed from the upper and lower FTO/metal contact pads regions, and the smaller three left and three right FTO/metal pads, as oriented in Figure 2.1d, using a cotton swab moistened with ethanol immediately after the spin cycle is complete. The FTO/metal pad cleaning must be done immediately before the sol-gel solution dries. (Removing the TiO₂ sol-gel layer is more important over the large upper and lower FTO/metal pad areas. The other six, smaller, FTO/metal pads on the sides will be coated with the metal top contacts, and therefore having clean FTO pads helps in case the contact probes poking through the evaporated metal layer.) After wiping the FTO/metal pads, each substrate is kept on a hotplate at 115 °C, to remove water, while the next substrate is prepared. After the last substrate is finished, the substrates are kept on the hotplate for an additional 20 minutes.

(v) Finally, the substrates are placed in a preheated furnace at 450°C for 30 min, regardless of whether the substrate is FTO or ITO coated glass. The films are then stored in air, in the dark, prior to QD film deposition.

2.V.b QD Layer Deposition

The QD layer is commonly deposited using multiple spin coating or dip coating cycles. The number of spin or dip cycles along with the QD concentration determines the QD film thickness. Both methods are highly tunable (*e.g.*, layer thickness and ligand exchange) and both result in solar cells of comparable performance. The choice of which method to use is largely a personal preference. Dip coating requires enough total volume to immerse the substrate. Therefore, the QD solution concentration is typically lower when

dip coating (e.g., 10-20 mg/mL) than in the case of spin coating (~30 mg/mL). As a result, dip coating is generally a slower deposition method, because each individual cycle deposits fewer QDs, but this may be preferred for finer control when very thin QD films are desired and for the potential to deposit more solar cells from a single QD synthesis. Higher (lower) solution concentrations will yield thicker (thinner) layers per cycle and thus quicker (slower) film fabrication. A disadvantage of spin coating is that some of the material is lost as it is spun off the substrate. Before starting, remember the French culinary phase, "mise en place," which refers to the importance of preparing and arranging all of the components and tools in an organized fashion prior to cooking, or making solar cells. Additionally, we highly recommend the tweezers visible in Figure 2.2 and Figure 2.3 (VWR 100494-780) because the wide tip prevents rotation of the substrate about the hold point. The procedures below apply to lead chalcogenide QDs that have native oleate ligands.

2.V.c Spin Coating Protocol

(i) Prior to spin coating, the QDs are dispersed in octane at a concentration of 30 mg/mL. The solution is filtered through a 0.2 μ m Nylon or PTFE filter to remove agglomerates and increase the uniformity of the film.

(ii) 80 µL of QD solution, enough to cover the middle portion of the substrate containing the six solar cell active areas, is dispensed onto a substrate using a micropipetter. The solution should be spread evenly to cover the entire surface. (If an air bubble forms, it is important to remove the bubble by perturbating the solution via puffs of air using the empty micropipetter.)

(iii) The substrate is spun at 2000 RPM for 30 seconds, with a 3 second ramp rate, in order to obtain a glassy film and dry the octane. (If there is any excess liquid on the back of the substrate, this should be dried on a scientific tissue before the ligand treatment.)

(iv) The QD film is then submerged in the 10 mM PbI₂ solution for 3 minutes to ensure complete exchange.

(v) When removing the substrate from the DMF solution, the film is tapped against the side of the beaker to let the excess DMF run back into the ligand solution.

(vi) The film is then submerged multiple times in neat acetonitrile to remove excess DMF and PbI₂. It is important to set the film on its edge in the acetonitrile and open the tweezers to release the DMF trapped between the tweezers and the substrate.

(vii) The film is then dried using a gentle stream of air to push the acetonitrile off the film edge. Steps 1-6 are done a total of four times to build up the PbI₂ layer (Figure 2.2a).

(viii) The MPA treated layer is spun in the same way, but 10 vol.% MPA-in-methanol is used as the ligand-exchange solution. The film is slowly lowered into the MPA solution, held for ~1 s, then steadily removed and rinsed in neat methanol. The film is dried with a gentle stream of air (~4 seconds total exposure time). This procedure is done a total of two times to build up the MPA layer. If excess MPA solution is not adequately rinsed, the film will develop white cloudy areas when the next QD layer is deposited from octane. Any pixels affected by this cloudiness will be Ohmic (not

exhibit rectifying behavior), so discard the film if too many pixels are affected. To avoid this problem, the film should be rinsed multiple times in the neat methanol. If the film begins peeling during the MPA treatment, as shown in Figure 2.2b, reduce the concentration of the MPA to 1 vol.% in methanol. Peeling during the MPA treatment is a greater issue if ZnO is used instead of TiO₂, in which case we recommend reducing the MPA concentration. We have found that the MPA concentration, within the range of 1 vol.% to 10 vol.%, does not produce statistically significant differences in the solar cell performance.



Figure 2.2 "Good" and "bad" QD films. (a) A typical film after spin coating in contrast to **(b)** a film that peeled during the MPA treatment.

An alternative spin coating approach involves performing the ligand treatments directly on top of the film while leaving the substrate in the spin coater. Our technique differs because of the long soak time in the PbI₂/DMF solution. By dip coating this treatment it is possible to process four films simultaneously by letting three of the films soak in the ligand treatment while the QD layer is being spin coated on the fourth film. While the QD layers may be treated by via deposition of ligand solution directly on the film in the spin coater, we prefer the soaking route described above for higher throughput.

2.V.d Dip Coating Protocol

When dip coating, the QDs are dispersed in hexane at a concentration of ~ 15 mg/mL. Prior to deposition, the QDs are filtered through a 0.2 µm Nylon or PTFE filter to remove agglomerates. Ligand solutions that are reused from prior depositions should be filtered as well. Traditionally, QD solar cells were dip coated with EDT ligand treatment. To dip coat QD layers with EDT, or other similar organic ligands, the following procedures are used:

(i) The substrate is lowered gently and vertically into the QD solution and then gently and vertically removed from the solution. When lowering the substrate into the QD solution, stop before any of the solution wets the tweezers. (If any of the QD solution is entrained in the tweezers, then a droplet may flow down the newly formed film and disrupt uniformity upon substrate removal.) The QD layer deposition occurs during the substrate withdrawal so the speed of lowering is not important. A good withdrawal speed is approximately 2 seconds to remove a 1" long substrate (~1.3 cm/s). Removing the substrate quickly yields thicker films, as more solution is trapped on the substrate, but uniformity and homogeneity usually suffer. If the film is non-uniform the substrate may be re-submerged into the QD solution. It is important to do this before ligand exchange. The substrate should be kept re-submerged in the QD solution for ~5-15 seconds to allow for dispersion of the non-uniform layer.

(ii) When the substrate is clear of the solution, tap the bottom edge of the substrate onto a paper towel/wipe to remove any excess QD solution. (If allowed to dry, the excess QDs may flake off during the ligand exchange.) The hexane should be completely dry before dipping into the ligand solution. Figure 2.3 shows smooth films formed from dip coating.

(iii) Next, the QD-coated-substrate is dipped into the ligand solution, which in this case is 1 mM EDT in acetonitrile. Similar dipping speeds are used for the ligand exchange, but a 1 second soak while the film is submerged is included prior to removal.

(iv) After removal from the EDT solution, the film should be allowed to dry. (If any droplets of solution are entrained on the film upon removal, they should be blown off with compressed nitrogen gas.)

(v) Once dry, the film is turned 90° and then it is dipped into the QD solution again and the process is repeated. Turning the substrate 90° helps to even out directional non-uniformities.

(vi) A profilometer is used to determine the QD film thickness.

(vii) When the QD film deposition is finished, the glass side of the substrate is cleaned with solvent-soaked (*e.g.*, methanol, ethanol, or acetonitrile) cotton swabs. On the active area side, the large upper and lower FTO/metal contact pad regions, as oriented in Figure 2.1e, should be cleaned carefully such that the cotton or solvent does not touch the six pixel areas.

(viii) Following cleaning of the FTO pads, the films are annealed in an N₂-filled glove box (O_2 at <5 ppm, H₂O <1 ppm) at 110° for 20 minutes. Annealing optimization

should be performed for different QD and ligand combinations. We refer the reader to Gao, *et al.*¹³³ for guidelines on optimizing the annealing step.

We also use dip coating to fabricated QD solar cells using the bilayer PbI₂ and MPA ligand treatments described in the spin coating section; the procedure is slightly modified: The QD layer is deposited as described in step (i) of Section 2.IV.d and the PbI₂ ligand exchange is performed as described in steps (iv-vii) of 2.IV.c. The MPA ligand exchange is performed as in step (viii) of 2.IV.c. When dip coating instead of spin coating, the thickness ratio of the total PbI₂-treated layer and the total MPA-treated layer is 2:1 (for example, 200 nm of PbI₂-treated QDs and 100 nm of MPA-treated QDs). The thickness is determined by profilometry and requires depositing many more layers than spin coating procedures.



Figure 2.3 Dip coated QD films. (a) The film after ~25 nm and **(b)** ~150 nm of EDTtreated ~0.63 eV PbSe QDs. The glass side of the substrates was cleaned in both cases. Imperfections may develop during the coating process. For example, there is a dark spot in the bottom-left, near the tweezers, which was a result of QD-agglomerates that float in the ligand exchange solution entrained in the film. This dark spot is not in an active solar cell area, however, and did not affect solar cell performance. On the other hand, some imperfections may not have significant impact on pixel performance, such as the light imperfection over the middle-right pixel.

2.V.e Top Contact Layer and Finishing the Solar Cell

After annealing, the back contact layers are deposited on the film by thermal evaporation. We deposit 15-20 nm of MoO_x and 100-150 nm of Al or Au. For deposition,

films are loaded into an evaporator and the chamber is evacuated to a base pressure of 10⁻⁷ - 10⁻⁸ Torr. The MoO_x layer is evaporated slowly at a rate of 0.02 nm/s. The Al or Au is then deposited at a rate of 1.5 nm/s. These depositions are done in a thermal evaporator with multiple sources to avoid exposing the film to air between MoO_x and Al or Au depositions. A false color cross-sectional scanning electron microscopy (SEM) image of a completed solar cell (Figure 2.1f) demonstrates highly uniform and smooth QD films that should result from following the protocol developed above. The finished solar cells are stored in a drawer, under ambient conditions, before and after characterization.

2.VI Characterization

Characterization is performed in an N_2 atmosphere glove box. Measuring the solar cells in air leads to a reduction in fill factor, which recovers when the cell is returned to inert atmosphere.

2.VI.a Current-Voltage Response

JV (current density vs. voltage) characterization of the solar cells is performed using an Oriel Sol3A (94043A) class AAA solar simulator system equipped with a 450 W Xenon arc lamp and calibrated to match AM1.5G. A metal plate is used to aperture (0.059cm²) each of the six pixels during characterization to prevent illuminating areas outside of the defined active area, which would artificially inflate the PCE.^{134,135} It should be noted that during the JV measurement of any single pixel, the other five pixels are illuminated and held at open circuit. The total pixel area (0.101 cm²) or the aperture area is used to calculate the current density in the dark or under illuminated conditions, respectively. The height of the solar cell stage is adjusted until the illumination intensity is 100 mW/cm², as determined by the current output of the calibrated Hamamatsu (S1787-04) silicon reference photodiode. A mismatch factor may be applied to correct the short circuit current (J_{sc}) value as appropriate depending on the QD size and cell responsivity.¹³⁴ Figure 2.4 shows example JV curves for solar cells with PbSe (blue) or PbS (red) QDs. While QD solar cells do not exhibit the hysteretic behavior observed in perovskite solar cells,¹¹⁸ measurement stress effects have been observed, such as a decrease in V_{oc} due to light soaking under open circuit conditions. We observe an efficiency standard deviation of ±10 % about the average. Deviations arise due to non-uniformities across the substrate area, as well as the measurement stress effects.



Figure 2.4 Example JV curves. Example J-V response of PbSe (0.78 eV) and PbS (1.2 eV) QD devices. The power conversion efficiency, fill factor, V_{oc} , and J_{sc} of the PbSe solar cell are 3.15%, 48.2%, 0.217 V, and 30.0 mA/cm², respectively. The efficiency, fill factor, V_{oc} , and J_{sc} of the PbS solar cell are 8.36%, 64.0%, 0.546 V, and 23.9 mA/cm², respectively. The architecture of these cells is shown in Figure 2.1.

2.VI.b Spectral Response

The external quantum efficiency (EQE) measurement is used to characterize current losses in the solar cell as a function of photon energy or wavelength. It is a measurement of the flux of electrons, measured as current density, in a solar cell with respect to the flux of photons incident on the solar cell. The EQE is also called the IPCE, or incident-photon-tocurrent-efficiency. Losses in the EQE may include: parasitic UV and IR absorbance in the hole or electron extracting layers (*e.g.*, FTO, TiO₂, or MoO_x), reflections at interfaces, inadequate absorber thickness leading to loss in the IR, and short carrier diffusion lengths in the QD layer or charge extraction layers. The measurement instrumentation involves a light source, monochromator, chopper, light filters, light guide, probe setup to measure current, a pre-amplifier, and a lock-in amplifier. More details on the instrumentation, measurement, and calculation may be found elsewhere.^{134,136-138}



Figure 2.5 Example EQE curves. Example EQE, reflectance, and IQE_{device} spectra of PbSe QD solar cells (0.72 eV). An IQE_{device} above 100% indicates that MEG is contributing to the collected current.¹²³ The architecture of this cell is shown in Figure 2.1.

Another important spectral response measurement is the internal quantum efficiency (IQE). One of the losses in solar cells arises from reflections, which are accounted for in the IQE measurement. Reflections prevent a fraction of light from reaching the QDs and therefore those incident photons are lost and not converted to current. The IQE may be calculated in two different ways: IQE of the device or IQE of the absorber material. In the former case, the IQE_{device} is QE after accounting for reflective losses off the entire device

stack. Thus, the IQE_{device} is the measured electron flux divided by the photon flux absorbed by the entire dielectric stack that makes up the solar cell. For example, Figure 2.5 shows an EQE and IQE_{device} for a PbSe QD solar cell. In the example solar cell, the IQE_{device} is greater than 100% in the UV region, indicating that MEG is contributing to the solar cell performance¹²³. In the other case, the IQE_{absorber} is the QE after accounting for reflective losses at all interfaces and absorptive losses in all materials except for the OD absorber layer. In other words, IQE_{absorber} is the measured electron flux divided by the photon flux absorbed only by the active layer (*i.e.*, the QDs). Thus IQE_{absorber} is always larger than IQE_{device}. Some instrumental setups allow for measuring the reflectance spectrum (specular ± diffuse reflectance) simultaneously with the EQE measurement. Alternatively, the reflectance spectrum may be obtained using a UV-Vis-NIR spectrophotometer equipped with an integrating sphere. To do so we make a witness QD solar cell on an un-patterned substrate in the same way as the patterned solar cells. The back contacts are deposited onto the entirety of the witness substrate. The reflectance spectrum of the device is then obtained by measuring the reflectance of the witness film in a Shimadzu UV-Vis-NIR-3600 spectrophotometer equipped with a 60 mm integrating sphere (8° incidence angle) and a NIST-calibrated specular reflectance standard (STAN-SSH, Ocean Optics). The IQE_{device}, for example, is then calculated as $EQE/(1-R_{device})$, where R_{device} is the reflectance spectrum of the witness cell. To measure the IQE_{absorber}, one needs to calculate the reflectance at each interface and the absorbance in each material. More details specific to QD solar cells are available in Semonin *et al.* and Law *et al.*^{123,136} Additional information regarding accounting for losses in the spectral responsivity of solar cells may be found elsewhere.^{134,137,138}

2.VII QD Synthesis

2.VII.a Reagents

1-octadecene (ODE, technical grade), oleylamine (OLAm, technical grade), oleic acid (OA, technical grade), PbCl₂ (99.999% trace metals basis), CdO (\geq 99.99% trace metals basis), S(NH₄)₂ (40-48 wt. % in H₂O), selenium (powder ~100 mesh, 99.99% trace metals basis), trioctylphosphine (TOP), hexane (reagent grade), and ethanol (200 proof, reagent grade). All reagents are purchased from Sigma Aldrich and are used as received.

2.VII.b General Synthetic Notes

The synthesis of CdS QDs is based on the synthesis published by Robinson, *et al.*,¹³⁹ but without drying the sulfur precursor, and Zhang, *et al.*¹²⁹ The synthesis of CdSe QDs is modified from that published by Peng, *et al.*¹⁴⁰ and Zhang, *et al.*¹³⁰ The syntheses of PbS and PbSe QDs by cation exchange reactions from CdS and CdSe, respectively, are modified from that published in Zhang *et al.*^{129,130}

At the beginning of a synthesis, reagents are degassed before heating. This is done by evacuating the flask atmosphere using the Schlenk line for 1-2 minutes, or until bubbling has ceased, then flushing with N₂ and repeating for a total of 3 cycles before the heating mantle is turned on. The vacuum base pressure should be 20–100 mTorr. When an injection is used to initiate a reaction, 16 gauge needles and 20 mL syringes are used regardless of the amount of liquid being injected. This ensures a quick injection, which will improve the size distribution of the product.

2.VII.c Synthesis of CdS QDs

(i) The precursor solution is prepared with 0.66 g CdO, 4 g OA, and 18 g ODE in a 100 mL round bottom flask.

(ii) The reagents are stirred and heated to 260 °C. The solution is further degassed by alternating between vacuum and N₂ while the solution temperature is <80 °C. At >80 °C the atmosphere in the flask is switched to N₂. (To minimize air leakage into the flask atmosphere, the N₂ pressure in the Schlenk line should be high enough such that excess N₂ escapes through the bubbler, which is part of the Schlenk line.)

(iii) Meanwhile, 880 μ L of (NH₄)₂S is added to 15 mL OLAm and stirred vigorously. This mixture outgasses aggressively and should not be capped. The ammonium sulfide will form a gel when added into the OLAm and should be allowed to completely dissolve before injection into the Cd-oleate solution.

(iv) The reaction is left at 260 °C until the burgundy color has disappeared and the solution turns clear, indicating that the CdO has been converted to Cd-oleate. It is important for all of the CdO to be reacted before the next step. (Gently shaking or rocking the flask helps to remove unconverted CdO from the flask walls.)

(v) The flask is removed from the heating mantle and allowed to cool to just above room temperature (32 °C).

(vi) The heating mantle is replaced and the temperature control is set to 32 °C.

(vii) The ammonium sulfide / OLAm solution is then injected into the flask and allowed to react for 1 hour.

(viii) After 1 hour, the heating mantle is removed and the reaction liquor is distributed into centrifuge tubes, each with 5-10 mL of reaction liquor. Hexane is then added until each tube contains 20-25 mL total solution. This step is important because trying to precipitate the QDs directly from the reaction liquor will result in oil instead of a solid precipitate after centrifugation.

(ix) Ethanol is then added until the transparent yellow solution is opaque (25 mL). The mixture is centrifuged at 7500 RPM for 5 min. The exact time and speed of centrifugation is not critical, as long as the result is a solid precipitate and a (mostly) colorless supernatant. (If a solid precipitate is not obtained, we recommend using a higher hexane:liquor ratio or using a lower solvent:antisolvent volume ratio.)

(**x**) The CdS QDs are dispersed in ~9 mL of toluene. It is important to only precipitate the product a single time, otherwise the QDs in toluene may form a gel that cannot be extracted into a syringe for injection. This reaction consistently produces QDs with a first exciton peak at 366 nm.

2.VII.d Synthesis of CdSe QDs

(i) The precursor solution is prepared by mixing 0.512 g CdO, 6.28 g OA, and 25 g ODE and heating in the same way as described in steps (i and ii) of section 2.VI.d.

(ii) While heating the reagents, 0.063 g (0.8 mmol) Se powder is added to 5 mL ODE and sonicated for 10 min. Also, 3 mL of 1 M TOPSe is mixed with 7 mL ODE and loaded into a syringe pump.

(iii) The timing of the sonication is not critical, except that the mixture should be actively sonicated immediately before loading a syringe for injection. The Se powder will settle out of the ODE if left for more than a few minutes. We recommend at least 10 minutes of sonication in order to disperse the Se powder well, but it can be sonicated much longer so that it does not settle before injection.

(iv) The TOPSe solution is made by stirring 0.1 mol Se powder in 100 mL TOP in the glove box for at least 3 hours. All of the Se powder should be dissolved to form a transparent, yellow-tinted solution before use in the synthesis. If kept in the glove box the TOPSe can be used over a long period of time. A strong yellow color or precipitate at the bottom of the bottle is an indication that the TOPSe has oxidized and should not be used.

(v) The Se/ODE mixture is injected at 260 °C and the temperature controller is set to 240 °C.

(vi) After 1 minute from injection, the TOPSe/ODE solution is added dropwise at \sim 1 drop/second. This is set by eye using the syringe pump. (It is also possible to do this step by hand, although we see better consistency with a mechanical syringe pump. If injecting the TOPSe/ODE solution by hand, it is important to be as steady as possible to improve the size distribution of the final CdSe.)

(vii) During the TOPSe/ODE addition, monitor the reaction by UV-Vis absorbance until the desired size is achieved. This step is most easily done by drawing small

aliquots (~0.1 mL) that are quenched in a cuvette filled with hexane (~2 mL). Aliquots should be taken every 5-10 minutes to track the growth of the QDs.

(viii) When the first exciton of the CdSe QD peak has reached 600 nm, the addition of the TOPSe/ODE mixture is stopped and 2 minutes later the heating mantle is turned off and removed, allowing the QDs to cool to room temperature. On average, there is ~3 mL of the TOPSe/ODE mixture leftover and the total reaction time is ~30 minutes. This will vary depending on the dripping speed, in general the slower additions of TOPSe/ODE result in greater monodispersity in the final sample.

(ix) The reaction liquor is split into enough 50 mL centrifuge tubes such that there is ~5 mL of liquor in each tube. Approximately 20 mL of hexane is added to each tube and each tube is then capped and shaken well. 25 mL of ethanol is added to each tube and the tubes are centrifuged at 7500 RPM for 5 minutes. Often, this first precipitation results in a slightly colored supernatant and it is discarded while keeping the precipitated QDs.

(x) The QD product is washed twice more by dispersing each QD precipitate in 10 mL of hexane, and then precipitating with an equal volume of ethanol. After the final wash, the QD product is dispersed in 9 mL ODE. Dispersing the QDs will require the aid of a vortex mixer. If the CdSe QDs will be stored for an extended period, it is advised to bring them into a glove box before the final dispersion in ODE.

(xi) A CdSe QD product with good size distribution will have a sharp first exciton peak and a clear second excitonic feature, as seen in Figure 2.6.



Figure 2.6 Absorption spectra from the CdSe synthesis. Example absorbance spectra of CdSe QDs with the peak of the first exciton at 515 nm (black) and 610 nm(red).

2.VII.e Cation Exchange Reaction from CdS (CdSe) to PbS (PbSe)

PbSe (PbS) QDs are synthesized by a cation exchange reaction from CdSe (CdS) QDs.

(i) The precursor solution is prepared by mixing 0.834 g (3 mmol) PbCl₂ and 10 mL (3 mmol) OLAm in a 100 mL round bottom flask.

(ii) The mixture is heated to 100 °C while stirring and degassing with alternating between vacuum and N₂. At 100°C, a needle is inserted into one septum, as shown in Figure 2.7a, to flow N₂ over the reagents for \sim 5 minutes and further remove any water not removed during degassing.

(iii) The mixture is heated to 140 °C and the vent needle is removed. As the suspension is heated, $PbCl_2$ and OLAm form a complex and the solution begins to turn clear and colorless (Figure 2.7a). At temperatures ≥ 140 °C, the solution will turn turbid and white again (Figure 2.7b). The solution temperature is maintained at 140 °C for 10 minutes. A milky white solution should be obtained before the CdSe (CdS) QDs are injected.

(iv) As the PbCl₂/OLAm complex is formed we have observed some differences in color at this stage of the reaction. Occasionally, the solution will stay clear until heated to a higher temperature (>145 °C) or the solution will have a pink hue after the complex forms. Neither case has had a detrimental effect on the synthesis.

(v) The reaction bath is heated or cooled to the injection temperature (90 °C to synthesize 1.3 eV PbS QDs, and 195 °C to synthesize 0.7 eV PbSe QDs) and 2-3 mL of CdSe (CdS) QDs (capped with Cd-oleate, 50-100 mg/mL in ODE) are injected using a 20 mL syringe and 16-gauge needle. Approximately 200 mg total of CdSe (CdS) QDs should be injected. There is an immediate color change to dark brown upon injection as the cation exchange reaction proceeds. The large diameter syringe and needle are important to ensure a swift injection of the CdSe (CdS) NCs. The resulting lead QDs will have a broad size distribution if the CdSe (CdS) QDs are not injected quickly enough.

(vi) The reaction is allowed to run for 30-60 seconds (depending on the desired size) before removing the mantle and immediately quenching by submerging the flask in a water bath. (If the reaction temperature is too low and/or the reaction time is too short, a mixture of CdS (CdSe) and PbS (PbSe) QDs will be obtained, including Janus particles, as discussed in earlier manuscripts.^{129,130})

(vii) At 70°C, 10 mL hexane is injected to assist cooling. At 30 °C, 8 mL OA is injected to replace the weakly bound OLAm ligands on the surface of the PbSe (PbS) QDs. The OA injection will raise the temperature of the reaction solution to \sim 45 °C and the

reaction should be allowed to cool below 30 °C again before exposing the solution to air.

(viii) The cooled product is poured into 2-50 mL centrifuge tubes, split evenly such that each tube contains 15 mL reaction product. Extra hexane (5 mL) is used to rinse the round-bottom flask and this is also added to the centrifuge tubes. Then, 20 mL of ethanol is added to each tube in order to precipitate the QDs.

(ix) The mixture is centrifuged for 5 minutes at 7500 RPM.

(x) The resulting supernatant should be (mostly) colorless and is discarded (Figure 2.8a). If the supernatant has a darker color, extra ethanol is added (2-4 mL) and the tubes are centrifuged again.

(xi) The solid QD precipitate in each tube is dispersed using 10 mL of hexane, the solutions are combined into one centrifuge tube, and the tube is centrifuged without addition of an antisolvent. This step precipitates the excess chlorides from the solution, which will result in a white precipitate (Figure 2.8d).

(xii) The QD solution is extracted into a syringe and then filtered through a $0.2 \ \mu m$ filter into a clean centrifuge tube. The latter step further removes excess chloride salts.

(xiii) A final wash is done by precipitating with ~20 mL ethanol (or until the solution is cloudy brown) and centrifuged as above.

(xiv) For dip-coating, QDs are dispersed in hexane at 10-20 mg/mL. For spin-coating, QDs are dispersed in octane at 30 mg/mL.



Figure 2.7 Pictures precursors for the cation exchange reaction. (a) As the PbCl₂/OLAm mixture is heated, it goes through a clear phase. **(b)** A milky white solution forms after heating the PbCl₂/OLAm mixture to \geq 140 °C.



Figure 2.8 Pictures of QDs during washing phase. The washing procedure for cation exchanged QDs: **(a)** the precipitate formed at the bottom of the centrifuge tube after precipitation and centrifugation; **(b)** QDs fully dispersed in hexane; **(c)** gray, cloudy solution that results from the precipitation with ethanol; **(d)** white precipitate of excess chlorides after centrifugation in neat hexane; and **(e)** final precipitation and centrifugation. Notice that the tube walls have some QDs stuck to them above the main solid QD precipitate, which is a sign that the QDs are well washed.

2.VII.f QD Characterization

After each synthesis, the QDs are characterized by UV-Vis-NIR absorbance spectroscopy. The absorbance spectra are used to determine the QD size, polydispersity,

and concentration. Polydispersity is gauged via the width of the first exciton peak. Figure 2.9 shows example of acceptable and unacceptable polydispersity of PbS (Figure 2.9a) and PbSe QDs (Figure 2.9b). The polydisperse QD batch should not be used or size selective precipitation should be performed to isolate more monodisperse QDs.



Figure 2.9 Absorption spectra from PbS and PbSe QD syntheses. Examples of (red) acceptable and (blue) unacceptable absorbance spectra of **(a)** PbS and **(b)** PbSe QDs.

2.VIII Discussion and Conclusions

The efficiency of QD solar cells has increased from 2.1 % in 2008¹⁴¹ to 11.3 % in 2016.¹⁴² This accelerated progress was accomplished through a combination of advances in the field revolving around the solar cell architecture and control of the QD surface, including band energetics and defect passivation. The solar cell architecture was improved by moving from a Schottky junction¹⁴¹ to a heterojunction with selective contacts for hole and electron extraction from the QD absorber layer.¹⁴³ Further architecture optimizations were made aimed at improving charge carrier collection efficiency through modification of the electric field at the junctions,^{144,145} for example, by using highly doped n-type MoO_x as the hole extracting contact layer.¹⁴⁶ In 2011, Semonin *et al.* showed that the use of two different ligand treatments during the deposition of the QD absorber layer (i.e., EDT-

treated QDs followed by hydrazine-treated QDs) led to significant improvements in QD solar cell performance.¹⁴⁷ Since then, QD solar cells have been made with two ligand treatments, such as tetrabutylammonium iodide (TBAI) followed by EDT.¹⁴⁸

Brown *et al.* then further opened the door to band alignment engineering within the QD absorber film by demonstrating control over conduction and valence band energy levels through varying the ligand molecules on the QD surface through solid state ligand exchange.¹⁰⁸ Likewise, the tunability of the QD Fermi level was demonstrated by control of the QD surface stoichiometry through solid state ligand exchange.¹⁴⁹ The range of beneficial ligand treatments in solar cells was later expanded with inorganic molecules, such as PbI₂, which also allowed QD solar cells to be made thicker than before, thereby absorbing a higher fraction of incident light.^{150,151} Beyond tuning the QD energetic alignment, control of the QD surface further encompassed surface trap passivation through both solid state ligand exchanges^{152,153} and synthetic protocols.^{154,155} For example, Ip *et al.* showed that insitu addition of CdCl₂ at the last stage of synthesis resulted in the reduction of mid-gap trap state density.¹⁵⁴ The trap reduction was attributed to partial passivation of the QD surface by halide anions.

Other synthetic advances, such as the cation exchange reactions described here, have similarly demonstrated reduced trap densities¹⁵⁵ and prolonged air stability¹⁵⁶ in lead-chalcogenide QDs. It is important to note that different synthetic procedures influence the QD surface termination. Traditional, lead(II) oxide-based, syntheses for leadchalcogenide QDs leave Pb-oleate ligands on the QD surface.¹⁵⁷ In contrast, the cation exchange reactions described here produce lead-chalcogenide QD surfaces terminated with a combination of Cd-oleate, Pb-oleate, and Cl-ions.^{130,150,158} Therefore, the QD surface

termination, the QD energetic alignment, trap density, and Fermi level, may vary even in the case of identical solid ligand exchanges performed on QDs synthesized by different methods. For example, solid-state ligand exchange may not remove the surface-bound Clions. These nuances influence solar cell performance differences among different research groups, and represent an array of both challenges and opportunities to continued advances in the field.

Further improvements in QD solar cells will be achieved through continued investigation of the solar cell architecture, control of OD surface through novel ligand exchanges, improved syntheses, and novel materials such new or as heterostructures.^{113,129,159,160} These advances can be accelerated through the ability to make in-house state-of-the-art prototype QD solar cells to serve as test beds for these investigations and for realizing the full potential of QD solar cells beyond the Shockley-Queisser limit.¹⁶¹⁻¹⁶³ Using the synthesis and film fabrication procedures described here, Chapter 3 will describe in greater detail the differences between QDs produced from the traditional PbO synthesis and those produced from the cation exchange synthesis described here.

Chapter 3: Chemical Analysis of PbS QDs with Metal Halide Surface Passivation

3.I Overview

The funding for my graduate work has been provided through an Energy Frontier Research Center of the Department of Energy called the Center for Advanced Solar Photophysics (CASP). CASP is made up of many institutions, including two national laboratories and multiple Universities around the U.S. The goal of CASP "is to explore and exploit the unique physics of nanostructured materials to boost the efficiency of solar energy conversion through novel light-matter interactions, controlled excited-state dynamics, and engineered carrier-carrier coupling." With the unique capabilities of the different institutions that make up CASP we study many types of quantum dots (QDs), making photophysical measurements on colloidal QDs, QD arrays, and optoelectronic devices.

In the study of QDs it has become apparent that the synthetic route, purification procedures, storage conditions, ligand treatments, etc. all contribute to the final properties of QDs and arrays. This causes difficulties when trying to compare reports between different laboratories, because even when researching nominally the same material there are variations that can heavily influence the measurement. In order to remedy this situation, CASP has set out to study a single, standardized QD sample.

I have synthesized QDs and deposited coupled QD arrays at NREL and then shipped samples of the colloidal solution and films to CASP members across the U.S. for measurements. This guarantees that throughout the synthesis, purification, and film deposition the QD samples are all the same. We have sought to understand this

standardized sample as completely as possible, in order to inform the field of our best materials and guide the design new and improved QD materials.

The standardized sample was chosen based on the QD material that produces the highest efficiency QD solar cells at NREL. This material is PbS QDs synthesized through a cation-exchange procedure of CdS QDs, denoted PbS_{CdS} and described in detail in Chapter 2. Many photophysical and optoelectronic measurements of interest require electronically coupled QD arrays, so the film formation step was also standardized. The choice of ligand treatment was also chosen based on high-efficiency QD solar cells in which we use two ligands in a dual treatment ligand exchange, described in detail in Chapter 2. In a layer-by-layer fashion, the first ligand (PbI₂) is used for four cycles, then the second ligand (MPA) is used to deposit two additional QD layers.

In the standard sample project we wanted to explore the effects of each ligand individually, along with how they interact with each other when using the dual treatment as in a device. As a result the standard sample turned into three film samples utilizing the ligands separately and together: 1) PbI₂, 2) MPA, and 3) PbI₂/MPA or the dual treatment.

The preliminary measurements from other CASP collaborators will be presented at the end of this chapter. Beyond being the standard sample coordinator, providing the samples and integrating the resulting data, my task was to characterize the QD material itself as fully as I could. I used many different elemental analysis techniques in conjunction in order to determine the underlying QD composition, which is the work presented in this chapter. Overall, this work will be paired with time-resolved microwave conductivity (TRMC), transient absorption (TA), time-resolved photoluminescence (TRPL), and photocurrent spectroscopies to give a complete description of the standard sample, from elemental composition to mobility and lifetime values.

3.II Introduction

QDs enable a wide variety of tunable material properties for optoelectronic devices, biomedical applications, and many other technologies. While a wealth of progress has been made from countless research efforts on this topic, the link between the chemistry of the materials and the material properties is still much weaker than desired. For instance, it is heavily debated whether the macroscopic properties of a QD film are better described by band transport, or a hopping mechanism; how the transport mechanism depends on the chemical identity of the coupling technique; the energetic position of the Fermi level with respect to the energy levels (or bands) and as a function of surface treatment; and what the chemical identity is that leads to mid gap defect states. A universal answer to these questions does not define all QD films. These anomalies prevent more rapid development of these highly novel and tunable materials systems.

With the large number of surface atoms in QDs it may seem that defects would dominate in QD materials, but theoretical calculations show that perfectly stoichiometric PbS QDs have no traps in the bandgap.¹⁶⁴ Along with this calculation, others have suggested that charge balance is the key to having mid-gap-trap-free QD materials.¹⁶⁵ Perfectly stoichiometric QDs have not yet been successfully synthesized in the laboratory because the high-energy facets of the truncated crystal structure tend to fuse together, creating bulk material. QD syntheses utilize long, organic molecules as ligands on the QD surface, keeping the individual QDs from agglomerating and providing solubility in non-polar organic solvents. Studies on charge balance also suggest that trap-free QDs can be synthesized by
optimizing the number of ligands on the QD surface, in favor of charge balance as opposed to complete surface coverage.¹⁶⁴

The long, organic ligands that offer easy solution processing simultaneously impede electrical transport in QD arrays. In order to use QDs for photovoltaic devices, these long organic ligands are exchanged to short or inorganic ligands resulting in an electronically conductive array. While colloidal QDs likely have few trap states, the ligand exchange process can lead to new states, both interface states—which cause a red-shift in absorption and photoluminescence—and new mid-gap trap states.^{166,167} Unpassivated QD surfaces can trap carriers when the lattice is not terminated sufficiently, so the chemical nature of new ligands must be carefully chosen to electronically couple the QDs while also passivating the QD surface. It has been suggested that traps in QD arrays are surface trap states because they are caused by the ligand exchange procedure.

Boyzigit, *et al.* theorize that these surface traps are electron-phonon interactions as opposed to specific chemical defects at the surface.¹⁶⁸ They report that phonons resulting from a "soft" nanocrystal surface can be stabilized by the correct choice of ligands and the stabilized surface results in lowering the overall number of trap states. Nelson, *et al.* also observed that when a QD array was heated above the melting temperature of the surface ligand it induced surface trap states.¹⁶⁹ They attribute this surface trap state to the surface mobility of ligand-bound metals causing a "liquid" surface that induces a trap state seen in fluorescence.

A great deal of work has been done to quantify trap state density and energetic position of trap states in PbS QDs, and a sample of measurements is shown below in Table 3.1. Trap state densities in QD arrays are dependent on the ligand, but generally fall in the range of $10^{15} - 10^{18}$ cm⁻³ with most measurements close to 10^{16} cm⁻³.^{43,170-173} This corresponds to ~1 trap per few thousand QDs. Changing the surface species can have a dramatic effect on the trap state density, for example one study found 1 trap per 400 QDs when using 3-mercaptoproprionic acid (MPA) as a ligand, but when concurrently treated with CdCl₂ the trap density decreased to 1 trap per 1800 QDs.⁴³ The range of densities and energy levels for traps reported in the literature likely arises from variations in the synthetic procedure and ligand treatments, which makes it difficult to make meaningful comparisons between different laboratories.

Energy of Trap (eV from CB)	Density of Trap state (cm ⁻³)	Reference	
0.26	2.7*10 ¹⁶		
0.36	(initial)	170	
	$1.8^{*}10^{17}$	170	
	(2 days air exposure)		
0.1	10 ¹⁸	171	
0.3	1014	1/1	
-	1017	42	
-	2*10 ¹⁶	45	
0.24	-	169	
0.27	-	174	
0.3	Highest (EDT)		
0.27	< ½ of EDT (MPA)	42	
0.23	Lowest (Br-)		
~0.4	-	167	

 Table 3.1: Energy of trap state and density of states at trap state energy.

Recently, cation and anion treatments that can bind to surface chalcogenide and lead, respectively, have been proven to improve photovoltaic device performance and increase the stability of lead chalcogenide QDs.^{39,40,45,46,98,175} Metal halide treatments have greatly increased the ability of PbSe QDs to resist oxidation, allowing device fabrication in

air and the first certification of a PbSe QD device.^{38,40,46,175} In addition to air stability, these treatments have been shown to decrease the number of trap states and resulted in the first measurement of nongeminate photoluminescence from an electronically coupled QD array, which will be shown in Chapter 4.¹⁰³ Introducing metal halides during the synthetic process has also been used to improve air stability, device performance and decrease the density of trap states.^{38-40,45,103} One way to introduce metal halides into PbS QDs is through the cation exchange method of the standard sample. In past reports, it has been shown that this exchange leaves residual cadmium and chloride in the QD product and the PbS_{CdS} QDs have improved optoelectronic properties.^{38,39,103,175}

As discussed in the Overview, the following chapter discusses the chemical characterization that is my part of the standard sample project. When helpful, the following analyses will be compared to the traditional Hines and Scholes PbS QD synthesis, which uses PbO and bis(trimethylsilyl)sulfide (TMS),²⁶ and will be labeled PbS_{PbO}.

3.III Results and Discussion

3.III.a Chemical Analysis

Figure 3.1a,b shows a schematic of the surface passivation that likely results from each of the synthetic routes studied here. This schematic is based on compositional analysis that will be expounded in this section. As an initial comparison, photovoltaic devices, which are one of the end-goals of this work with CASP, were fabricated from the two synthetic techniques. Each device was made in ambient, following the spin coating procedure found in the literature.⁹⁸ **Figure 3.1**c,d shows average JV scans and the external quantum efficiency (EQE) curves for representative devices of the data summarized in

Figure 3.1e,f. The overall spectral shape for each type is similar and there is very little difference between the integrated current for each device type, matching the similarities in the J_{SC} seen in the device statistics shown in **Table 3.2**.



Figure 3.1: Overview of PbS_{cds} and PbS_{Pb0} comparison. (a,b) Schematic showing the surface chemistry of each synthesis, PbS_{Pb0} is shown in (a) and PbS_{CdS} is shown in (b) along with the legend. (c) JV scans of example devices made from the different synthetic methods. (d) EQE spectra of devices made from PbS_{Pb0} and PbS_{CdS} showing very similar EQE and resulting current. (e) Histogram of the V_{OC} and (f) histogram of power conversion efficiency for devices made from PbS_{Pb0} and PbS_{CdS} . While there is variation in the devices between batches, the PbS_{CdS} QDs consistently result in higher V_{OC} and efficiency than devices made from PbS_{Pb0} QDs.

Table 3.2: Average solar cell performance parameters. This table contains devices made from the two synthesis techniques representing over 40 individual devices.

	Voc (mV)	Jsc (mA/cm ²)	FF (%)	Eff (%)
PbS _{Pb0}	420 ± 104	20 ± 1.6	47 ± 8	4.1 ± 1.7
PbScds	464 ± 69	21 ± 1.4	57 ± 5	5.7 ± 1

To determine the origin of the improvement in photoluminescence¹⁰³ and devices that is observed using cation-exchange-prepared QDs, we compare the atomic composition of PbS_{CdS} QDs to PbS_{Pb0} QDs. Elemental analysis was used to determine the variation in composition between the PbS_{CdS} and the PbS_{Pb0} QDs. Inductively coupled plasma (ICP) was used to yield the inorganic composition, *i.e.* the amount of lead, sulfur, and cadmium in the samples. Glow Discharge Mass Spectrometry (GDMS) is a highly sensitive technique used to quantify the impurity elements in a matrix (in this case PbS). By pairing ICP and GDMS measurements we can construct a complete picture of the composition of the QD samples; the GDMS results are shown in Figure 3.2a. In both cases the Pb:S ratio is 1.6, similar to previous literature reports for this size of QD.⁵² We find that the PbS_{CdS} is a higher purity sample; the main impurities are cadmium and chloride, while other atoms (Si, K, etc.) are present at lower levels when compared to the PbS_{PbO} sample, Figure 3.2a. The excess chloride and cadmium in the PbS_{CdS} most likely reside at the surface of the QD based on the etching of Cd when exposed to chlorinated solvents shown in reference 38 and ligand exchange data shown below. Chloride and cadmium passivation are believed to be consistent with the air stability and higher V_{0C} , respectively, as will be shown in subsequent chapters.



Figure 3.2: Elemental analysis and NMR for PbS_{CdS} **QDs. (a)** Results from GDMS showing the impurity atoms detected in each sample. The PbS_{Pb0} sample shows higher purity while the PbS_{CdS} has notable amounts of Cd and Cl, which contribute to the air stability and higher V_{oc}. **(b)** NMR spectra normalized to the concentration of the PbS QDs in solution shows the difference in ligand coverage between the PbS_{Pb0} (blue) and PbS_{CdS} (red). The peak demarcated with (*) is due to the benzene solvent and the peak with (#) is the internal standard, dibromomethane, used for quantitative analysis. A magnified portion of the NMR spectrum is displayed in the green box and shows the slight shift in the vinylic hydrogen peak. **(c)** Absorption and PL measurements on PbS_{Pb0} and PbS_{CdS} samples in solution.

Nuclear magnetic resonance (NMR) was used to quantify the number of ligands attached the QD surface. Using an internal standard, the ligand coverage was calculated for both PbS_{Pb0} and PbS_{cds} QDs of similar sizes and the NMR spectra are seen in Figure 3.2b. The internal standard is used to calculate the concentration of oleate molecules in the solution and the concentration of QDs is determined based on a calibration curve using the absorption of the solution at 400 nm.^{50,176} We found that PbS_{cds} had lower ligand coverage than the PbS_{Pb0} counterpart. This is most likely due to residual chloride filling surface sites that would usually be occupied by oleate ligands, due to the PbCl₂ precursor for PbS_{cds} QDs. The difference in oleate ligand coverage from Figure 3.2b (5.7 OA/nm² for PbS_{Pb0} and 3.3

 OA/nm^2 for PbS_{CdS}) corresponds to a difference of about 75 more ligands per PbOsynthesized QD. While chloride cannot be measured in ICP analysis, the XPS data shows a Pb:Cl ratio of ~3, which is 82 chloride ions per QD for this size. Along with the added cadmium at the surface, this excess chloride results in charge neutral PbS_{CdS} QDs—within error—even though there are significantly less oleate ligands at the QD surface.

The chemical shift of the vinylic hydrogen signal (6.1 ppm) shows a small, but consistent shift due to the different chemical environment on the surface of the QD. We postulate that this is due to cadmium on the surface of the QD, because PbS QDs made from PbCl₂ and TMS⁴⁰ do not show a shifting of the vinylic hydrogen peak (Figure 3.3a,b). These QDs have a similar Cl surface passivation, but do not contain cadmium, so the shift is attributed to the presence of surface cadmium. The peak is also shifted upfield, toward the vinylic peak of CdS QDs, which are terminated purely by Cd-oleate ligands (Figure 3.3c,d). This shifting suggests that the residual cadmium from the cation exchange is on the surface of the QD as Cd-oleate, causing a shifted vinylic signal from the pure Pb-oleate capped QDs. The shifting could be due to the difference in chemical environment (Pb vs Cd bound), the strength of the various metal-oleate bonds to the QD surface, or the rate of exchange between bound and free oleate ligands. FTIR and ICP experiments are used to help elucidate the nature of the Cd found at the QD surface.



Figure 3.3: Reference NMR spectra for PbS QDs. (a) NMR spectra for PbS_{PbO} , PbS_{CdS} , and PbS_{PbCl2} . **(b)** Zoomed in portion of the graph in (a) showing the vinylic hydrogen peak for each of the different QD syntheses techniques. The peak is slightly shifted for the PbS_{CdS} shown in blue. **(c)** This NMR spectra show the PbS QD syntheses compared to the CdS QDs. **(d)** This zoomed in portion of figure (c) shows the shift of the vinylic hydrogen peak for the CdS QDs compared to both spectra for the PbS QDs.

Tetramethylethylenediamine (TMEDA) is a chelating agent that can be used to remove surface species from the QD core. The metal-oleate ligands have a higher affinity for TMEDA than binding to the QD surface letting one easily separate the metal-oleate species from the bulk QD sample. The FTIR spectra shown in Figure 3.4a,b compares the species removed using TMEDA (labeled M-oleate, yellow trace) to neat Pb-oleate (maroon) and neat Cd-oleate (green). Based on the comparison shown enlarged in Figure 3.4b, the oleate complexes removed by TMEDA are a mixture of Pb- and Cd-oleates. This is confirmed by ICP analysis of the TMEDA removed oleates, shown in Figure 3.4c, where the Pb:Cd ratio is 0.7. More Cd-oleate ligands are removed from the QD surface during the TMEDA exposure than Pb-oleate ligands. The TMEDA treatment can be done multiple times to remove the majority of surface species but here, we have endeavored to show that Cdoleate is present as a ligand species on this QD sample



Figure 3.4: FTIR and ICP analysis of PbS_{CdS} **QD ligands. (a)** FTIR spectra showing the individual metal-oleates and the oleate species removed from the QD surface using TMEDA. **(b)** This region of the spectra has been enlarged to show the different peak positions of Pb-and Cd-oleate. The ligands removed from the QD sample are plotted in yellow and the broad peaks show a mixture of Pb- and Cd-oleate was removed from the QD surface. **(c)** ICP-OES measurements of the Pb:Cd ratio for neat PbS_{CdS} QDs (red), the surface species removed with TMEDA (purple), and the QD sample after one exposure to TMEDA (orange). **(d)** ICP-OES measurements showing the Pb:Cd ratio for PbS_{CdS} QDs treated with different ligands. The neat QDs (red) show the largest Cd content, while the PbI₂ treatment (green) results in the lowest Cd content. The EDT (teal) and MPA (blue) show comparable amounts of residual Cd, but some Cd was removed during the ligand exchange procedure.

In Figure 3.4d a second ICP study shows how the Cd content is influenced by the

ligand exchange processes used to make conductive QD arrays. The organic ligands (which

both most likely bind through the thiolate moiety) have equal amounts of Cd, slightly less than the neat oleate-capped QDs. This is in contrast to the PbI₂ ligand treatment and is consistent with the manner in which each ligand binds. The EDT and MPA ligands undergo an acid-base reaction with oleate ligands bound at the QD surface, producing oleic acid and a thiolate that replaces the oleate. In this scheme, one would expect to have a very small influence on the amount of Cd on the QD surface. In the case of PbI₂, the solvent (dimethylformamide, DMF) is used to strip the ligands off of the QD surface¹⁷⁷ and then the QD is passivated by PbI₂ in solution. In this scheme, the DMF removes metal-oleate complexes (probably forming many clusters with iodide and chloride as well) and therefore the Cd content in the final QD array is very low.

Combining the data from ICP and NMR the composition of the QDs can be obtained. The QD core is stoichiometric PbS (within the constraints of the GDMS results, which show a few impurity atoms that are incorporated at <1 atom per QD) with a shell of Pb- and Cdoleate along with surface Cl passivation. Based on the atomic ratios measured in ICP and the ligand coverage calculated from NMR, the PbS core is surrounded by Pb_{0.86}Cd_{0.14}OA_{1.1}Cl_{0.9}. This ligand shell is varied and is capable of binding in many different ways, as X-type, L-type, or bound-ion-pairs. This variety of surface passivation could be the reason for the excellent air-stability and PL properties of the PbS_{CdS} QDs compared to their PbS_{PbO} counterparts passivated solely with Pb-oleate.

3.III.b Photoluminescence

The PL spectra and the integrated PL intensity were monitored as a function of temperature, from 18 K to 300 K. As presented in detail in Chapter 4, the PbS_{CdS} QD samples vs. PbS_{Pb0} QDs exhibit markedly different temperature dependent and excitation

intensity dependent behavior. Similar conclusions are drawn here, but for purposes of evaluating the treatments associated with the standard sample, we focus on the PbS_{Cds} QDs and the effects of the ligands.



Figure 3.5: Temperature dependent photoluminescence for QD films. (a,b) show the low temperature photoluminescence on films made from PbS_{CdS} and PbS_{PbO} , respectively, along with the impact of the three different ligand treatments (PbI₂, pink trace; MPA, green trace; and dual treatment, black dashed trace). **(c)** Temperature dependent PL peak position for the different ligands on PbS_{CdS} . **(d-f)** Temperature dependent PL traces for the ligand treatments: PbI_2 (d), MPA (e), and PbI_2/MPA (f). Regardless of the ligand treatment, there is measureable PL at room temperature, but the room temperature PL for the MPA treatment is significantly red-shifted from the treatments with PbI_2 . This shift is highlighted in panel (c).

Steady-state photoluminescence (PL) was measured in solutions (Figure 3.2c) and films (Figure 3.5) for both QD samples. The Stokes shift for the PbS_{cds} measured in solution is slightly smaller (78 nm) than the PbS_{Pb0} (86 nm) and the PbS_{cds} has a larger PLQY (56 % compared to 23 %) showing that the cation exchange results in higher quality QD material. PL from treated films shows the effects of various ligand treatments on QD film properties.

The temperature dependent spectral profiles for all samples are shown in Figure 3.5d-f. PbI₂ and PbI₂/MPA films share common features: an initial red shift as the temperature is raised and a subsequent blue shift when approaching room temperature (see Figure 3.5c). The spectral envelopes are almost purely Gaussian at low temperature, but exhibit asymmetry and tailing toward the blue at higher temperatures. These characteristics were previously established to be related to population transfer within the bandtail density of states.¹⁷⁸ Strong quenching is observed, although the PL is not entirely quenched at room temperature, unlike in films of conventional PbS_{PbO} ODs.¹⁷⁹ The temperature dependent spectra of the MPA film reveal the existence of at least two distributions of emitting species. This is especially apparent at intermediate temperatures, where the distributions have nearly equal weight. Such behavior has been previously reported and ascribed to relatively shallow and weakly emissive trapped charges.¹⁸⁰ The existence of the two distributions broadens the PL spectrum and distorts the temperature dependent peak shift from what is observed for PbI₂ and PbI₂/MPA (Figure 3.5e). The monotonic blue shift with increasing temperature reflects the increased prevalence of the higher energy PL emission as thermal activation redistributes population away from the trapped charge states. The intensity of the emission monotonically decreases from 18K to 295 K for the PbI₂ and PbI₂/MPA films, whereas it increases slightly from 18-100 K in the MPA film, before decreasing toward room temperature (Figure 3.5e). This rise may be a further indication of trapped charges for QDs capped with strongly bound thiolates, similar to reference 181.

The low temperature photoluminescence spectra are normalized and plotted in Figure 3.5a,b. The PbS_{PbO} sample (Figure 3.5b) shows strong red shifting with the MPA

treatment, while the PbI₂/MPA film only red-shifts slightly compared to the PbI₂ film (Figure 3.5a). The thiol group on the MPA ligand may introduce hole-trap states¹⁸¹ which explain the red-shifting induced by the MPA ligand; both from MPA alone and as the secondary treatment in the bilayer films. The intermediate PL peak is an indication that the MPA treatment in the PbI₂/MPA film also treats the PbI₂ layer, suggesting that the two ligands do not have perfectly distinct regions in the film. The PbS_{Cds} QDs respond very differently to the ligand treatments (Figure 3.5a). While the widths of the PL peaks change with the ligand treatment, the significant red-shifting induced by the MPA in the PbS_{Pb0} sample is not seen here. This suggests that the thiolate hole trap is not produced to the same extent in the PbS_{cds} sample. The halide passivation (from the synthetic method, or added by the PbI₂ treatment) helps to minimize the traps at the QD surface, manifesting here as an absence of the red-shifting in the low temperature PL spectrum.

As shown in Figure 3.5a, the MPA film exhibits a broad (0.22 eV) PL spectrum at 18 K, with the peak centered at 1.06 eV. PbI₂ shows a red-shifted (1.04 eV) and narrowed band (0.16 eV). When the PbI₂ treatment is followed by the MPA treatment (PbI₂/MPA), the band center blue shifts to about 1.08 eV. Interestingly, when normalized to the peak value, the PL from MPA effectively encompasses the PL from the PbI₂ and PbI₂/MPA films. The red shifted spectrum of the PbI₂ supports our hypothesis that the inorganic treatment brings the QDs close together, coupling them strongly. On the other hand the spectra of the PbI₂/MPA film shows how the MPA treatment impacts not only the new layers deposited on top, but also the underlying PbI₂ layers because the spectra for the PbI₂/MPA film is shifted from the PbI₂ film instead of producing a combination of the PL peaks observed in the PbI₂ and MPA treatments.

3.III.c Collaborative Work

PbS QD films with the three different ligand treatments were studied through many different characterization techniques including transient absorption spectroscopy (TA), field effect transistors (FETs), time-resolved photoluminescence (TRPL), time-resolved photocurrent (TPC) and time-resolved microwave conductivity (TRMC). A summary of the preliminary results of these studies is reported in Table 3.3. Analysis of FET and TRMC data is still ongoing and will require more measurements in order to give meaningful results.

The marked differences between the ligand treatments are clear when measuring the mobility and lifetime. The PbI₂ treatment results in high mobility films, but with a short lifetime. Conversely, the MPA treatment results in lower mobility films with a longer lifetime. When building a bilayer film, the mobility stays high, close to the mobility of the PbI₂ films while the lifetime is longer than that of the PbI₂ film. This suggests that this particular combination of ligands provides the right balance of mobility and lifetime to produce high efficiency photovoltaic devices.

One interesting observation from this data is that while many of the techniques result in similar trends, the absolute numbers are very different and some trends do not hold perfectly from one measurement to the next. This shows us that the measurement of "mobility" or "lifetime" while referring to nominally the same parameter may be measuring a slightly different property of the material depending on the excitation and probe type. **Table 3.3: Preliminary results from collaborative measurements.** A summary of results from techniques measuring mobility and lifetime to allow for easy comparison.

	Mobility (cm ² /Vs)				Lifetim	e
	PbI ₂	MPA	PbI ₂ /MPA	PbI ₂	MPA	PbI ₂ /MPA
TRPL				192 ns	247 ns	224 ns
TA (fast)				860 ps	1.6 ns	1.2 ns
(intermediate)				114 ns	273 ns	211 ns
FETs	7.6*10-4	3.1*10-6	1.3*10 ⁻³			
(electron)	1.3*10-4	5.8*10-4	2.6*10 ⁻³			
(hole)	1.2*10 ⁻⁵	5.6*10 ⁻⁷	1.0*10 ⁻⁵			
TPC	0.16	0.06	0.075	17 ns	32 ns	77 ns

3.IV Methods

3.IV.a Synthesis of PbS QDs

 PbS_{CdS} QDs were synthesized following the procedures outline in detailed in reference 98 and in Section 2.VII.

3.IV.b Film Formation

Detailed spin-coating steps are found in Chapter 2. The individual ligands (PbI_2 and MPA) are usually built up to 4 layers each and for the dual treatment, 4 layers with PbI_2 are followed with 2 layers of the MPA treated QDs. All films are annealed in an N₂-filled glovebox on a hotplate set to 110°C for 20 minutes.

3.IV.c NMR

PbS QDs are dried from octane and placed under vacuum overnight in order to remove any excess solvent. Benzene-d₆ or toluene-d₈ are used to disperse the dried QD

powder and the residual solvent signals are used to calibrate the shift positions.¹⁸² The concentration is calculated using optical absorption measurements and dibromomethane is used as the internal standard for quantitative analysis. A Bruker 400 MHz NMR was used to collect ¹H NMR spectra using a relaxation time of 45 seconds.

3.IV.d ICP-OES

PbS QDs were dried from octane and placed under vacuum overnight to remove residual organic solvents. HNO₃ (70%, \geq 99.999% trace metals basis) was used to dissolve the QDs, sometimes with the help of HCl (trace metals basis). The acid-QD mixture was vortexed and sonicated in order to ensure the complete dissolution of the QD material. The solution was then filtered and diluted to at least 3 different concentrations, with a final concentration of 5 vol% acid in water. Samples were analyzed by the Laboratory for Environmental and Geological Studies at the University of Colorado, Boulder.

3.IV.e Photoluminescence

See section 4.V.e for temp dependent PL methods. Photoluminescence samples were fabricated as described above in the film fabrication section on sapphire substrates.

3.V Conclusion

In conclusion, the cation exchanged QDs show improved air stability, have fewer impurities and produce higher efficiency devices than PbS QDs produced from the traditional Hines synthesis. Residual cadmium and chloride at the QD surface contribute to the oxidative stability and changes the surface composition, e.g. reducing the number of oleate ligands on the QD surface. Optical and electrical measurements of the QD films show that by using a bilayer ligand treatment it is possible to tune the mobility and lifetime of the QD array to be optimal for charge transport and extraction. In this chapter I have shown the detailed elemental composition of PbS_{CdS} QDs and the next chapter will discuss in greater detail the photoluminescence properties of the films fabricated from these QDs.

Chapter 4: Nongeminate Radiative Recombination of Free Charges in Cation-Exchanged PbS Quantum Dot Films

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4.I Abstract

Using photoluminescence (PL) spectroscopy we explore the radiative recombination pathways in PbS quantum dots (QDs) synthesized by two methods. We compare conventionally synthesized PbS from a PbO precursor to PbS synthesized using cation-exchange from CdS QDs. We show that strongly coupled films of PbS QDs from the cation-exchange luminesce with significant efficiency at room temperature. This is in stark contrast to conventional PbS QDs, which have exceedingly weak room temperature emission. Moreover, the power dependence of the emission is quadratic, indicating bimolecular recombination, a feature previously unreported in coupled PbS QD films. We interpret these results in terms of a greatly reduced defect concentration for cation-exchanged QDs that mitigates the influence of trap-assisted recombination. Cation-exchanged QDs have recently been employed in highly efficient and air-stable lead chalcogenide QD devices, and the reduced number of trap states inferred here may lead to improved current collection and higher open circuit voltage.

4.I.a Graphical Abstract



4.II Introduction

One of the keys to optimal solar cell performance is to approach the so-called "radiative limit," which dictates that at open-circuit the primary recombination mechanism should be radiative decay at or very near the band gap energy.¹⁸³ For GaAs solar cells, the limit is approached due to the near-unity internal emission efficiency, and optimization of the external PL efficiency is a performance metric.¹⁸⁴ Although the photoluminescence (PL) of colloidal quantum dots (QDs) is often reported in order to show band gap energy, size distribution, and reasonably effective surface passivation, the emission from processed QD films relevant for solar cells is much less often reported. We have found that the PL at room temperature from a strongly coupled QD film is most often exceedingly weak (<<1%) even in cases where the PL efficiency of the colloidal QDs is high prior to film formation (10-60%).^{178,179,185} We recently characterized PL in a series of PbS QD films with varying degrees of coupling and conclusively showed that the PL quantum yield (PLQY) vs.

PLQY for most lead chalcogenide QD films are inversely related using conventional QD synthesis and film formation procedures. Photogenerated charge-carriers in coupled QD arrays can sample a large number of QDs at high temperatures, inevitably leading to strongly quenched PL even with a relatively low concentration of defects.¹⁸⁵

QD solar cells are on a reasonably steep trajectory of power conversion efficiency (PCE) vs. time,¹⁸⁶ but the recent incremental gains involve improvements not clearly related to defect passivation, for example using structured TiO₂ in order to trap light more efficiently.¹⁸⁷ Often, the fill factor (FF) appears to be the most improved feature of champion solar cells, as opposed to the open-circuit voltage (V_{OC}), which is far below its theoretical limit. The FF has a complicated dependence on device characteristics and can depend on factors not related to the material quality, while the V_{OC} is more directly influenced by defect states. In order to steepen the efficiency vs. time curve, a better defined methodology for reducing defect density would be helpful for improvements in V_{OC} and for enabling the use of thicker active layers that can approach nearly ideal J_{SC} values.

Performing ligand exchanges changes the surface passivation of the QDs, in some cases providing improved defect passivation and surface protection against photooxidation or other forms of degradation.⁶⁴ A variety of chemical methodologies have been used to control the QD surface chemistry, these include, but are not limited to, *in situ* passivation during the synthesis of the QDs,^{40,42,43,54} using shorter ligands to replace native ligands that can also provide additional passivation or protection to QDs in films,^{97,188,189} or adding a second metal chalcogenide material to encapsulate the QD in a core-shell structure. Coreshell structures have been shown to reduce the number of surface traps in lead chalcogenide QDs, revealing improved PL in solution and resulting in improved V_{OC} in QD

devices.^{34,190} The apparently reduced defect density is presumably due to replacing atoms likely to have dangling bonds with a shell material that is less prone to forming inter-gap energy states (i.e., a type-I structure). The dual benefits of reduced dangling bonds and protection from oxygen make this strategy attractive. However, a wide-bandgap shell can limit the short-circuit current in a device by confining carriers within the core due to the band offset between the core and the shell.

A modified core-shell type approach that utilizes a thin layer of lead halide instead of a metal chalcogenide has been demonstrated computationally and experimentally to be beneficial. Calculations suggest that a thin PbI₂ layer surrounds PbSe QDs after iodide salt treatment, which passivates surface states and makes QDs oxidatively stable.¹⁹¹ Similar results have been reported for chloride salt treatments on PbSe QDs, leaving them more air stable and with higher PLQY yields than their all-organic capped counterparts.⁴⁰ These photophysical observations have translated to improved performance in recent QD devices, primarily through passivation protection from oxidation.¹⁰⁵ In fact, all recent record efficiency PbS QD devices have used some form of halide treatment during fabrication of the QD absorber layer.^{43,97,105,187} Protection from oxidation and the removal of intrinsic surface-related inter-gap defect levels are interconnected variables in most device studies with lead chalcogenide QDs, thus the microscopic origins of improved performance remain unclear. In fact a recent study of different iodide PbS QD treatments found that the defect density was always higher in iodide treated films compared to EDT treated films.¹⁹²

In addition to PL measurements, transient absorption (TA) spectroscopy is often used to characterize excited state lifetimes and elucidate recombination mechanisms. For isolated QDs, a model including quantum confined Auger recombination involving

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multiexcitons can successfully reproduce the TA data as a function of pump fluence.^{193,194} For coupled QDs, the same model can be employed and produces results that reasonably reproduce the data, but important parameters, such as the biexciton lifetime, change considerably and appear to depend on the film conductivity, calling into question the validity of the exciton model. Especially problematic would be the presence of separated charge carriers within the film.^{12,195} Moreover, the lifetime observed at low pump fluence, typically greater than 100 ns for uncoupled QDs, decreases significantly with increased QD coupling, further complicating the analysis. In many cases, there is a clear inverse relationship between the degree of QD coupling and the low fluence lifetime measured by time-resolved terahertz or TA. The shortened lifetime is further evidence for increased deleterious defect densities that exists after most ligand-exchanges that leads to trapassisted recombination hastened by a high charge-carrier or exciton mobility.^{196,197}

In order to analyze data sets that may span large ranges of temperatures, excitation densities, and unknown strengths of inter-QD coupling (and exciton binding energies), we begin with a general model that encompasses both bulk recombination of free-charge carriers and excitonic recombination. The model includes terms that are linear, quadratic, and cubic in the excited state population. The linear terms involve geminate electron-hole radiative or nonradiative recombination and trap-assisted nonradiative decay, (often via a Shockley-Read Hall (SRH) mechanism), with rate constants k_X^r , k_X^n , and k_A^n , respectively. The quadratic terms include nongeminate electron-hole radiative recombination (C_B^r) and exciton-exciton nonradiative (C_{XX}^n) recombination coefficients. The latter term is often associated with an Auger mechanism. The cubic term describes nonradiative Auger recombination of free carriers (C_A^n).¹⁹⁸ This model is expressed in Equation 4.1 as a change in excited state population density (N_t) vs. time. The superscripts on each rate constant/coefficient denote if it is radiative (r) or nonradiative (n).

$$N'_{t} = -(k^{n}_{A} + k^{r}_{X} + k^{n}_{X})N_{t} - (C^{r}_{B} + C^{n}_{XX})N^{2}_{t} - C^{n}_{A}N^{3}_{t}$$
(4.1)

Under conditions of strong QD coupling and low fluence, the linear term involving charges (k_A^n) dominates at room temperature. The other linear term involving excitons (k_X^r, k_X^n) are relevant only in weakly coupled films or at low temperatures where exciton dissociation is negligible. At higher excitation density, quadratic terms become important, with the C_B^r pathway commonly observed in high performing solar cells, including PbMAI₃ perovskite films.¹⁹⁹ We note that the nonradiative pathway involving bimolecular charge-carrier recombination is often seen in organic solar cells with low dielectric constant (i.e., via a Langevin or related mechanism).²⁰⁰ The quadratic term with coefficient C_{XX}^n is negligible at room temperature for systems with small exciton binding energy (i.e. most bulk inorganic semiconductors). For QDs in a film, the term is only relevant when the barrier to exciton dissociation is similar to or larger than k_BT . At even higher photon fluxes or in film regions where charges accumulate (i.e. at a junction under open circuit), the cubic Auger term can dominate, typically leading to fast and mobility dependent nonradiative decay.

With uncertainty about the degree to which each term in Equation 4.1 contributes, extracting the rate constants/coefficients from a direct time-resolved measurement can be challenging. However, by measuring steady-state PL intensity vs. incident excitation intensity (proportional to N_t), we can extract the mechanism of radiative recombination by determining the order of the kinetic process (i.e., linear or quadratic). We find that in cation-exchanged QD films the radiative recombination regime switches from linear to

quadratic with increased temperature and that PL is not strongly quenched. This is in stark contrast to conventionally synthesized PbS QDs of the same size that show greater than two orders of magnitude quenching above ~200 K.¹⁷⁸ In addition, TA analysis suggests that at very low fluence within the linear recombination regime the excited state lifetime is increased significantly (i.e., k_A^n is reduced) when the cation-exchange method is used to synthesize the QDs. Taken together, these observations imply that greatly improved surface passivation enables carriers to undergo many more phonon-assisted tunneling events without nonradiative decay, leading to the opportunity for radiative decay at room temperature and open circuit. This improvement should have a direct impact on V_{0C} as well as the maximum thickness of QD films that can be employed in order to capture a higher fraction of available solar flux.

4.III Results and Discussion

In Figure 4.1 are shown PL spectra of 3 nm diameter PbS QDs synthesized by cation exchange from CdS QDs, with a first exciton at 930 nm (~1.3 eV), cast into a film on a sapphire substrate using dip-coating with 1,2-ethanedithiol (EDT) to replace the native oleic acid (OA) ligands. The room temperature Stokes shift of 0.15 eV is typical for small PbS QDs when fast energy transfer within the distribution competes with PL.^{179,201} The inset highlights the peak PL energy as a function of temperature, showing an initial red shift, then a strong blue shift as the temperature increases.



Figure 4.1 Temperature dependent photoluminescence. PL of 3 nm diameter PbS QDs synthesized by cation exchange, cast into a film using EDT. Dashed line is the room temperature absorption spectrum. Inset: PL peak position vs. temperature.

The initial red-shift of the PL peak energy as the temperature is raised is indicative of band-tail behavior,^{178,202,203} while the general blue-shift is consistent with previous literature which shows an increase in bandgap with increased temperature.¹⁷⁸ More notably, the EDT-treated PbS QDs made by cation exchange show significant emission at room temperature. Strong emission at room temperature is also observed in uncoupled QDs, such as QDs capped with OA or long-chain thiol ligands, because the excitons are not dissociated regardless of the temperature,¹⁷⁹ and intra-QD excitonic radiative recombination is competitive with nonradiative recombination. However, coupled PbS QD films have previously shown 2-3 orders of magnitude of quenching at room temperature compared with ~20 K. This is thought to be due to deep trap states on the surfaces of QDs, which charge carriers readily find when they are able to sample a large number of QDs during hopping transport through the film. The reasonably strong room temperature emission of these cation-exchanged QD films suggests that the trap state density normally responsible for quenching emission has significantly decreased.



Figure 4.2: FTIR spectra of neat QD films and EDT treated films. In **(a)** the film was deposited by drop casting and the same film was measured again after an EDT soak. In **(b)**, a film of OA capped QDs was deposited, then an EDT film was made by dipcoating. Using the absorbance at the first exciton, the FTIR data were normalized to make a direct comparison.

In order to prove that the QD films are not composed of isolated QDs, Fourier transform infrared spectroscopy (FTIR) measurements were performed to demonstrate a complete ligand exchange. FTIR spectra show complete removal of the OA peaks (Figure 4.2) to within the instrument sensitivity. Field-effect transistors (FET) were fabricated in order to further demonstrate strong electronic coupling in the films. Current-voltage scans (Figure 4.3) reveal an n-type film with a mobility of 3.8×10^{-3} cm²/Vs, which is higher than typical mobility values observed for conventional PbS QDs of this size treated only with short-chain organic molecules (~ $1-2 \times 10^{-3}$ cm²/Vs).^{43,45,204} FETs are majority carrier devices and generally should be insensitive to the presence of intra-gap states because the high gate bias quickly fills those states and thus should not contribute to the FET measurement, but shallow defects would impact the mobility. The improvements in the FET mobility and

the improved PL at room temperature suggest that the cation exchanged QDs have less mid-gap deep defects and fewer shallow defects. The n-type behavior suggests that the normally anion-rich EDT-capped PbS¹⁸¹ surface has become more stoichiometric or slightly cation-rich. This may be due to residual Cd²⁺ from the cation exchange process binding to surface sulfur sites.¹⁵⁰ Chloride ions may also be adding electron density to the lattice if they replace surface sulfur.^{43,46} Furthermore, a lower EDT packing density due to fewer available Pb²⁺ binding sites may reduce the density of thiolate groups at the surface that might otherwise lead to p-type behavior. The chemistry of the surface, including the locations and densities of Cl⁻ and Cd²⁺, is not fully understood and requires further theoretical and experimental studies.



Figure 4.3: Output and transfer characteristics of PbS_{Cds} **QD FETs.** FET measurements of 3.0 nm cation-exchanged PbS QDs treated with EDT. (a) Output characteristics showing n-type response. (b) Transfer characteristics shown along with the fits for the source-drain voltages that fall below the saturation voltage. The fits shown in red are used to calculate the mobility (see Appendix A1). (c) Transfer characteristics with the square-root of current vs voltage. The fits are shown in red for source-drain voltages above the saturation voltage and used to calculate mobility.

Table 4.1: FET mobility for PbS_{cds} **QDs with EDT.** The mobility is extracted from the fits for each source-drain voltage shown in Figure 4.3. The saturation voltage was estimated to be \sim 15 V, from Figure 4.3a. The mobility from the 15 V transfer curve is calculated in both the linear and saturated regimes because the switch between the two regimes is not exact.

V _{SD} (V)	5	10	15	15	20	25	30	Average
μ _n (cm²/Vs)	2.5*10 ⁻³	3.9*10 ⁻³	5.1*10 ⁻³	2.1*10 ⁻³	3.9*10 ⁻³	4.1*10 ⁻³	5.3*10 ⁻³	3.8*10 ⁻³

In Figure 4.4 the integrated PL across the relevant spectral region (~0.8-1.4 eV) is plotted on a log-log scale as a function of incident laser power. In all cases, the power is kept far below the threshold for multiphoton absorption in a single QD ($\langle N_{abs} \rangle \langle \langle 1 \rangle$). The black squares show data for uncoupled QDs at room temperature, revealing a slope of 0.95. A slope near one is indicative of geminate recombination of the initially created electronhole pair. At low temperature (blue circles), the slope for a coupled QD film is also ~1 due to excitonic recombination resulting from minimal thermal energy available for exciton dissociation. At room temperature (red squares), however, the slope changes to 1.9, indicating that nongeminate bimolecular recombination of free charges, the second term in Equation 4.1, is now dominating the radiative decay.



Figure 4.4 Power dependence of the PL intensity. Integrated PL intensity vs. incident laser power and calculated intensity at 514 nm for a film of OA-capped PbS QDs at room temperature and the same QDs after exchange of OA with EDT at two different temperatures.

Figure 4.5 displays the integrated PL intensity over the entire relevant spectral range vs. temperature for two samples, conventional PbS QDs and cation exchanged PbS QDs, both subsequently ligand-exchanged with EDT. The notable differences between the two curves are the slopes of PL quenching at intermediate temperatures and the strength of persistent emission as room temperature is approached. We note that there are no substantial differences in overall PLQY or temperature dependence for isolated QDs made by the different synthetic methods (data not shown). The first term in Equation 4.2 is the previously developed model of PL quenching, derived by Zhang et al ¹⁷⁹. This term expresses the kinetic competition between excitonic radiative decay and exciton dissociation leading to PL quenching. We note that exciton dissociation by itself is not a decay mechanism (and thus does not appear in Equation 4.1), but is a potential mechanism for PL quenching in the presence of defects, thus justifying its presence in Equation 4.2. The

model fits the conventional PbS QD PL vs. temperature well, but deviates from the cationexchanged QD PL considerably. The second term in Equation 4.2 is an additional pathway to radiative recombination for free charge-carriers that were born from exciton dissociation via the first term.

$$\Phi_{PL}(T,N) = \frac{k_X^r}{k_X^r + k_{CT}(T) + k_X^n} + \Phi_{PL}^{bi}(N) \frac{k_{CT}(T)}{k_X^r + k_{CT}(T) + k_X^n}$$
(4.2),

where $k_{CT}(T)$ is the exciton dissociation rate constant, expressed in Equation 4.3. We previously confirmed that the exciton dissociation rate constant can be equated with the temperature-dependent hopping rate constant used in dark transport measurements, thus the form follows as:

$$k_{CT}(T) = \alpha \exp\left(-\left(\frac{T*}{T}\right)^{\nu}\right)$$
(4.3),

where α is the attempt frequency, T^* is the characteristic temperature, and the exponent ν is related to the transport regime.⁴¹ Here, for simplicity we have assumed $\nu = 1$, which represents nearest-neighbor hopping.

The bimolecular recombination yield (Φ_{PL}^{bi}) as a function of carrier density *N* is given by:

$$\Phi_{PL}^{bi}(N) = \frac{c_B^r}{c_B^r + k_A/_N + N c_A^n}$$
(4.4),

which expresses the competition between rates of radiative bimolecular decay, $C_B^r N^2$, vs. the sum of the rates of relevant processes ($C_B^r N^2$ itself, unimolecular trapping, k_A , and Auger decay, $C_A^n N^3$).

Using Equation 4.2 to fit the data for cation-exchanged QDs, we find that the bimolecular recombination term is non-zero since the PL does not strongly quench at high temperature. The non-zero value for bimolecular recombination shows that carriers are

able to recombine with each other radiatively before being trapped and non-radiatively decaying. We note that the term Φ_{PL}^{bi} is excitation power dependent as expected (Figure 4.5 inset), following a roughly quadratic dependence at low fluence before exhibiting saturation at high fluence due to the influence of higher-order nonradiative recombination (e.g., Auger decay).

In previous work on conventional PbS QDs we have demonstrated that higher mobility, correlated with higher α via the Einstein-Smoluchowski relation ($\mu = (e/2kT)d^2 \alpha$), leads to faster trap-assisted nonradiative recombination.¹⁷⁹ However, we have shown here that both the mobility and room temperature PLQY of the cation-exchanged films are higher than those of the conventional QD films, thus invalidating the previously established inverse relationship between those quantities. From the relationship between α and μ , one might expect higher α for cation-exchanged films; however, the opposite is true, as a tends to be smaller than for conventional QDs ($\sim 10^8 \text{ s}^{-1}$ to $\sim 10^9 \text{ s}^{-1}$) despite the fact that the inter-OD distance d should be identical. This likely reflects the fact that the films of cationexchanged QDs are n-type instead of p-type, and thus the mobilities of holes, being the minority carriers, are probed. Hole mobilities tend to be roughly an order of magnitude smaller than electron mobilities for QDs of this size.²⁰⁵ Because the parameters a and Φ_{PL}^{bi} have a similar effect on the shape of the quenching curves (higher Φ_{PL}^{bi} mimics lower a), their influences are difficult to separate from each other. For this reason, a is held fixed for determination of Φ_{PL}^{bi} vs. power. More complex behavior may not be captured by the temperature-dependent PL data and thus other experiments are necessary to elucidate the full dynamical picture.



Figure 4.5 Temperature dependent PL intensity. Integrated PL as a function of temperature for conventional PbS QDs (\blacksquare) and for cation-exchanged PbS QDs (\bullet). Inset: Log-Log plot of the power dependence of Φ_{PL}^{bi} .

The transient absorption curves shown in Figure 4.6 were collected at various excitation densities; calculated $\langle N_{abs} \rangle$ values are shown at the right of the figure, where $\langle N_{abs} \rangle$ is calculated from the measured pump fluence and the absorption cross section.¹⁹⁵ A trace at similarly low $\langle N_{abs} \rangle$ values is shown for an EDT-treated PbS QD film of a similar size but made by conventional synthesis (dashed curve). At the lowest excitation densities (black curves), only terms linear in the photoexcited carrier density contribute to the decay, and thus the nonradiative trap-assisted recombination term, involving k_A^n , dominates. The rate constant is at least one order of magnitude smaller for the cation-exchanged QDs with PbCl₂ than with conventional QDs, which further underscores the reduction in deleterious trapping that occurs in the cation-exchanged QDs. We attempted to simultaneously fit the series of power dependent decay curves to a model of either

quantum-confined Auger decay, free-carrier/bulk-like Auger decay, or a generic model including linear, quadratic, and cubic decay terms. None of these models fitted the full data set satisfactorily, although the bulk Auger decay model was a reasonable fit through most excitation densities. Inclusion of the quadratic term improved the fit slightly, but given our prior estimate of the yield of bimolecular decay (at most a few percent), it is not surprising that the fit was not greatly improved. Further investigation of the appropriate kinetic scheme for this situation is ongoing.

The TA measurements further reveal that the onset of a power dependent sub-ns decay occurs well below the $\langle N_{abs} \rangle = 1$ value. This is also observed in the steady-state PL power dependence, where saturation of the quadratic behavior occurs at excitation intensities of about 200 mW/cm², higher than solar intensities but far below the regime of multiple photon absorption per QD. This is likely due to diffusion assisted Auger recombination of charge-carriers, similar to that proposed by Gao, *et al.*²⁰⁶ and reported in several investigations of coupled QD film dynamics.^{195,196}



Figure 4.6 Transient absorption for cation exchanged PbS QDs. Transient absorption at the peak of the lowest exciton bleach signal (~930 nm) for various excitation powers at 800 nm for a cation-exchanged PbS QD film. The calculated average exciton occupancy is shown

at right. The dashed curve shows the bleach recovery for low excitation intensity of a film of conventional PbS QDs, also at 930 nm.

The connection between V_{OC} and radiative recombination of free carriers is expressed in Equation 4.5:

$$qV_{OC} = qV_{OC-Ideal} - kT |\ln \eta_{ext}|$$
(4.5),

where *q* is the elementary charge, *V*_{OC} is the open-circuit voltage, *V*_{OC-Ideal} is the theoretical V_{OC} , k is Boltzmann's constant, T is the temperature, and η_{ext} is the external luminescence efficiency.¹⁸³ The V_{0C} loss for conventionally synthesized PbS QDs would expected to be > 0.25 V since η_{ext} is < 10⁻⁴. For cation-exchanged PbS QDs, the bimolecular recombination efficiency was found to be as high as ~0.02, but at solar intensities it is ~0.005. (This PLQY is still very low compared to QDs in solution due to the QDs being electronically coupled. As discussed in Zhang, et al.¹⁷⁹ the amount of coupling can be directly related to the PLQY quenching at room temperature, so the PLQY is generally low for coupled films. Even with a low PLQY from the QD array the important point of this study is that room-temperature PLQY from a coupled QD film has not been high enough to be measured until now.) Using η_{ext} = 0.005, the V_{0C} loss, from equation 5, is around 0.14 V, or at least 0.1 V smaller than with conventional QDs. It should be pointed out that this is the minimum loss because η_{ext} is defined as only PL exiting from the front of the solar cell, which is inevitably lower than the η_{int} measured here by reference to absolute PLQY measurements. Whereas other loss mechanisms contribute to the ~0.5 V V_{OC} deficit now commonly measured for QD solar cells, the clear observation of bimolecular radiative recombination signifies the approach of the regime achieved by other high-performing solar cells for which PL at open circuit is an important metric. In Table 4.2 the performance parameters for devices fabricated from the traditional synthesis and the cation exchange are shown. The V_{OC} is the main difference

between the two devices, with the J_{SC} being very similar. This illustrates the impact that trap states have on the V_{OC} in photovoltaic devices.

Table 4.2: Comparison of photovoltaic performance for PbS_{Pb0} and PbS_{CdS} QD devices.

	Voc (mV)	Jsc (mA/cm ²)	FF (%)	Eff (%)
PbS _{Pb0}	465	26	55	6.4
PbS _{cds}	509	26	63	8.4

4.IV Methods

4.IV.a Reagents

See Chapter 2: for a full list of reagents used in the following methods. Chapter 2:

4.IV.b PbS QD Synthesis

The cation exchange of CdS to PbS QDs is described in detail in Chapter 2:. See Section 2.VII.c for the synthesis of CdS QDs and Section 2.VII.e for the cation exchange to produce PbS QDs.

4.IV.c Film Fabrication

Films for PL and TA experiments were deposited on sapphire substrates by dipcoating with the QD in hexane solution and 1 mM EDT in acetonitrile. See Section 2.V.d for a detailed description of the dip coating technique. This process was repeated 20-30 times in order to build up an optically dense film with an OD ~0.1-0.2 at the lowest energy exciton peak.

4.IV.d Transient Absorption

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Pump-probe data were collected using a femtosecond transient absorption spectrometer (Helios, Ultrafast Systems). The laser source was a 4 W Ti-sapphire amplifier (Libra, Coherent), operating at 1 kHz and 100 fs pulse width. The fundamental beam at 800 nm was split, and a small portion (<5 mW) was used to generate the near-infrared continuum (800 – 1700 nm) in a 1 cm thick sapphire rod. Another portion was attenuated with neutral density filters and used as the excitation source after being modulated at 500 Hz. The spot size was approximately 1 mm and 300 mm for the pump and probe beams, respectively. The probe beam was split equally and directed to two different InGaAs array detectors. The portion that did not traverse the sample was used to cancel out laser fluctuations while the beam sent through the sample was collected and binned as either "pump on" or "pump off", depending on the timing with respect to the 500 Hz excitation beam. The time delay was varied with an exponential distribution of time points out to 5 ns and averaged for 1 sec at each delay. Between two and ten scans were subsequently averaged. Fitting was performed in Igor Pro using a variety of kinetic schemes. The calculated $\langle N_{abs} \rangle$ values are determined from the pump fluence, the absorption crosssection at 800 nm, and the measured spot size.

4.IV.e Temperature Dependent Photoluminescence

For temperature dependent PL experiments, the films were mounted in a closed loop He flow cryostat (18 K – 325 K) fitted with sapphire windows that was evacuated to 1 × 10⁻⁴ Torr. The sample was cooled to 18 K and then heated slowly in 20 K steps, with an equilibration time of 10 minutes at each temperature. Collecting PL spectra during cooling instead of heating produced the same results. The 514 nm line of an Ar-ion laser was used to excite the sample, with a beam size of approximately 2.5 mm and power varying from

0.5 to 150 mW. Each spectrum required roughly one minute of exposure time. The excitation beam was modulated at 500 Hz, and the sample emission was routed through a monochromator with a 300 groove/mm grating blazed at 1250 nm. A dual, balanced Ge photodiode was used in concert with a lock-in amplifier to detect the signal. The spectral sensitivity of the entire system was determined with a calibrated tungsten lamp, and PL spectra were corrected accordingly.

4.V Conclusion

In conclusion, we have found cation-exchanged PbS QDs to possess a much smaller deleterious trap state density than traditionally synthesized PbS QDs. This allows coupled films of PbS QDs to emit fairly strongly (PLQY ~ 1%) at room temperature through bimolecular charge-carrier recombination, previously not seen in PbS QD films. The presence of halide and residual Cd²⁺ ions during the cation exchange process may result in improved surface defect passivation. Improving the external luminescence efficiency will increase the *V*_{oc} in devices made from PbS QD films, which has been one of the major limiting factors to increasing the efficiency in QD solar cells. Combining cation-exchanged QDs with additional surface treatments under development should lead to even better luminescence efficiency at open circuit and more efficient QD solar cells. Such PL measurements should be used as a metric for the development of new surface treatments with the caveat that the PL should scale with the light intensity as shown in Figure 4.4.

While this chapter has focused on the PbS QDs produced from the cation exchange synthesis, Chapter 5 will shift focus to PbSe QDs; their increased air-stability and the ability to produce high efficiency photovoltaic devices. Chapter 5 also explores the question of

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how the starting material impacts the cation exchange reaction and provides insight into the mechanism of cation exchange in the QDs.

Chapter 5: Air Stable and Efficient PbSe Quantum Dot Solar Cells based on ZnSe to PbSe Cation-Exchanged Quantum Dots

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5.I Abstract

We developed a cation-exchange reaction that produces air stable PbSe QDs from ZnSe QDs and PbX₂ (X=Cl, Br, or I) precursors. The resulting PbSe QDs are terminated with halide anions and contain residual Zn cations. We characterized the PbSe QDs using UV-Vis-NIR absorption, photoluminescence quantum yield spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and transmission electron microscopy. Solar cells fabricated from these PbSe QDs obtained an overall best power conversion efficiency of 6.5 % at one sun illumination. The solar cell performance without encapsulation remains unchanged for over 384 days in ambient conditions, and after 50 days the device was certified at 5.9 %.

5.II Introduction

Colloidal quantum dots (QDs) are being investigated due to their beneficial optical and electrical properties, such as band gap tunability, strong absorption over a broad wavelength range, intrinsically large dipole moments, good photo-stability, and multiple exciton generation (MEG).^{13,18,20} To exploit these desirable properties, researchers are exploring the use of QDs in various applications such as solar cells, light-emitting diodes (LEDs),^{207,208} bio-imaging,²⁰⁹ and field effect transistors (FETs).²¹⁰ QD based solar energy conversion strategies are attracting considerable interest because solar energy is renewable, eco-friendly, and sustainable. The main factors that determine the efficiency of QD based solar cells include an optimized solar cell device structure and improved interfacial contact between the QD and charge separating layers. Research efforts have improved the transport characteristics of the *n*-type window layer (e.g. TiO_2 , ZnO, CdS) and *p*-type PbE (E = S or Se) QDs.^{96,211} Specifically PbSe QD solar cells are attractive because of their potential to exceed the Shockley-Queisser limit and approach the Ross-Nozik limit via MEG.^{1,3} For example, Semonin *et al.* fabricated a QD solar cell with a peak external quantum efficiency (EQE) of more than 100% using PbSe QDs.¹⁰ However, performance of PbSe QD based solar cells tends to quickly degrade upon exposure to air due to oxidation of the photoactive QD layers. Optical shifts observed in steady-state absorption and photoluminescence (PL) suggest that surface oxidation induces important changes in the electronic structure of the QDs related to the reduction in their diameter.^{212–214} Improving the stability of QD systems is an important task that should enable a greater degree of reproducibility and uniformity.

Strategies to enhance the optical and electrical properties as well as improve the physical, chemical, and photo-stability of PbSe QDs have been developed including PbSe/CdSe²¹⁵ and PbSe/PbS²¹⁶ core/shell structures as well as PbS_xSe_{1-x}²¹⁷ alloy structures. Although core/shell structures improve the air stability, the electrical transport in films made from core/shell QDs can be impeded by the localization of one or both charge carriers in the core, rendering subsequently fabricated charge separation architectures useless. Therefore, surface treatments that result in stable QDs without impeding charge

transport have gained interest in the literature. As a result, several robust methods for improving the stability of QDs *via* surface treatments have been developed. Halide treated PbS QDs have shown promise in improving solar cell^{39,97} performance and similar halide terminated PbSe QDs follow similar trends.^{38,40} Bae *et al.* improved the air stability of PbSe QDs by employing chlorine gas and hypothesized that a surface passivation layer of PbCl_x forms to protect the PbSe core.⁴⁶ Woo *et al.* developed an NH₄X surface treatment and hypothesized that the improved stability results from the formation of a PbX₂ (X = Cl, Br, or I) passivation layer that protects the {100} facets.¹⁹¹ Zhang *et al.* studied the use of Pbhalide precursors in a direct heat-up synthesis of PbE QDs and found improved air stability of the halide terminated QDs.⁴⁰

Another approach to synthesizing air stable PbSe QDs is through a cation-exchange reaction.³⁸ Cation-exchange reactions are an increasingly popular approach to synthesizing QDs because morphologically well-defined nanocrystals, prepared by traditional hot injection methods, can be used as an anion template for the preparation of compositionally pure and alloyed nanocrystal structures. Some of these are otherwise inaccessible by direct synthetic methods.²¹⁸ Additionally, there is evidence that residual metal ions present during the reaction can effectively passivate deleterious defect states leading to improved performance.²¹⁹ Such improvements from metal cations have been explored experimentally⁴³ and theoretically.¹⁶⁵ We found evidence that improvements in QD solar cell performance is likely a combination of both halide and metal passivation.³⁸ Accordingly, cadmium and halide treated PbSe QDs have been developed for QD photovoltaics. Zhang, *et al.* developed a cation-exchange reaction starting from presynthesized CdSe QDs to produce PbSe QDs and found that PbSe QD solar cells with ~6%

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power conversion efficiency could be fabricated in ambient conditions. However, those solar cells degraded from 6 % to 4 % in a few days when stored in air making further improvements necessary. Therefore, we extend the cation-exchange reaction developed by Zhang, *et al.* to ZnSe as the starting QD material to synthesize air stable, PbSe QDs.³⁸



Figure 5.1 Diagram of PbSe_{ZnSe} **QDs.** A schematic illustration of the QDs resulting from the cation-exchange reaction by the Pb-halide precursor and ZnSe QDs.

5.III Results and Discussion

We developed a cation exchange procedure that produces PbSe from ZnSe QDs (denoted PbSe_{ZnSe}). Pre-synthesized ZnSe QDs and PbX₂ (X = Cl, Br, or I) are the precursors for size-tunable, air-stable PbSe QDs with both halide anion and zinc cation passivation. The cation exchange reaction is depicted in Figure 5.1, which is similar to the methodology reported by Zhang, *et al.*³⁸ First, ZnSe QDs are synthesized following previous reports,²²⁰ using diethyl-zinc (Et₂Zn) and tri-*n*-octylphosphine selenide (TOP-Se) as zinc and selenium precursors. The resulting ZnSe QDs have a 1st exciton peak at 3.3 eV (Figure 5.2c) that, according to literature reports, corresponds to a diameter of ~3.3 nm (shown as the shaded region in Figure 5.2c.^{221,222} The cation exchange reaction is described in the

Methods section below. Briefly, ZnSe QDs dispersed in ODE are injected into a complex of PbX₂ with oleylamine (OLAm) at temperatures ranging from 80-200 °C. The reaction is allowed to procede for 1-30 minutes and then cooled to room temperature; oleic acid (OA) is injected into the final solution to both exchange the native OLAm ligands and to help remove the QDs from residual PbX₂/OLAm. The absorption spectra of the PbSe QDs are shown in Figure 5.2a for a variety of growth times.



Figure 5.2 Absorption spectra and size tracking for PbSe and ZnSe QDs. (a) Evolution of absorption spectra of PbSe QDs exchanged from ZnSe in a PbI₂/OLAm heterogeneous solution at different injection temperatures. **(b)** The diameter of the resulting PbSe QD domain as calculated from standard sizing curves. The colored markers correspond with the temperatures used in (a). **(c)** Absorption spectrum of precursor ZnSe QDs.

After injection of the ZnSe QDs, the cation exchange occurs rapidly as evidenced by the appearance of a sharp 1st exciton peak in the near-IR (Figure 5.2a, bold traces) and the transformation of the XRD peaks from those corresponding to ZnSe (Figure 5.3, black trace) to those of PbSe (Figure 5.3, red trace). If the reaction is allowed to proceed, the PbSe QDs continue to grow (Figure 5.2a, shaded traces). Higher injection temperatures result in larger diameter PbSe QDs and induce a faster subsequent growth phase. The diameter of

the PbSe QDs (Figure 5.2b) can be tuned over a broad range (~1.8 nm to ~7 nm). However, when the size of the PbSe QDs is calculated based upon the 1st exciton peak and standard sizing curves,²²³ we find that the product diameter is smaller than the precursor ZnSe diameter when the injection temperature is less than 150-160°C (Figure 5.2 shaded box compared to circles). These observations indicate that the cation exchange reaction is thermally activated. Cation-exchange reactions have been described in terms of a temperature-dependent, reaction-zone width.³¹ For complete cation exchange, the reaction-zone width should be larger than the precursor QDs. Our results suggest that the zone width is larger than ~3 nm only when the injection temperature is >150 °C.



Figure 5.3 XRD of ZnSe and PbSe QDs. XRD patterns of ZnSe QDs (black trace) and cation exchanged PbSe QDs (red line). The standard for zinc blende (black sticks) and rock salt (red sticks) are shown with the corresponding XRD pattern.

For injection temperatures less than 150° C partial exchange occurs and there are two possible reaction pathways that are consistent with our results: (1) after partial cation exchange, the PbSe component continues to grow at the interface of the ZnSe/PbSe, analogous to what was observed in the PbS_{CdS} reaction³⁶ and/or (2) the partial cation exchange is accompanied by dissolution of the remaining ZnSe component.²²⁴ We find that the size distribution of the PbSe QDs changes with injection temperature and growth time. The size distribution improves at higher temperatures and larger product sizes. Once the temperature is high enough to achieve complete exchange, the size distribution of the ZnSe QDs is preserved. As growth continues, the particle size distribution increases due to Ostwald ripening (size-defocusing regime). The XRD patterns and TEM images (Figure 5.4) suggest a single phase of PbSe particles following injection of ZnSe QDs at 150°C. Also, the UV-Vis spectra do not exhibit high-energy features that could be assigned to residual ZnSe. This is in contrast to the partial cation exchange of CdS to PbS results, which do show features of the residual CdS in the TEM, XRD, and UV-Vis.³⁶ These observations suggest that after partial exchange residual ZnSe dissolves, leaving single phase PbSe QDs. We have not attempted to find reaction conditions that would preserve the partially exchanged nanostructures.



Figure 5.4 TEM and XRD of PbSe_{ZnSe} **QDs. (a)** TEM, and **(b)** HR-TEM images of cation exchanged PbSe QDs. **(c)** XRD pattern of cation exchanged PbSe QDs. The red lines are the known positions for rock salt PbSe and blue lines are the known positions for zinc blende ZnSe, we see no residual ZnSe phase after the exchange.

These observations are consistent with that found in the direct synthesis of PbE QDs from PbX₂/OLAm heterogeneous mixtures.⁴⁰ In that reaction, PbE QD growth is governed by diffusion of monomers in a viscous heterogeneous reaction bath. The viscosity increases from PbI₂ to PbCl₂, which results in faster diffusion in the PbI₂ mixture, causing the growth to approach the reaction-controlled regime and the size-distribution to defocus. Here the

size-defocusing regime is reached only when the reaction is allowed to proceed well beyond the initial cation exchange step.

In contrast to both the diffusion controlled direct synthesis of PbS and PbSe and the cation exchange from CdSe/CdS, the PbSe_{ZnSe} QDs described here enable the production of PbSe QDs with Cl, Br, or I termination while retaining good size distributions. We compared the stability of the PbSe QDs when employing various PbX₂ precursors by storing the product QDs in tetrachloroethylene (TCE) under ambient conditions for 50 days and monitoring the absorbance. The degree of hypsochromic shift of the first exciton feature monitored by UV-Vis (Figure 5.5a) is an indicator of the degree of oxidation, which varies as PbCl₂ > PbBr₂ > PbI₂. We rationalize this trend by considering the hard and soft Lewis acid and base theory (HSAB). Pb²⁺ is a borderline acid; iodide is a soft base; bromide is a borderline base and chloride is a hard base. This suggests that iodide and bromide would have improved coordination of surface bound Pb²⁺ ions compared to chloride, which could help explain the increased effectiveness of iodide and bromide at protecting the surface compared to chloride.



Figure 5.5 Stability of various PbSe QD syntheses in air. (a) Stability comparison of PbSe QDs cation exchanged from ZnSe using PbX_2 (X = I, Br or Cl) with an injection temperature 150°C. **(b)** Stability comparison of PbSe QDs synthesized from four reaction protocols.

We also compared the stability of PbSe QDs synthesized from different formulations by preparing PbSe QDs with a first exciton peak at ~1550 nm from four different reaction protocols; (1) standard PbO synthesis²⁸ (PbSe_{PbO}); (2) PbSe synthesized directly using the PbCl₂/OLAm diffusion based synthesis⁴⁰ (PbSe_{PbCl₂}); (3) PbSe cation exchanged from CdSe in PbCl₂ (PbSe_{CdSe});¹⁶⁵ and (4) the cation exchange from ZnSe/PbI₂ presented here (PbSe_{ZnSe}). We stored the samples in TCE under ambient conditions, and compared their absorbance spectra. The position of the first exciton peak was recorded every 10 days for 50 days and the results are shown in Figure 5.5b. All of the QDs terminated with a halide show better stability than the PbO synthesized QDs that are terminated solely by oleate ligands. While the difference is not large, there does appear to be an advantage to the cation exchanged QDs that have both halide termination and some residual metal cations (Cd, Zn).



Figure 5.6 XPS analysis of PbSe_{znSe} **QDs.** HR-XPS spectra of ZnSe/PbI₂ synthesized PbSe QDs when injection temperature 150°C (**a**) Pb 4f spectral region (**b**) Se 3d spectral region (**c**) I 3d spectral region (**d**) Zn 2p spectral region.

We focused all subsequent experiments on the ZnSe/PbI₂ synthesized PbSe QDs. Residual zinc and iodide from the exchange reaction is observed in high-resolution x-ray photoelectron spectroscopy (XPS) (Figure 5.6). We observe a shift of both the Pb 4f peak (Figure 4a) and Se 3d peaks to higher binding energies relative to PbO synthesized QDs suggesting a Pb-I terminated QDs.³⁹ Such shifts are consistent with our study of PbS QDs that had been treated with NH₄I⁵⁸ (where no Zn is present) and a study where PbSe QDs had been treated by NH₄Cl.¹⁹¹ The detection of I and Zn spectral features (Figure 5.6c and d, respectively) confirms that Zn and I are present in the PbSe QD films. For 2.8 nm diameter PbSe QDs we find the ratio of Pb/Se to be 2.4, Pb/I to be 3 and Pb/Zn to be 27. From the combination of these XPS elemental ratios and the XRD it is reasonable to conclude that iodide anions partially terminate the QDs along with oleate ligands. While the precise location of the Zn cations cannot be deduced by the experiments conducted here, it is likely that they also reside near the surface, as observed in other reports.³⁸



Figure 5.7 Device characterization for PbSe_{ZnSe} **QD solar cells. (a)** Schematic illustration of the photovoltaic device structure. **(b)** Cross-sectional SEM (scanning electron microscopy) image of a completed device, with false color added for clarity. **(c)** EQE (external quantum efficiency) spectrum and **(d)** JV curve of a high efficiency device made from PbSe_{ZnSe} QDs with PbI₂ and MPA ligands.

QD solar cells were fabricated from PbSe QDs (963 nm first exciton peak), following a metal halide solid-state fabrication procedure.³⁹ First, a film of QDs is deposited on the n-

type window layer (TiO₂) by dip-coating using PbI₂ in *N*,*N*-dimethylformamide (DMF) to remove the native oleate ligands. A thinner PbSe QD layer is deposited on the back using 3mercaptoproprionic acid (MPA) in methanol (MeOH). The full device structure (Figure 5.7 a and b) consists of FTO/TiO₂/PbSe_{PbI₂}/PbSe_{MPA}/Au (details provided in experimental section). The total thickness of the QD photoactive layer is *ca*. 200 nm (Figure 5.7b, SEM analysis). We hypothesize that the PbSe_{MPA} treatment acts as an electron blocking layer, thereby reducing interfacial recombination at the PbSe QD/Au interface. Chuang *et al.* reported a similar approach using TBAI and 1,2-ethanedithiol (EDT) ligands to produce a PbS_{TBAI}/PbS_{EDT}⁹⁷ bilayer device. Semonin *et al.* also employed two ligands, EDT and hydrazine (Hy), to produce a PbSe QD bilayer (PbSe_{EDT}/PbSe_{Hy}) device.¹⁰

The external quantum efficiency (EQE) (Figure 5.7c) is close to 80% throughout the visible region and ~30% at the 1S absorption feature at 980 nm. To characterize the device, we measured the photocurrent density-voltage (JV) curves under AM1.5 illumination in an inert atmosphere (Figure 5.7d). The best cell exhibited a power conversion efficiency (PCE) of 6.5 %, with an open circuit voltage (V_{oc}) of 528 mV, a short circuit current density (J_{sc}) of 24 mA/cm², and a fill factor (*FF*) of 50.6 %. Similar to Semonin *et al.*, we find that the device efficiency improves after 1-4 days.¹⁰ We stored the solar cell in air without any encapsulation for one year, while tracking the device performance (Figure 5.8), and find that the device performance is stable for 384 days. After 50 days of storage in air, the cell was certified by the NREL certification team and achieved a 5.9 % PCE (Appendix A2). This is the first certification of a PbSe QD solar cell.



Figure 5.8 Stability of PbSe_{ZnSe} **QD solar cell in air.** Long-term stability measurement of PbSe_{ZnSe} QD device performance, stored in air without encapsulation. Blue markers show the average PCE and the error bars show the standard deviation across the device pixels. The red star is the externally-verified efficiency from the NREL certification team.

We postulate that I⁻ ions from the cation exchange reaction are responsible for the stability exhibited by devices made from the PbSe_{ZnSe} QDs. Halide ions greatly improve the air stability of PbSe QDs, rendering the surface resistant to oxidation.^{38,40,46} Figure 5.5b clearly shows that synthetic routes for PbSe QDs utilizing halide precursors result in air stable QDs, also the XPS data discussed above shows a very low Zn content, while I ions are much more prevalent. Residual iodide ions from the cation exchange reaction, along with the iodide from the ligand exchange, fully passivate and protect the PbSe QD surface, so that device fabrication and storage in air does not affect the QD film. Looking at Figure 5.5b, the PbSe_{PbCI2} QDs show similar air stability to the cation exchanged QDs. Residual Zn²⁺ ions may passivate other surface states, contributing to better device efficiency, but do not play a large role in improving the air stability.

5.IV Methods

5.IV.a Reagents

Lead Iodide (PbI₂), Lead Chloride (PbCl₂), Lead Bromide (PbBr₂) (99.999%), Oleylamine (OLAm, tech. grade, 70 %), Oleic acid (OA, tech. grade, 90 %), Diethyl-Zinc (Et₂Zn, 0.5 M in toluene), 1-Octadencene (ODE, tech. grade, 90 %), Selenium powder (99.99 %), Tri-*n*-octylphosphine (TOP, tech. grade, 90 %), Trioctylphosphine oxide (TOPO, tech. grade, 90 %), 3-Mercaptoproprionic acid (MPA, > 99 %), Tetrachloroethylene (TCE, > 99.9 %), Hexane (95 %), and Ethanol (> 99.5 %) were purchased from Sigma Aldrich and used without further purification.

5.IV.b ZnSe QD Synthesis

ZnSe QDs were synthesized using the methodology reported by Kim *et al.*²²⁰ For a typical reaction, HDA (1.449 g, 6 mmol) and TOPO (9.3 g, 24 mmol) were heated to 125°C and degassed under vacuum for 2 hours in a three neck flask. The solution was then heated to 320 °C under N₂ atmosphere. In order to make the injection solution, Et₂Zn (1.2 mmol) and 1.2 mL of 1 M TOP-Se stock solution were mixed in 3 mL of TOP in a glove box. The injection solution was rapidly added to the three-neck flask at 320 °C. The solution was maintained at 270°C for 1 hr, then cooled to room temperature. The resulting ZnSe QDs were isolated by precipitation with ethanol and subsequently re-dispersed into ODE.

5.IV.c ZnSe to PbSe Cation Exchange

The cation-exchanged PbSe QDs were synthesized using a modified procedure similar to that reported in Zhang *et al.*³⁸ and described in Section 2.VII.e. OLAm (10 mL)

and PbI₂ (1.2 mmol) were heated to 140 °C and kept under vacuum for 1 hr to degas and remove water. The mixture was then cooled or heated under N₂ atmosphere to reach the desired reaction temperature. ZnSe QDs (80 mg) in ODE were injected under N₂ and the reaction was maintained at temperature for 3-30 min and then cooled to 40 °C using a water bath. 8 mL of OA was added to the reaction solution and stirred for 20 min. The QDs were washed twice by precipitating with 40 mL of ethanol, centrifuging to remove the solids, and then re-dispersing in hexane. Table 5.1 summarizes the reaction temperature, growth time, and the resulting position of the first exciton peak in the absorption spectra for the PbSe_{ZnSe}. This table reflects the results presented in Figure 5.2a.

Table 5.1 Reaction conditions highlighting the size control of the cation exchange. The final growth time listed in the middle column results in the largest (longest wavelength first excitonic peak) QD diameter. In order to synthesize smaller particles the reaction must be quenched earlier.

Injection Temperature	Final Growth Time	First Exciton Position
(°C)	(min)	(nm)
80	30	850-1050
120	20	940-1180
150	10	980-1370
180	5	1250-1180
200	3	1420-1880

5.IV.d Characterization

Absorption spectra were measured by Shimadzu UV-Vis-NIR 3600 spectrophotometer. Photoluminescence quantum yield (PLQY) data was obtained using a LabSphere integrating sphere with excitation provided by a LED. TEM images and HR-TEM were taken on FEI Tecnai G2 20-Twin electron microscope with an accelerating voltage of 200kV. Carbon-coated copper grids were deposited by dipping in QDs dispersed in hexane. HP-XRD patterns were obtained using a Bruker D8 Discover diffractometer using Cu Kα radiation. XPS results were obtained using the Physical Electronics 5600 photoemission system using Al Kα radiation. A more detailed discussion can be found in reference 225. Briefly, the XPS spectra were calibrated using known metallic transitions, and all samples shown here did not exhibit photocharging. Solar cell devices were measured following the procedures found in Section 2.VI.

5.IV.e Device Fabrication

Devices were fabricated as described in Section 2.V by dip coating with a bilayer ligand treatment using PbI₂ and MPA (Section 2.V.d). 16 layers of PbSe QDs were deposited using PbI₂, and then 2 layers were deposited using MPA. 100 nm of gold was deposited by thermal evaporation as the back contact. Devices were stored in air in the dark and transferred into an N₂-atmosphere glove box for characterization.

5.V Conclusions

In summary, we developed and synthesized size tunable PbSe QDs *via* a cation exchange reaction from ZnSe QDs and Pb-halide precursors. We found improved PbSe QD air stability with iodide passivation and these QDs exhibit better solution air stability than other halide (bromide or chloride) ions. Improving the air stability of cation-exchanged PbSe QDs enabled us to fabricate photovoltaic devices with 6.5 % power conversion efficiency. Furthermore, the device showed excellent stability (>91 % of the best efficiency) for one year under ambient conditions. The next chapter will stay focused on PbSe QDs, specifically how we use what we know about the surface passivation to further increase the oxidative stability of the PbSe QD arrays. Chapter 6 will also discuss my efforts to address the *V*_{oc} deficit in QD devices (that was addressed in Chapter 4 for PbS QDs), specifically with low-bandgap materials that are relevant for MEG applications

Chapter 6: Exploration of Metal Chloride Uptake for Improved Performance Characteristics of PbSe Quantum Dot Solar Cells

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Marshall, A. R.; Young, M. R.; Nozik, A. J.; Beard, M. C.; Luther, J. M. Exploration of Metal Chloride Uptake for Improved Performance Characteristics of PbSe Quantum Dot Solar

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6.I Abstract

We explored the uptake of metal chloride salts with +1 to +3 metals of Na⁺, K⁺, Zn²⁺, Cd²⁺, Sn²⁺, Cu²⁺, and In³⁺ by PbSe QD solar cells. We also compared CdCl₂ to Cd acetate and Cd nitrate treatments. PbSe QD solar cells fabricated with a CdCl₂ treatment are stable for more than 270 days stored in air. We studied how temperature and immersion times affect optoelectronic properties and photovoltaic cell performance. Uptake of Cd²⁺ and Zn²⁺ increase open circuit voltage while In³⁺ and K⁺ increase the photocurrent without influencing the spectral response or first exciton peak position. Using the most beneficial treatments we varied the bandgap of PbSe QD solar cells from 0.78 eV to 1.3 eV and find the improved V_{oC} is more prevalent for lower bandgap QD solar cells.

6.II Introduction

Lead Chalcogenide quantum dots (QDs) are actively researched for optoelectronic devices due to unique and customizable opto-electronic features;^{203,226} tunable bandgap,

control over workfunction,^{64,189} ease of synthesis,^{27,227} and enhanced multiple exciton generation (MEG).^{10,12,66,228-230} Colloidal solutions of PbSe QDs have been extensively explored for fundamental studies^{12,20,21,205,231-237} and incorporated into photovoltaic, proof of principle, architectures.^{10,95,238-244} Nevertheless, PbSe QD solar cells have received less attention than PbS QD solar cells mainly due to more problematic air-stability. A common theme in PbSe QD studies involves not exposing the QDs to oxygen or water,^{237,245,180} which can be accomplished within a controlled atmosphere glove box or by encapsulating the QD films, such as by matrix infilling.²⁴⁶ Recently Zhang and co-workers developed new synthetic protocols that resulted in high efficiency (5-6%) PbSe QDSCs fabricated in ambient conditions.^{38,189} Despite these improvements, device characteristics still lag behind the best PbS QD solar cells with 9.9% power conversion efficiency.¹⁸⁶

Core-shell structures and over-coating of QD films have been investigated as a means to increase both the stability and transport properties in QD solids.^{246–256} Recently, new synthetic strategies based upon Pb halide precursors improved the stability and resistance to ambient oxygen, leading to colloidal, air-stable PbSe QDs.^{38,40,257} Zhang *et al.* first demonstrated that a PbCl₂–oleylamine complex as the Pb precursor resulted in PbSe QDs that were resistive to oxidation. PbSe QD solar cells could be fabricated in ambient conditions (rather than in an oxygen-free glove box) and achieved a power conversion efficiency of \sim 2 %.⁴⁰ In a subsequent report the authors demonstrated further improvements by using a synthetic technique to first synthesize CdSe QDs of the desired size and then convert them to PbSe by a cation exchange reaction with the same PbCl₂–oleylamine complex. Solar cells fabricated in air from the resulting PbSe QDs produced a record power conversion efficiency of 6.2 %.³⁸

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Inorganic and short molecular ligands (as small as single-atoms) are being explored mainly as a means to improve the charge-carrier mobilities in QD films.^{58,236,258-261} But, ligands also have a significant effect on the valence band position in QD films, which requires thoughtful design of devices made using new ligand treatments.^{64,189} Halide-based ligands and surface treatments show the deepest valence band positions of all the studied ligands and have been shown to enhance the air-stability of QD films.^{64,105,189} According to Ip *et al.* removing native ligands exposes trap states and the halide anions passivate those exposed states.⁴³ For example, Crisp, *et al.* developed a PbI₂ surface treatment for PbS QD solar cells resulting in >6 % efficient devices that are stable in ambient conditions.¹⁸⁹ Also, the five most recently published record reports for QD solar cells have employed halide passivation of PbS QDs to achieve high efficiencies.^{42,43,97,105,187}

As with many solar cell technologies, a major limiter of QDSCs in general is the low open circuit voltage (V_{oc}) compared to the ideal V_{oc} for a given bandgap. Furthermore, the V_{oc} for PbSe QDSCs is lower than that of corresponding bandgap PbS QD devices. The highest V_{oc} reported for PbSe is 520 mV, while PbS has achieved 655 mV with QDs of the same 1.3 eV bandgap.^{38,262} Here we show that using a combination of the cation-exchange synthesis and post film processing metal halide treatments, we can utilize air-stable PbSe QDs, produce highly efficient devices at lower bandgap, and increase either the J_{SC} or V_{oc} by choice of treatment.

6.III Results and Discussion

PbSe QD samples with various band gaps ranging from 0.78 to 1.3 eV were synthesized according to Zhang, *et al.* using a method based on cation exchange from CdSe.³⁸ 400 nm thick, PbSe QD films were assembled onto TiO₂-coated F:SnO₂ by dip coating using 1 mM 1,2-ethanedithiol (EDT) in acetonitrile to remove the native ligands. The key step for this work involves submersing the films in methanol (MeOH) saturated with metal salts, prior to evaporating the top contact, for various times and at various bath temperatures. A control device was soaked in neat MeOH to ensure that the solvent was not the cause of any changes in device performance observed.

Introducing metal impurities into nanocrystals can, in some cases, dope them *n*- or *p*-type depending on the charge state of the dopant.^{263–267} Additions of metal impurities may also heal defect states. For example, Choi, *et al.* showed that thermally diffusing In metal into a CdSe QD film resulted in band-like electronic transport, which they attributed to the filling of sub- and mid- gap defect states due to the incorporation of In into CdSe QDs.²⁶⁶ Here we developed a process of introducing metal cations along with halide anions by simply immersing the as-formed QD solids in a MeOH solution containing the dissolved metal halides. We studied the following metal salts: NaCl, CuCl₂, SnCl₂, CdCl₂, ZnCl, KCl, InCl₃, Cd(acetate)₂ and Cd(NO₃)₂. We chose metals with varying oxidation states (+1 to +3), and good solubility in MeOH. We find strong effects on optoelectronic properties of PbSe QD devices with certain treatments.

First, the PbSe QD films were soaked for 1 second in MeOH solutions at 45°C. In Figure 6.1, the current-voltage characteristics of 0.88 eV PbSe QD solar cells are categorized into treatments that had minimal or detrimental effects (Figure 6.1a), treatments that improved the short circuit current density (J_{SC}) (Figure 6.1b), and treatments that enhanced the open circuit voltage (V_{OC}) (Figure 6.1c). NaCl and ZnCl₂ had little effect on the device performance, while CuCl₂ and SnCl₂ had detrimental effects. Both KCl and InCl₃ increased the short-circuit current while CdCl₂ increased the V_{OC} by over 100

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mV (Figure 6.1b,c). Two non-halide Cd^{2+} salts were explored ($Cd(acetate)_2$ and $Cd(NO_3)_2$), and from these studies we conclude that addition of Cd^{2+} increases the *V*_{oc}, but that the NO_3 - anion has a negative effect on overall performance by decreasing the current and fill factor (Figure 6.1c).



Figure 6.1: JV scans for PbSe QD solar cells with various salt treatments. (a) JV curves for treatments that had no effect or were detrimental to the device performance. (b) Two treatments, KCl and InCl₃ drastically improved the current density of devices, from 21 to 27 mA/cm² without reducing the V_{OC} . (c) JV curves for the PbSe QD films treated in cadmium salts. All cadmium salts, regardless of the anion, increased the V_{OC} by at least 100 mV.

We find that of all the metal salts studied, $CdCl_2$ exhibits the most beneficial effects; therefore, we further explored $CdCl_2$ treatments. Using a bath temperature of 45°C, the soak time was varied from 1 to 20 seconds (Figure 6.2a). We find an 80 mV increase in the V_{oc} after only 1 second of $CdCl_2$ treatment. Longer soak times cause a decrease in the J_{SC} and fill factor, which we attribute to the formation of transport barriers between QDs as too much Cd is incorporated into the PbSe film, and thus increasing series resistance in the device and limiting charge collection.

To support our assessment, the spectral position of the first exciton absorption peak for QDs with E_g of 1.3 (Figure 6.2b) and 0.8 eV (Figure 6.2c) continually blue shifts with treatment time. The peak position can be correlated to the core (PbSe) size of the QD and we use a previously published sizing curve to estimate the effective diameter of the PbSe QDs in the film;^{52,223} the 1S peak position has also been used as a tool to determine the average core size in PbSe/CdSe core/shell QDs³⁷. Initial formation of the film using EDT causes a redshift of 14 meV (for 0.8 eV QDs) and 45 meV (for 1.3 eV QDs) and is well documented in the literature.^{66,195,205,252} As the CdCl₂ soak times increase, the peak position shows a general (but very slight) blue shift. Over a 40 second time window this blue shift is ~15 meV for 1.3 eV QDs corresponding to a change in effective diameter of only 1.3 Å (3.29 nm neat EDT film, to 3.16 nm after 40 sec), which is much less than the thickness of one monolayer of Pb or Se. The larger, 0.8 eV PbSe QDs showed a similar effect with a change in effective diameter of 1.4 Å (4.87 nm neat EDT film, to 4.73 nm after 40 sec, Figure 6.2b).

The minimal shift of the first exciton after a 1-second soak in $CdCl_2$ (3 meV) combined with the large increase in V_{OC} (~100 mV) leads us to postulate that the Cd ions do not rapidly replace Pb, but first passivate specific QD surface sites. Pietryga *et al.* show significant spectral shifts when performing a cation exchange on the surface of PbSe QDs, even for shells <1 nm thick.³⁷ Comparing the spectral shifts measured in Fig. 2 using the CdCl₂ treatment to this previous work, these QDs do not show a CdSe shell forming during the first 1 second of treatment. After longer treatment times (or higher temperatures) the Cd will begin to replace Pb atoms at the surface, perhaps even forming a thin shell, which explains the lower current in devices with long CdCl₂ treatment times.

We next studied the temperature of the soak treatments. Using the 1-second soak time, the temperature of the treatment was varied from 20 °C to 40 °C (Figure 6.2c-e). At the highest temperature there is a decrease in J_{SC} for some devices, showing that higher

temperatures promote fast ion-absorption in the film. The optimal temperature was 30 °C, where a small amount of Cd was incorporated, improving the *V*_{oc} without a deleterious loss in current. In recent studies on the valence band and Fermi energy levels in PbS QD films, EDT and CdCl₂ ligands have similar energy levels.^{64,189} The co-passivation of CdCl₂ and EDT should not alter the valence band or Fermi level energies significantly compared to the EDT treatment alone. Hence, the *V*_{oc} enhancement is not a result of a larger bandgap or shifting energy levels in the film, but from trap passivation at the QD surface.



Figure 6.2: Effect of treatment time and temperature on PbSe QD solar cells. (a) All $CdCl_2$ treatments improved the V_{OC} over that of the untreated device, but longer soaks resulted in decreased current and increased series resistance. (b) The 1S exciton peak position in original QD solution, in a film treated with EDT and as a function of $CdCl_2$ soak time for 2 different QD sizes. Top shows 3.2 nm PbSe with first exciton near 1.3 eV (color coded to match panel A) and bottom shows 4.8 nm PbSe with first exciton of 0.83 eV. (c) V_{OC} , (d) J_{SC} , and (e) power conversion efficiency as a function of $CdCl_2$ soak temperatures (1 sec soak time) for QD films with bandgap (E_{g-Abs}) ranging from 0.78 to 1.3 eV.

The V_{OC} gains are more pronounced for lower bandgap samples, and thus the optimization of the CdCl₂ treatment results in the highest efficiency PbSe QD devices reported to date for low-bandgap films (below 1.1 eV, Figure 6.3b). Note that we use the

peak of the lowest energy exciton in the solution absorption spectrum to estimate the bandgap of the QDs (E_{g-Abs}) and to inform about the physical size of the QD. However, the bandgap of the films in solar cells are generally determined using a Tauc plot (details in Appendix A3). As an alternative to the 1S absorption feature, a recent publication estimated the bandgap of PbS QDSC using the onset of the EQE.¹⁰⁰ Using the EQE spectra to estimate the absorption of the films, we make a Tauc plot and find the *x*-intercept of a linear fit to the low energy side in order to calculate the bandgap (E_{g-EQE}); this value is used to calculate theoretical performance parameters, as below in the discussion of V_{OC} deficit. The E_{g-EQE} is always found to be lower in energy than the E_{g-Abs} ; the four sizes studied here show E_{g-EQE} of 0.73, 0.77, 0.93, and 1.1 eV for E_{g-Abs} of 0.78, 0.88, 1.07, and 1.3 eV, respectively.



Figure 6.3: Device structure with efficiency and V_{oc} **as a function of bandgap. (a)** Scanning Electron Microscopy (SEM) image showing the cross-section of a typical PbSe QD device. **(b)** JV curves for the top performing devices with $E_{g-EQE} = 0.73$ to 1.1 eV fabricated using the 1 second, 30°C, CdCl₂ treatment. **(c)** The V_{oc} deficit calculated as a percentage of the maximum theoretical V_{oc} using the Shockley Queisser analysis for each film's E_{g-EQE} . The untreated devices are shown as open triangles and the CdCl₂-soaked films are shown as colored triangles matching the legend in panel B. The CdCl₂ treated devices reach a higher percentage of the maximum allowable V_{oc} .

Recently, the large V_{OC} deficit in QDSCs has been acknowledged as a major limiting factor in overall power conversion efficiency, and likely results from trap-assisted recombination.^{183,268} Given the large increase in V_{OC} with the Cd-based soak treatment presented in this work, we show the percentage of the theoretical V_{OC} (using the Shockley-

Queisser formalism)¹ achieved in devices before and after the CdCl₂ treatment (Figure 6.3). The CdCl₂ treatment reduces the V_{OC} deficit by as much as 20%, most significantly for the lower bandgap material (larger diameter PbSe QDs) and represents a promising approach to improving the performance of QDSCs.

Secondary-ion mass spectrometry (SIMS) and inductively coupled plasma mass spectrometry (ICP-MS) were used to assess the cadmium and indium incorporation of the treated PbSe films. Films were dip coated using EDT in the same manner as described for device fabrication, then the films were exposed to either neat MeOH, or saturated MeOH solutions of CdCl₂ or InCl₃. In Figure 6.4, we show the depth-dependent SIMS profile for the measured Se, In, and Cd content. The In signal in the InCl₃ treated film is two orders of magnitude higher than in the MeOH and CdCl₂ treated films, and similarly the relative amount of Cd in the CdCl₂ treated film is an order of magnitude higher than in the MeOH or InCl₃ treated film. These results demonstrate that a 1-second soak in a salt solution results in a significant incorporation of the metal cation evenly throughout the entire thickness of the QD solid. The ICP samples were prepared by digesting the treated films in nitric acid. The ICP data (Table 6.1) is in agreement with the SIMS and shows clear indication of Cd and In uptake by the films upon the 1 second soak.



Figure 6.4: Secondary ion mass spectrometry of treated PbSe QD films. Secondary ion mass spectrometry (SIMS) shows the ¹¹³In, ¹¹⁴Cd, and ⁸⁰Se signals from 3 treated films. The absolute counts were normalized by the ⁸⁰Se signal. The methanol rinse (left) is the reference for a neat QD film. The film treated with CdCl₂ (middle) shows a substantial and uniform increase in the amount of ¹¹⁴Cd detected by SIMS throughout the thickness of the film. The InCl₃ treated film likewise shows a uniform increase in the ¹¹³In signal (right). The surface of the film is shaded in purple and the gray shading indicates the ITO layer below the PbSe QD film. The ¹¹³In signal increases and other signals begin to decrease once the ITO layer is reached. The bulk of the QD film is represented by the un-shaded region.

Table 6.1: ICP of treated PbSe QD films. ICP results from films treated with MeOH, CdCl₂, and InCl₃. The Se signal is included to show the variation between the concentrations of the different samples.

	Se (ppb)	Cd (ppb)	In (ppb)
MeOH-only	3946	47.0	<0.14
CdCl ₂	3849	810.0	4.1
InCl ₃	4085	45.2	332.3

The Cd content was also measured using SIMS as a function of immersion time in the CdCl₂ solution. CdCl₂ treated films show a 5-fold increase in the amount of Cd. The difference in Cd content between the different time soaks is not noticeable within the sensitivity of the SIMS measurement, but the 1S absorption peak continues to shift (as shown in Figure 6.2b) and long treatment times lead to reduced transport. This implies

that the initial immersion quickly incorporates Cd into the film, passivating trap states on the QD surfaces and causing the increase in V_{OC} . An excess of Cd limits transport though, as seen in the J_{SC} decrease for long treatment times and elevated bath temperatures. This excess Cd measured in SIMS and ICP is not present as inclusions of CdCl₂ as seen from the XRD patterns in Figure 6.5. The XRD pattern before and after the CdCl₂ treatment are indistinguishable.



Figure 6.5: XRD pattern of treated and un-treated PbSe QDs. XRD pattern for EDT treated thin films of PbSe QDs, with (red trace) and without (blue trace) the CdCl₂ treatment. The black trace shows neat, CdCl₂ powder. The bottom traces are of thick, dropcast samples of PbSe treated with EDT, then CdCl₂. Neither the dipcoated nor dropcast films show XRD peaks indicating leftover CdCl₂ from the treatment.

Halide treatments have been shown in many cases to provide QDs with protection from oxidative attack.^{46,191,257} We find that chloride post-treatments (specifically CdCl₂ and InCl₃) improve the air-stability of devices. The InCl₃ device shows better air stability than an untreated device (Figure 6.6a, blue triangles, especially apparent around days 10-20). CdCl₂ shows the best air-stability overall (Figure 6.6a). We attribute this stability to the passivation of the surface–Cd fills defect states,²⁶⁹ leading to an improved *Voc*, while Cl lowers the work function^{64,189} making the films resistive to oxidation. Comparing these devices to one treated with Cd(acetate)₂ (Figure 6.6b), we can see the affect of Cd without Cl: the V_{OC} increase is apparent in Figure 6.1 and the air stability is enhanced slightly. The device completely degrades between 5 and 27 days, similar to the InCl₃ treated device. The co-passivation of Cd and Cl in the device results in PbSe QDSCs that can be stored in air for over 270 days and maintain ~80 % of their initial efficiency.



Figure 6.6: Long-term air stability of PbSe QD solar cells. (a) The efficiency of multiple devices is graphed as a function of days after fabrication while being stored in air, normalized to the efficiency on the first day. Devices with no chloride treatment (green squares) were not functional within the first few days of air exposure. The InCl₃ treatment (blue triangles) offers some protection; devices were still functional after almost a month in air, albeit less so than at the beginning and degraded to 0% under long-term air exposure. The CdCl₂ treatment (red circles) offered the best protection, losing little efficiency (in some cases <20% relative to initial values), even up to 270 days of air storage. Individual devices are denoted with different symbols and connecting lines. **(b)** A PbSe device treated with Cd(acetate)₂ shows similar, but slightly worse stability to the InCl₃ treatment.

6.IV Methods

6.IV.a PbSe QD Synthesis

PbSe QDs were synthesized following a previously published procedure, through a

cation exchange of CdSe QDs.³⁸ See Section 2.VII.e for detailed procedures. In this chapter,

four different sizes of PbSe QDs were used to determine the effects of the treatments on

various band gaps. In

Table 6.2 the reaction conditions for each PbSe band gap are recorded.

Table 6.2: PbSe QD synthesis conditions. The initial CdSe QD starting materials and injection temperatures are shown for the four sizes of PbSe QDs used in this chapter.

CdSe QD 1 st Exciton	Injection Temperature	Result: PbSe QD 1 st Exciton
500 nm	140 °C	950 nm
564 nm	160 °C	1155 nm
580 nm	190 °C	1410 nm
612 nm	195 °C	1590 nm

6.IV.b Photovoltaic Devices

The TiO_2 sol-gel is prepared following the procedure found in Section 2.V.a. The QD layer is fabricated using a layer-by-layer dip coating process that is outlined in Section2.V.d. PbSe QDs are dip coated from hexane with 1 mM 1,2-ethanedithiol in acetonitrile; approximately 20 layers results in 250-350 nm thick films.

This film is then treated with a saturated CdCl₂ solution in MeOH (~25mg/mL) at various temperatures. The film is soaked in the CdCl₂/MeOH solution for 1 second then washed thoroughly with reagent grade isopropanol. The films are annealed on a hotplate at 111°C in the glove box for 20 min before the evaporation of 20-50 nm molybdenum trioxide and 200 nm aluminum. This completes the full device stack of FTO/TiO₂/PbSe QDs/MoO_x/Al. The devices were always stored in air while the EQE and JV curves were measured in an oxygen-free environment.

6.IV.c ICP-MS
PbSe QD films were dip coated using 1mM EDT on glass substrates, then 1 second treatments were done at 30°C in neat MeOH, CdCl₂, and InCl₃. The films were dissolved in 70% HNO₃ in water, trace metals basis. The solutions were then diluted with water (trace metals basis) and HNO₃ to make solutions of 5 vol% HNO₃ in water. The samples were submitted to the Laboratory for Environmental and Geological Studies (LEGS) at the University of Colorado, Boulder for ICP-MS analysis.

6.IV.d Secondary Ion Mass Spectrometry (SIMS)

Films were dip coated in a manner mimicking device fabrication (without the TiO₂ layer) for SIMS analysis. PbSe QDs in hexane (15 mg/mL) and 1 mM EDT in acetonitrile were used to dipcoat a film 200nm thick onto an ITO substrate. MeOH and metal chloride soak treatments were done for 1 second with the solutions at 35°C. The films were analyzed in a Cameca IMS 5f instrument with a Cs⁺ primary ion beam and positive secondary ions.

6.V Conclusion

We report on the inclusion of metal and halide ions, post film fabrication, as a means of enhancing the efficiency of low bandgap PbSe QDSCs by simply exposing QD solids to metal halide solutions in MeOH. We find that CdCl₂ has the best enhancement. The addition of Cd drastically reduces the *V*_{oc} deficit by passivating limiting defects and the combination of Cd and Cl enhances the air-stability of QDSCs. Larger diameter PbSe QDs show the most improvement from the CdCl₂ treatment. Devices are stored in air for over 270 days and retain close to 80% of the original efficiency. This work aids in the advancement of QDSCs by enabling air-stable, high efficiency PbSe devices, especially

for low bandgap films, which are ideal for studying MEG in QD solar cells. In Chapter 7 I transition into discussing a new material that we have shown has great potential to produce high efficiency photovoltaic devices: perovskite QDs. This new QD material produces devices with high *V*_{oc} on the first device attempts, theoretically because perovskite materials are "defect-tolerant" materials. While the bandgap of perovskite QDs is not ideal for single-junction solar cells, the work presented in the next chapter is useful for fabricating tandem devices.

Chapter 7: Quantum Dot-Induced Phase Stabilization of α-CsPbI₃ Perovskite for High-Efficiency Photovoltaics

Adapted with permission from:

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7.I Abstract

We show nanoscale phase stabilization of CsPbI₃ quantum dots (QDs) to low temperatures that can be used as the active component of efficient optoelectronic devices. CsPbI₃ is an all-inorganic analog to the hybrid organic cation halide perovskites, but the cubic phase of bulk CsPbI₃ (α -CsPbI₃)—the variant with desirable band gap—is only stable at high temperatures. We describe the formation of α -CsPbI₃ QD films that are phase-stable for months in ambient air. The films exhibit long-range electronic transport and were used to fabricate colloidal perovskite QD photovoltaic cells with an open-circuit voltage of 1.23 volts and efficiency of 10.77%. These devices also function as light-emitting diodes with low turn-on voltage and tunable emission.

7.II Introduction

Hybrid organic-inorganic halide perovskites, with the common formulation ABX₃ (where A is an organic cation, B is commonly Pb²⁺, and X is a halide), were first applied to photovoltaics (PVs) as methylammonium lead triiodide (CH₃NH₃PbI₃) in 2009.²⁷⁰ Perovskite PV devices processed from solution inks now convert >22 % of incident sunlight into electricity, which is on par with the best thin-film chalcogenide and silicon devices, but durability of the semiconductor presents a major technical hurdle to commercialization. Under environmental stress, CH₃NH₃PbI₃ dissociates into PbI₂ and CH₃NH₃I, the latter of which is volatile.⁸⁶

Thus, an all-inorganic structure without a volatile organic component is highly desired. The all-inorganic Pb-halide perovskite with the most appropriate band gap for PV applications is cubic (α) CsPbI₃ ($E_g = 1.73$ eV) because geometrical constraints of the perovskite structure require a large +1 A-site cation, and Cs⁺ is the most feasible. However, below 320 °C, the orthorhombic (δ) phase ($E_g = 2.82$ eV) is thermodynamically preferred.²⁷¹ Nevertheless, groups have explored CsPbX₃ compounds as PV materials, but films of CsPbI₃ undergo immediate transformation to the δ phase when exposed to ambient conditions.²⁷² Attempts to stabilize the α phase through alloying with Br have been explored because CsPbIBr₂ shows a much reduced δ to α phase transition temperature of 100 °C.²⁷¹ However, the composition change leads to an undesired increase in the band gap. We show that nanocrystal surfaces can be used to stabilize α -CsPbI₃ at room temperature, far below the phase transition temperature for thin film or bulk materials. We further show that we can control the electronic coupling of quantum dots (QDs) to produce air-stable, efficient PV cells (initial efficiency above 10%) based on this all-inorganic material.

Many physical properties differ between nanometer-sized and bulk crystalline materials of the same chemical compound. One such example is the structural phase in which the constituent atoms are arranged. For example, the semiconductors CdS and CdSe embody a rock salt structure at high pressure. However, the solid-solid phase transition point between the rock salt phase and the hexagonal wurtzite phase can vary greatly in

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temperature and pressure as a function of crystal size.^{84,85} Manipulated size-dependent phase diagrams have been explored in a variety of material systems with advantageous properties of the crystals emerging at reduced dimensions in oxides (such as TiO₂), lanthanides (such as NaYF₄),²⁷³ metals (such as Ag),²⁷⁴ and ferroelectrics (such as the perovskite BaTiO₃).²⁷⁵

Synthetic protocols of colloidal halide perovskite QDs have recently been reported.^{74,75,276–281} CsPbX₃ QDs exhibit improved room-temperature cubic-phase stability and attractive optical properties for a wide range of applications.^{75,76,78–81} Experiments on size- and shape-dependent optical properties,^{75,94,282,283} surface chemistry,⁸⁸ and other photophysics²⁸⁴ are being explored for CsPbBr₃ QDs. However, previous studies were unable to achieve α -CsPbI₃ QDs that were stable enough for extensive characterization or to be used in PV cells.

7.III Results/Discussion

We present an improved synthetic route and purification approach to CsPbI₃ QDs. Once purified, the QDs retain the cubic phase for months in ambient air and even at cryogenic temperatures. A method for perovskite QD film assembly is described that allows for efficient dot-to-dot electronic transport while retaining the phase stability of the individual QDs. The PV cells produced from this approach have the highest power conversion efficiency (PCE) and stabilized power output (SPO) of any all-inorganic perovskite absorber, produce 1.23 V at open circuit (among the best of any perovskite PV cells), and also function as light emitting diodes (LEDs), emitting visible red light with low turn-on voltage.



Figure 7.1: Characterization of CsPbI₃ QDs. (a) UV-Visible absorption spectra and photographs of CsPbI₃ QDs synthesized at a) 60 (3.4 nm), b) 100 (4.5 nm), c) 130 (5 nm), d) 150 (6.8 nm), e) 170 (8 nm), f) 180 (9 nm), g) 185 °C (12.5 nm), average size from TEM shown in parentheses. (b) Normalized photoluminescence spectra and photographs under UV illumination of the QDs from (A). (c) High resolution transmission electron micrograph (HRTEM) of CsPbI₃ QDs synthesized at 180 °C. (d) XRD patterns of QDs synthesized at (from bottom to top) 60, 100, 170, 180, and 185 °C confirming that they crystallize in the cubic phase of CsPbI₃.

7.III.a Synthesis and Purification

The tunability of the band gap via size control due to quantum confinement is shown in Figure 7.1. The series of CsPbI₃ QDs, with varied size (band gap), were synthesized by the addition of Cs-oleate to a flask containing PbI₂ percursor—as first described by Protesescu *et al.*⁷⁵–here, using injection temperatures between 60 and 185 °C to control the size (Figure 7.1a). This produces QDs solubilized by non-crystalline iodide and oleylammonium surface ligands.⁸⁸ Unpurified QDs transform to the δ phase within several days, as in previous reports.^{92,285} However, we developed a process to purify the QDs by using methyl acetate (MeOAc), an antisolvent that removes excess unreacted precursors without inducing agglomeration. Using the extraction procedure, we found that the QDs are stable in the cubic phase for months with ambient storage.

The excitonic peak of CsPbI₃ shifted between 585 and 670 nm, corresponding to QD sizes between 3 and 12.5 nm, respectively. The corresponding normalized photoluminescence (PL) spectra of the samples are shown in Figure 7.1b, along with a photograph of the QDs in hexane. Upon ultra- violet (UV) excitation, emission was in the orange (600 nm) to red (680 nm) color range, corresponding to a band gap between 2.07 and 1.82 eV. The full width at half- maximum of the PL for the smallest QDs was 83 meV and increased slightly for the larger sizes, whereas the PL quantum yield varied from 21 to 55% for different sizes.

In contrast to the instability of the cubic phase of bulk CsPbI₃ at room temperature, QDs have been reported to retain the cubic phase because of the large contribution of surface energy (Figure 7.1d).^{75,82} The softer basic nature of I⁻ as compared with Br⁻ results in weaker acid-base interactions between the halide and the oleylammonium ligand (a hard acid) in the case of CsPbI₃, compared with that of CsPbBr₃.^{92,286} Therefore, the isolation of CsPbI₃ QDs is more difficult than that of CsPbBr₃ QDs because of the loss of ligand during extraction, causing agglomeration and conversion to the orthorhombic phase. Thus, we found that MeOAc, which isolates the QDs without full removal of the surface species, is critical to the phase-stable devices described below.

The high-resolution transmission electron micrograph (TEM) of the sample synthesized at 180 °C (Figure 7.1c) shows an interplanar distance of 0.62 nm, which is consistent with the (100) plane of α -CsPbI₃.^{82,94,287} In Figure 7.2, a and b, powder x-ray diffraction (XRD) patterns and UV-visible absorption spectra confirm the absence of diffraction peaks of the high-energy (~3 eV) sharp absorption characteristic of orthorhombic phase formation,⁸² even after 60 days of storage in ambient conditions. Additionally, the QDs remained in the cubic phase even after the solution was cooled to 77 K, further demonstrating the expanded temperature stability of the cubic phase.



Figure 7.2: Phase stability of colloidal and powder CsPbI₃ **QDs. (a)** Powder XRD patterns and **(b)** UV-Visible absorption spectra, normalized at 370 nm, of CsPbI₃ QDs

synthesized at 170 °C and stored in ambient conditions for a period of 60 days. Inset shows the slight blue shift that is seen in the excitonic peak with extended storage. **(c)** Rietveld refinement fitting of CsPbI₃ NC XRD pattern revealing pure cubic phase CsPbI₃.

Rietveld refinement of the XRD patterns, shown in Figure 7.2c allowed us to quantify the contribution from cubic and orthorhombic phases. No detectable orthorhombic phase was found. Additionally, lattice parameters of three different size CsPbI₃ QD samples were estimated (Table 7.1). The lattice parameter values showed a size dependence and were lower than the previously measured experimental value (6.2894 Å at 634 K) of bulk α -CsPbI₃.²⁸⁷ Our measurements were performed at 297 K whereas high temperatures are required to characterize bulk α -CsPbI₃. A similar increase in lattice parameter with decreasing particle size has been reported in other systems and attributed to electrostatic relaxation with decreasing crystal size.²⁸⁸

Table 7.1: Results	s of the	Rietveld	refinement.
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QD Size (TEM)	a (Å)	R _{wp}	QD Size (Rietveld)
8 nm	6.231 ± 0.002	3.42	9 ± 1 nm
9 nm	6.220 ± 0.002	6.50	10 ± 1 nm
15.5 nm	6.189 ± 0.002	7.79	17 ± 2 nm

7.III.b Assembling Conductive Arrays

In order to use these highly phase-stable α -CsPbI₃ QDs in optoelectronic devices, we developed a method to cast electronically conductive QD films. The QDs were first spin-cast from octane, then dipped in a saturated MeOAc solution of either Pb(OAc)₂ or Pb(NO₃)₂ (neat MeOAc was used as a control). This process was repeated multiple times—typically

three to five—to produce QD films with thicknesses between 100 and 400 nm. The optical absorption and PL spectra (Figure 7.3a, for three samples with indicated reaction temperature) show that in each case, the film absorbance and PL was red-shifted ~20 nm from that of the QDs in solution, whereas the tunable emission properties of the films indicate that quantum confinement is preserved. Fourier-transform infrared (FTIR) spectra show the removal of organic ligands from the film with exposure to neat MeOAc (Figure 7.3b), given the near absence of C–H modes near 3000 cm⁻¹ or below ~2000 cm⁻¹ belonging to oleylammonium, oleate, or octadecene.



Figure 7.3: CsPbI₃ QD film characterization. (a) UV-visible absorption (solid lines) and PL spectra (dashed lines) of CsPbI₃ QDs in solution (blue) and cast as films (black) for QDs synthesized at 100, 150, and 180 °C. (b) FTIR spectra showing the IR transmission of a CsPbI₃ NC film as cast (black) and after treating with MeOAc (red).

We therefore attribute the preserved phase stability of the QDs in the films to the size of the crystals (given the quantum confined optical properties) independent of the surface species. However, we found that prolonged annealing at temperatures >200°C

causes further grain growth and thus induces a phase transition to the orthorhombic phase (Figure 7.4 and Table 7.2). Additional strategies to preserve the phase in sintered QD films are being explored.²⁸⁹ We have observed α -CsPbI₃ with edge length up to 50 nm using the solution-phase synthesis described here. To make the δ -CsPbI₃ QDs analyzed in Figure 7.4, a 1/3 scale of the standard reaction was performed at 170 °C. The reaction was maintained at 170 °C while slowly adding excess Cs-oleate solution (1.5 mL total) until the reaction solution turned bright yellow (15.5 minutes). The reaction was then quenched in an icewater bath and purified once by centrifugation. We see a conversion of the particle shape from cubes to spheres (Figure 7.4a, b) when the particles go through the α to δ phase transition; a reflection of the underlying crystal structure change.



Figure 7.4: Characterization of α **- and** δ **-CsPbI**₃ **QDs.** High-resolution TEM images of (a) α - and (b) δ -CsPbI₃ QDs showing the distinctly different faceting of the two phases. (c) UV-visible absorption spectra of the cubic and orthorhombic phase QDs shown in (a) and (b), respectively. (d) XRD patterns of the two QD samples compared to reference patterns for α -CsPbI₃ and δ -CsPbI₃. The asterisks denote peaks that correspond to CsI.

We performed temperature dependent XRD analysis on films of QDs drop cast onto

a Si wafer. The temperature was ramped uniformly using an *in-situ* heating stage in a N2

atmosphere at 1 °C/min. An XRD scan was acquired each minute. Using Rietveld refinement, we quantified the contribution of α - and δ -CsPbI₃ phases in select XRD scans as the QD sample was heated up to 350 °C. At 206 °C, the sample remained entirely in the cubic phase with an estimated crystal size enlarged to 70 ± 20 nm. Once the sample temperature reached 213 °C, however, the resultant XRD pattern was consistent with a sample that contains 90 wt.% δ -CsPbI₃ and 10 wt.% α -CsPbI₃. The mixed phase makes the refinement fitting challenging, however we get values consistent with the 206 °C XRD pattern. Table 7.2 shows a summary of the fitting.

Sample (temperature of scan)	a (Å)	Size (nm)	
206 °C	6.207 ± 0.006	70 ± 20	
213 °C Orthorhombic (90 wt.%)	a = 10.11 ± 0.05 b = 4.66 ± 0.1 c = 18.07 ± 0.1	100 ± 100	
213 °C Cubic (10 wt. %)	6.2 ± 0.1		

Table 7.2: Grain size extracted from Rietveld refinement of XRD-T.

Due to the air stability of α -CsPbI₃ QDs in arrays we are able to fabricate optoelectronic devices, discussed below.

7.III.c Photovoltaic Devices

We fabricated PV cells with CsPbI₃ QD films as the photoactive material. A schematic of device architecture shown in Figure 7.5a, scanning electron micrograph (SEM) cross-section image is shown in Figure 7.5b. The reverse-scan current density-voltage (JV) curves show an open-circuit voltage (Voc) of 1.23 V, and 10.77 % PCE for a 0.10 cm² cell made and tested completely in ambient conditions (relative humidity ~15 to 25 %) (Figure

7.5c). In Figure 7.5d, the spectral response of the PV cell is shown, indicating a band gap of 1.75 eV for this film. We compare QD devices to thin-film $CsPbX_3$ perovskite solar cells following literature reports, which have thus far reported at 9.8 % PCE and SPO as high as 6.5 %.^{82,83,272}



Figure 7.5: CsPbI₃ **photovoltaic and LED devices. (a)** A schematic (with HRTEM image of QDs) and **(b)** SEM cross-section of the CsPbI₃ PV cell. **(c)** Current-voltage curves of a device measured in air over the course of 15 days. The black diamond represents the stabilized output of the device at 0.92 V. **(d)** External quantum efficiency (black, left ordinate) and integrated current density (blue, right ordinate) of the device. **(e)** EL spectra of CsPbI₃ solar cell (CsPbI₃ synthesized at 170 °C) under forward bias. The inset shows a photograph of the luminescent device. **(f)** PL (dotted lines) and EL (solid lines) spectra of completed devices fabricated using CsPbI₃ QDs synthesized at 170 and 180 °C demonstrating size quantization effects in the completed devices.

Furthermore, the PCE improved from its initial value over the course of 60 days storage in dry but ambient conditions (Figure 7.6a). In Figure 7.6b, we show the SPO of the cell by measuring the current density while the device is biased at 0.92 V. The SPO is an important parameter in perovskite literature because of the varying results when different scan rates or scan directions are used.



Figure 7.6: Stability of CsPbI₃ **QD solar cells multi-day, SPO and hysteresis. (a)** The device was periodically measured over a 64-day period. Performance parameters were extracted from a 1 V/s voltage swept from forward bias to short-circuit. Between measurements the device was stored in the dark in a desiccator. (b) Measured current response (black) of the device over 120 s when held at a constant voltage of 0.92 V. The corresponding power is shown in green. (c) Hysteresis characterization of CsPbI₃ PV cells. Forward scan (dashed lines) and reverse scan (solid lines) current density-voltage curves of a typical CsPbI₃ QD solar cell at different scan rates along with the stabilized power output near the maximum power point.

In Figure 7.6c we show forward and reverse scans at various scan rates along with the SPO. We find that decreasing the scan rate improves the forward scan, while having very little impact on the reverse scans. The device stabilizes very close to the reverse scans, but in-between the forward and reverse scans at the slowest scan rate. The QD devices show improved *JV*-scan efficiency, operational stability, and tolerance to higher relative humidity levels (Figure 7.7, Figure 7.8, and Table 7.3). The V_{oc} is remarkably higher than that of other QD solar cells (typically <0.7 V) and among the highest V_{oc} in all perovskite PV cells for band gap values below 2 eV.



Figure 7.7: CsPbI³ **QDs versus bulk CsPbX**³ **films in humid air.** *JV*-curves of TiO_2 /perovskite/spiro-OMeTAD/MoO_x/Al solar cells with **(a)** CsPbI₃ QDs, **(b)** bulk CsPbI₃, **(c)** and bulk CsPbI₂Br perovskite active layers. The devices were measured following fabrication (red curves) and after storage for 2 days in the dark in ambient conditions (blue curves). The ambient relative humidity was 40-60%.



Figure 7.8: Long-term stabilized power output in humid air. Current density-voltage curves of TiO₂/perovskite/spiro-OMeTAD/MoO_x/Al solar cells with **(a)** CsPbI₃ QDs, **(b)** bulk CsPbI₃, **(c)** and bulk CsPbI₂Br perovskite active layers. **(d)** The stabilized power output (SPO) of the solar cells shown in (a-c) conducted in ambient conditions, without active heating/cooling, over the course of 3600 s. The bias voltages used were 0.92 V, 0.3 V, and 0.88 V, respectively. **(e)** SPO measurements conducted for 7200 s at 85 °C on a CsPbI₃ QD solar cell (J_{SC} = 10.71 mA/cm², V_{OC} = 1.19 V, FF = 0.642, efficiency = 8.16%) near the maximum power point of the device at this elevated temperature (bias voltage = 0.65 V).

For all of these measurements the devices were completely un-encapsulated. The relative humidity of the ambient air was 40-60 % during the course of all of these experiments.

	Test	Jsc (mAcm ⁻²)	V _{oc} (V)	FF	Efficiency (%)
CsPbI ₃ QDs	Initial	10.3	1.23	0.743	9.5
	Day 2	6.65	1.07	0.358	2.55
Bulk CsPbI3	Initial	15.4	0.4	0.393	2.42
	Day 2	0.47	0.32	0.289	0.044
Bulk CsPbI2Br	Initial	10.8	1.1	0.689	8.18
	Day 2	0.43	0.85	0.472	0.17

Table 7.3: Stability data for various types of CsPbX₃ **PV cells.** The 2nd day measurement was performed after 2 days of storage in 40-60% relative humidity.

We have not optimized the device architecture or the QD film-treatment scheme. We found that dip-coating spin-cast films in neat MeOAc and MeOAc saturated with Pb(OAc)₂ or Pb(NO₃)₂ all work reasonably well (JV-scanned PCE >9 %) in PV devices. Large diffusion lengths and mobility values have been measured in CsPbBr₃ QDs by means of terahertz spectroscopy;²⁹⁰ however, a better understanding of the electronic coupling is critical to maximizing long-range transport in QD perovskite films.

7.III.d Light Emitting Diodes

Given the PL properties of these perovskite QDs, we explored their use as LEDs. The PV devices produced bright visible electroluminescence (EL) when biased above VOC (Figure 7.5e, inset). The EL had a low turn-on voltage near the band gap of the CsPbI₃, with increasing intensity at larger applied biases (Figure 7.5e). These spectra provide direct evidence that quantum confinement is retained in the complete devices, which is critical to retaining the improved cubic-phase stability, as seen by the shift in both the EL and PL

spectra of devices with different-size QDs (Figure 7.5f). The synthesis of normally unstable material phases stabilized through colloidal QD synthesis provides another mechanism for material design for PVs, LEDs, and other applications.

7.III.e Removal of Oleic Acid

In the literature, there has been debate about the ligands on the surface of CsPbI₃ QDs;^{88,89,291,292} whether oleylammonium iodide binds as a bound ion pair or if oleate molecules bind to surface Pb and Cs atoms. One recent report claims that excess oleic acid (OA) contributes to the instability of colloidal CsPbI₃ QDs and replaces the OA with a phosphinic acid (diisooctylphosphinic acid, DIPA).²⁹² Following this synthetic technique, we compared the colloidal QDs synthesized using DIPA to those synthesized using OA and fabricated devices from each (Figure 7.9). The DIPA-QDs were more difficult to wash, because the DIPA does not bind to the surface of the QD, presumably leaving a lower ligand density than that found on the OA-QDs. This caused a slight red-shift in the absorption spectra we believe due to QD agglomeration during the isolation steps. Devices fabricated from the two synthetic techniques were identical (Figure 7.9b), but the SPO showed a significant improvement when using the DIPA synthesis (Figure 7.9c). The OA-QD device degrades slightly over the 2 minutes of applied voltage, while the DIPA-QD device shows higher power output and no degradation.



Figure 7.9: Comparison of syntheses for CsPbI₃ **QDs. (a)** Absorption and PL (scaled for the absorption at the excitation wavelength). The DIPA synthesis is more challenging to purify, probably due to having less ligands on the surface of the QD. This makes the QDs agglomerate during the isolation steps and cause the red-shifted absorbance and PL, and resulting in a slightly lower PL efficiency than the OA-synthesized QDs. (b) *JV*-curves for CsPbI₃ QD devices made from QDs synthesized by each method. These devices were fabricated with six layers of the Pb(NO₃)₂ treatment. **(c)** SPO for each device. Even though initial scans for each device were comparable, the DIPA device stabilized at a higher efficiency. Also, the OA-QD device showed a slight decrease in SPO over time, while the DIPA-QD device did not lose efficiency over 2 minutes.

7.III.f Metal Halide Post-Treatment

The other area of interest is using new surface treatments to affect the device performance parameters, similar to the work in Chapter 6. In order to increase the stability of α -CsPbI₃, the Goldschmidt tolerance factor shows that a larger cation in the A-site will stabilize the cubic crystal structure. The Cs cation is too small for the α phase to be thermodynamically favored, causing the conversion to the δ phase at room temperature. Using a larger A-site cation as a surface treatment may help stabilize the α -CsPbI₃ QD material over a long period of time.

We began exploring surface treatments to assist with the phase stabilization and keep the QDs from agglomerating into bulk material. While a full analysis of new surface treatments is ongoing and the subject of a future publication, I focus on one surface treatment as an example of the fine control surface treatments afford—in direct comparison to the lead chalcogenide systems. RbI is employed as a new ligand to replace the lead salt ligands used to make the first CsPbI₃ QD devices.



Figure 7.10: Effect of RbI on CsPbI₃ **QD Solar Cells. (a)** JV scans for $Pb(NO_3)_2$ treated CsPbI₃ QDs compared to the RbI treatment using two different solvents: MeAc and IPA. **(b)** SPO for the different ligand treatments. The solar cells treated with RbI stabilize closer to the JV scan efficiency, while the $Pb(NO_3)_2$ treated solar cell stabilizes 0.6% lower than the JV scan efficiency.

First, note that the solvent used for the ligand treatment has an effect on the photovoltaic device performance. As discussed in Section 7.III.a the anti-solvents traditionally used for QD purification (alcohols or acetone) cause the CsPbI₃ QDs to agglomerate and/or dissolve. These solvents have a detrimental effect on films as well, lowering the V_{OC} of the photovoltaic devices. In Figure 7.10, the isopropyl alcohol (IPA, blue trace) causes a lower V_{OC} than either of the ligand treatments with methyl acetate (MeAc). Second, the SPO for the RbI treatments is closer to the JV scan than the SPO for the Pb(NO₃)₂ treatment. Due to hysteresis in perovskite photovoltaics, the SPO has become the more trusted measurement for determining the true efficiency of these devices. Therefore, having an SPO that is similar to the JV scan implies that there is little hysteresis and the device is semi-stable under operating conditions.

7.IV Methods

7.IV.a Reagents

All chemicals were purchased from Sigma Aldrich and used without purification, unless otherwise noted. Cesium carbonate (Cs₂CO₃, 99.9%), lead (II) iodide (PbI₂) 99.9985%, Alfa Aesar), oleic acid (OA, technical grade 90%), oleylamine (OLAm, technical grade 70%), 1-octadecene (ODE, technical grade 90%), toluene (anhydrous 99.8%), hexane (reagent grade \geq 95%), octane (anhydrous, \geq 99%), 1-butanol (anhydrous 99.8%), methyl acetate (MeOAc, anhydrous 99.5%), lead (II) acetate trihydrate (Pb(OAc)₂·3H₂O, 99.999%), lead (II) nitrate (Pb(NO₃)₂, 99.999%), rhodamine-6G (99%), ethanol (EtOH, 200 proof, \geq 99.5%), titanium ethoxide (\geq 97%), hydrochloric acid (HCl, 37% in water), 2,2',7,7'-Tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD, Lumtec, ≥99.5%), chlorobenzene (anhydrous, 99.8%), 4-tert-butylpyridine, bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI), and acetonitrile (anhydrous, 99.8%).

7.IV.b Synthesis of Cs-oleate

0.5 g of Cs₂CO₃, 2 mL OA and 50 mL ODE were added to a 100 mL 3-necked round bottom flask and stirred under vacuum for 30 min at 120 °C. The flask was purged with N₂ for 10 min and then placed back under vacuum. This process of alternately applying vacuum and N₂ was repeated 3 times to remove moisture and O₂. The reaction was considered complete when the solution was clear, indicating that the Cs₂CO₃ had reacted with the OA. The Cs-oleate solution in ODE was stored in N₂ until it was needed for the NC synthesis.

7.IV.c Synthesis of colloidal CsPbI₃ QDs

CsPbI₃ QDs were synthesized following the previous report by Protesescu, *et al.*⁽¹¹⁾ with a few modifications, most notably scaling up the synthesis 10 times to have sufficient product for device fabrication. In our present work, various sizes of colloidal CsPbI₃ QDs were synthesized by tuning the reaction temperature. PbI₂ (1 g) and ODE (50 mL) were stirred in a 500 mL round bottom flask and degassed under vacuum (~0.1 Torr) at 120 °C for 1 hour. The flask was then filled with N₂ and kept under constant N₂ flow. OA and OLAm (5mL each, pre-heated at ~70 °C) were injected. The flask was put under vacuum again until the PbI₂ completely dissolved and the solution was no longer releasing gas (15 – 30 minutes). The temperature was then varied depending on the desired NC size (60 °C for 3.4 nm, 100 °C for 4.5 nm 130 °C for 5 nm 150 °C for 6.8 nm 170 °C for 8 nm, 180 °C for 9 nm QDs and 185 °C for 12.5 nm). The Cs-oleate (~0.0625 M, 8 mL) precursor, pre-heated at 70 °C under N₂ atmosphere, was swiftly injected into the reaction mixture. The reaction mixture turned dark red and the reaction was quenched by immediate immersion of the flask into an ice bath (5-7 seconds after injection).

7.IV.d Isolation of CsPbI₃ QDs

Due to the ionic nature of the CsPbI₃ QDs and the proposed ionic binding of the ligands, polar non-solvents traditionally used to wash QDs from reaction solutions instead dissolve the CsPbI₃ QDs. A variety of low polarity non-solvents were tested: 1-butanol, acetone and ethyl acetate destabilized the QDs and resulted in a yellowish suspension, while MeOAc successfully extracted cubic phase CsPbI₃ QDs. The synthesized CsPbI₃ QDs were precipitated by adding 200 mL MeOAc (ratio of NC reaction solution:MeOAc is 1:3) and then centrifuged at 8000 RPM for 5 min. The wet pellet of QDs in each centrifuge tube

was redispersed in 3 mL hexane, precipitated again with an equal volume MeOAc and centrifuged at 8000 RPM for 2 min. *Note: Adding excess MeOAc makes the QDs agglomerate and grow during the washing procedure.* The QDs were dispersed in 20 mL of hexane and centrifuged again at 4000 RPM for 5 min to remove excess PbI₂ and Cs-oleate. The solution of colloidal CsPbI₃ QDs was kept in the dark at 4 °C for 48 hours to remove excess unreacted precusor. The NC solution was decanted and centrifuged again at 4000 RPM for 5 min before use. For device fabrication, the hexane was dried and the QDs were dissolved in octane at a concentration of ~50 mg/mL. The temperature range of the synthesis is determined by the solubility of the precursors; Cs-oleate will not dissolve in ODE below 60 °C and PbI₂ begins to precipitate out of the reaction solution above 185 °C.

7.IV.e Characterization

UV-visible absorption spectra were recorded using a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer. Steady state photoluminescence (PL) and room temperature PL quantum yields were measured using a Horiba Jobin Yvon fluoromax-4 spectrophotometer. For quantum yield measurements, the QDs were dispersed in toluene using rhodamine 6G in EtOH as a reference. UV-visible absorption and PL experiments were done in solution and on thin films (prepared as described below). Powder X-ray diffraction data were recorded using a Bruker D8 Discover X-ray diffractometer with a Hi-Star 2D area detector using Cu K α radiation (1.54 Å). Transmission electron microscopy (TEM) studies were carried out using FEI T30 at 300 kV. TEM grids were prepared by dropping a dilute colloidal solution of QDs in a hexane-octane mixture onto the carbon coated copper grids.

To further explore the structural properties of the QDs, Rietveld analysis of the XRD data was performed using Materials Analysis Using Diffraction (MAUD)²⁹³ software (Figure

7.2, Table 7.1, Figure 7.4, and Table 7.2). In this analysis, the background structural parameters (atomic coordinates, occupancies, lattice parameters, *etc.*), and microstructural parameters (particle size, lattice strain, residual stress, *etc.*) are refined through a least-squares method. This XRD refinement shows that the cubic model provides quantitative fits of the experimental XRD patterns, while using the experimentally measured lattice parameters of the orthorhombic phase²⁸⁷ cannot be fitted with the XRD pattern. Due to the extreme peak broadening and increased background of the smallest size, Rietveld refinement of smaller sized CsPbI₃ nanocrystals is not possible, however peaks of cubic CsPbI₃ nanocrystals are observed to be present in the XRD data of all NC sizes.

7.IV.f Film Fabrication

Ligand solutions were made by sonicating 20 mg of (Pb(OAc)₂ or Pb(NO₃)₂) in 20 mL of anhydrous MeOAc for 10 minutes. The excess salt was removed by centrifugation at 4000 RPM for 5 minutes. The QDs (~50 mg/mL in octane) were spin-cast at 1000 RPM for 20 sec followed by 2000 RPM for 5 sec on the substrate and swiftly dipped 2-3 times in the ligand solution. The film was then rinsed using neat, anhydrous MeOAc, then dried with a stream of air. Films grown using only MeOAc were simply treated with a single rinsing step. This procedure was repeated for 3-5 cycles in order to build up 100 – 500 nm thick films.

7.IV.g Device Fabrication

 TiO_2 was deposited on FTO coated glass in the same way as the lead chalcogenide photovoltaic devices, described in Section 2.V.a. The CsPbI₃ NC photoactive layer was deposited using the procedure described above, resulting in a total thickness of ~150 nm. The hole-transporting layer was spin-coated from a solution consisting of 72.3 mg of spiro-

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OMeTAD in 1 mL of chlorobenzene, 28.8 μ L of 4-TBP, and 17.5 μ L of Li-TFSI solution (520 mg/mL in acetonitrile). All of the spin-coating processes were performed in ambient. MoO₃ (15 nm) and Al (200 nm) electrodes were deposited according to the procedure described in Section 2.V.e.

7.V Conclusion

Herein, we have shown greatly improved phase stability of all-inorganic halide perovskite materials. We utilize colloidal QDs to stabilize CsPbI₃ in the cubic perovskite phase, which is highly desirable for optoelectronic applications. We then developed a ligand exchange that removes the organic capping group, enabling electronic coupling of the nanocrystal film yet still preserving cubic phase stability. This results in the highest reported solar cell efficiency for an all-inorganic perovskite and we have recently fabricated devices performing higher than any QD PV cells. The devices can also be operated as LEDs when forward biased and show low turn-on voltages, while exhibiting exceptional phase stability compared with bulk or thin film versions of the same chemical composition. Further exploration of surface chemistry and ligand treatments will enable better control over the formation of conductive arrays, improving PV cell performance and long-term operational stability.

Chapter 8: Conclusion and Outlook

8.I Conclusions

In this thesis I have shown how the photophysical properties of QD materials can be tuned using surface chemistry modifications and how we exploit those properties to improve photovoltaic devices. We are able to use surface modifications to tune QD arrays of both lead chalcogenide and perovskite QDs with ligand exchange procedures and new synthetic techniques. The surface composition that results from the cation exchange synthesis produces lead chalcogenide QDs that are air-stable and show enhanced photophysical properties, and by changing the ligands during the CsPbI₃ QD synthesis I show improved stabilized power output.

Post-treating coupled QD arrays also influences the properties of the film. I have shown the efficient uptake of metal halide salts into PbSe QD arrays in order to control the transport properties and increase air-stability. Using these metal salt treatments I minimize the V_{oc} deficit in low-bandgap PbSe QD devices. This is an important step towards increasing the overall efficiency of low-bandgap PbSe QD devices, which are important for MEG-enhanced photovoltaics.

I also show the first fabrication of a perovskite QD solar cell, using CsPbI₃ stabilized in the cubic phase. I show that native ligands can be removed using methyl acetate and by employing a similar metal salt treatment as with the lead chalcogenide QDs I am able to tune the film properties without changing the QD composition.

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8.II Outlook

In the field of lead chalcogenide QDs, the energy level and density of trap states in the material has been a topic of discussion for many years. While many new surface treatments show promise in reducing trap states in this material, the physical or chemical identity of these trap states is still elusive. The initial measurements and hypotheses of trap states are presented in the introduction of Chapter 3. This information would be of great interest to the community and would provide researchers with a more directed path forward as new coupling strategies are explored for QD arrays. Another important advancement will be the measurement of MEG with the new ligand treatment schemes that are currently used in high-efficiency photovoltaic devices. In the past, it has been shown that the coupling strategy influences the MEG efficiency and with the plethora of new treatment schemes these measurements would be beneficial for the community.

CsPbX₃ QDs are still a very new material that will be the subject of many studies in the next few years. While we generally try to understand CsPbX₃ QDs in the framework of the metal chalcogenide QD systems, there are clear differences that require new in-depth analysis on surface chemistry and ligand effects. The highly ionic nature of the CsPbX₃ QD core requires the community to rethink how ligand exchanges and solvents interact with a QD surface. The high-efficiency devices our group was able to produce from CsPbI₃ QDs show immense potential for this material—especially for implementation as the top cell in a tandem photovoltaic device—so working to understand the surface chemistry will have high rewards. This material has the best properties of almost any high-bandgap material and the ability to solution process devices makes it highly amenable to low-cost fabrication. Overall, QD materials have proven to be highly useful in modern technology and with the recent advances will make their way into the solar cell market, possibly as stand-alone devices, but certainly in the context of tandem devices.

References

- (1) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of P-n Junction Solar Cells. *J. Appl. Phys.* **1961**, *32* (3), 510–519.
- (2) Nozik, A. J. Nanoscience and Nanostructures for Photovoltaics and Solar Fuels. *Nano Lett.* **2010**, *10* (8), 2735–2741.
- (3) Ross, R. T.; Nozik, A. J. Efficiency of Hot-carrier Solar Energy Converters. *Journal of Applied Physics* **1982**, *53* (5), 3813–3818.
- (4) Nozik, A. J. Photoelectrochemistry: Applications to Solar Energy Conversion. *Annual Review of Physical Chemistry* **1978**, *29* (1), 189–222.
- (5) Hanna, M. C.; Lu, Z.; Nozik, A. J. Hot Carrier Solar Cells. *AIP Conference Proceedings* **1997**, *404* (1), 309–316.
- (6) Green, M. A. Third Generation Photovoltaics: Ultra-High Conversion Efficiency at Low Cost. *Prog. Photovolt: Res. Appl.* **2001**, *9* (2), 123–135.
- (7) A. Martí, A. Luque. *Next Generation Photovoltaics: High Efficiency through Full Spectrum Utilization*; 2003.
- Hanna, M. C.; Nozik, A. J. Solar Conversion Efficiency of Photovoltaic and Photoelectrolysis Cells with Carrier Multiplication Absorbers. *J. Appl. Phys.* 2006, 100 (7), 74510-074510–074518.
- (9) Beard, M. C.; Midgett, A. G.; Hanna, M. C.; Luther, J. M.; Hughes, B. K.; Nozik, A. J. Comparing Multiple Exciton Generation in Quantum Dots To Impact Ionization in Bulk Semiconductors: Implications for Enhancement of Solar Energy Conversion. *Nano Lett.* **2010**, *10* (8), 3019–3027.
- (10) Semonin, O. E.; Luther, J. M.; Choi, S.; Chen, H.-Y.; Gao, J.; Nozik, A. J.; Beard, M. C. Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell. *Science* **2011**, *334* (6062), 1530–1533.
- (11) Nishihara, T.; Tahara, H.; Okano, M.; Ono, M.; Kanemitsu, Y. Fast Dissociation and Reduced Auger Recombination of Multiple Excitons in Closely Packed PbS Nanocrystal Thin Films. *J. Phys. Chem. Lett.* **2015**, 1327–1332.
- (12) Beard, M. C.; Luther, J. M.; Semonin, O. E.; Nozik, A. J. Third Generation Photovoltaics Based on Multiple Exciton Generation in Quantum Confined Semiconductors. *Acc. Chem. Res.* **2012**, *46* (6), 1252–1260.
- (13) Nozik, A. J.; Beard, M. C.; Luther, J. M.; Law, M.; Ellingson, R. J.; Johnson, J. C. Semiconductor Quantum Dots and Quantum Dot Arrays and Applications of Multiple

Exciton Generation to Third-Generation Photovoltaic Solar Cells. *Chem. Rev.* **2010**, *110* (11), 6873–6890.

- (14) Ekuma, C. E.; Singh, D. J.; Moreno, J.; Jarrell, M. Optical Properties of PbTe and PbSe. *Phys. Rev. B* **2012**, *85* (8), 85205.
- (15) Santoni, A.; Paolucci, G.; Santoro, G.; Prince, K. C.; Christensen, N. E. Band Structure of Lead Sulphide. *J. Phys.: Condens. Matter* **1992**, *4* (32), 6759.
- (16) Dutta, A. K.; Ho, T.; Zhang, L.; Stroeve, P. Nucleation and Growth of Lead Sulfide Nanoand Microcrystallites in Supramolecular Polymer Assemblies. *Chem. Mater.* 2000, *12* (4), 1042–1048.
- (17) Lipovskii, A.; Kolobkova, E.; Petrikov, V. Synthesis and Characterization of PbSe Quantum Dots in Phosphate Glass. *Appl. Phys. Lett.* **1997**, *71* (23), 3406–3408.
- (18) Semonin, O. E.; Luther, J. M.; Beard, M. C. Quantum Dots for next-Generation Photovoltaics. *Mater. Today* **2012**, *15* (11), 508–515.
- (19) Davis, N. J. L. K.; Böhm, M. L.; Tabachnyk, M.; Wisnivesky-Rocca-Rivarola, F.; Jellicoe, T. C.; Ducati, C.; Ehrler, B.; Greenham, N. C. Multiple-Exciton Generation in Lead Selenide Nanorod Solar Cells with External Quantum Efficiencies Exceeding 120%. *Nature Communications* 2015, *6*, 8259.
- (20) Schaller, R. D.; Klimov, V. I. High Efficiency Carrier Multiplication in PbSe Nanocrystals: Implications for Solar Energy Conversion. *Phys. Rev. Lett.* 2004, *92* (18), 186601.
- (21) Padilha, L. A.; Stewart, J. T.; Sandberg, R. L.; Bae, W. K.; Koh, W.-K.; Pietryga, J. M.; Klimov, V. I. Aspect Ratio Dependence of Auger Recombination and Carrier Multiplication in PbSe Nanorods. *Nano Lett.* **2013**, *13* (3), 1092–1099.
- (22) Cunningham, P. D.; Boercker, J. E.; Foos, E. E.; Lumb, M. P.; Smith, A. R.; Tischler, J. G.; Melinger, J. S. Enhanced Multiple Exciton Generation in Quasi-One-Dimensional Semiconductors. *Nano Lett.* **2011**, *11* (8), 3476–3481.
- (23) Cunningham, P. D.; Boercker, J. E.; Foos, E. E.; Lumb, M. P.; Smith, A. R.; Tischler, J. G.; Melinger, J. S. Correction to Enhanced Multiple Exciton Generation in Quasi-One-Dimensional Semiconductors. *Nano Lett.* **2013**, *13* (6), 3003–3003.
- (24) Brus, L. Electronic Wave Functions in Semiconductor Clusters: Experiment and Theory. *J. Phys. Chem.* **1986**, *90* (12), 2555–2560.
- (25) Brus, L. E. Electron–electron and Electron-hole Interactions in Small Semiconductor Crystallites: The Size Dependence of the Lowest Excited Electronic State. *J. Chem. Phys.* **1984**, *80* (9), 4403.

- (26) Hines, M. a.; Scholes, G. d. Colloidal PbS Nanocrystals with Size-Tunable Near-Infrared Emission: Observation of Post-Synthesis Self-Narrowing of the Particle Size Distribution. *Adv. Mater.* **2003**, *15* (21), 1844–1849.
- (27) Zhang, J.; Crisp, R. W.; Gao, J.; Kroupa, D. M.; Beard, M. C.; Luther, J. M. Synthetic Conditions for High-Accuracy Size Control of PbS Quantum Dots. *J. Phys. Chem. Lett.* 2015, 6 (10), 1830–1833.
- (28) Law, M.; Beard, M. C.; Choi, S.; Luther, J. M.; Hanna, M. C.; Nozik, A. J. Determining the Internal Quantum Efficiency of PbSe Nanocrystal Solar Cells with the Aid of an Optical Model. *Nano Lett.* **2008**, *8* (11), 3904–3910.
- (29) Steckel, J. S.; Yen, B. K. H.; Oertel, D. C.; Bawendi, M. G. On the Mechanism of Lead Chalcogenide Nanocrystal Formation. J. Am. Chem. Soc. 2006, 128 (40), 13032– 13033.
- (30) Steckel, J. s.; Coe-Sullivan, S.; Bulović, V.; Bawendi, M. g. 1.3 Mm to 1.55 Mm Tunable Electroluminescence from PbSe Quantum Dots Embedded within an Organic Device. *Adv. Mater.* **2003**, *15* (21), 1862–1866.
- (31) Son, D. H.; Hughes, S. M.; Yin, Y.; Alivisatos, A. P. Cation Exchange Reactions in Ionic Nanocrystals. *Science* **2004**, *306* (5698), 1009–1012.
- (32) Luther, J. M.; Zheng, H.; Sadtler, B.; Alivisatos, A. P. Synthesis of PbS Nanorods and Other Ionic Nanocrystals of Complex Morphology by Sequential Cation Exchange Reactions. *J. Am. Chem. Soc.* **2009**, *131* (46), 16851–16857.
- (33) Casavola, M.; van Huis, M. A.; Bals, S.; Lambert, K.; Hens, Z.; Vanmaekelbergh, D. Anisotropic Cation Exchange in PbSe/CdSe Core/Shell Nanocrystals of Different Geometry. *Chem. Mater.* **2011**, *24* (2), 294–302.
- (34) Neo, D. C. J.; Cheng, C.; Stranks, S. D.; Fairclough, S. M.; Kim, J. S.; Kirkland, A. I.; Smith, J. M.; Snaith, H. J.; Assender, H. E.; Watt, A. A. R. Influence of Shell Thickness and Surface Passivation on PbS/CdS Core/Shell Colloidal Quantum Dot Solar Cells. *Chem. Mater.* 2014, *26* (13), 4004–4013.
- (35) Ren, F.; Zhao, H.; Vetrone, F.; Ma, D. Microwave-Assisted Cation Exchange toward Synthesis of near-Infrared Emitting PbS/CdS Core/Shell Quantum Dots with Significantly Improved Quantum Yields through a Uniform Growth Path. *Nanoscale* 2013, 5 (17), 7800.
- (36) Zhang, J.; Chernomordik, B. D.; Crisp, R. W.; Kroupa, D. M.; Luther, J. M.; Miller, E. M.; Gao, J.; Beard, M. C. Preparation of Cd/Pb Chalcogenide Heterostructured Janus Particles via Controllable Cation Exchange. ACS Nano 2015, 9 (7), 7151–7163.
- (37) Pietryga, J. M.; Werder, D. J.; Williams, D. J.; Casson, J. L.; Schaller, R. D.; Klimov, V. I.; Hollingsworth, J. A. Utilizing the Lability of Lead Selenide to Produce

Heterostructured Nanocrystals with Bright, Stable Infrared Emission. J. Am. Chem. Soc. **2008**, 130 (14), 4879–4885.

- (38) Zhang, J.; Gao, J.; Church, C. P.; Miller, E. M.; Luther, J. M.; Klimov, V. I.; Beard, M. C. PbSe Quantum Dot Solar Cells with More than 6% Efficiency Fabricated in Ambient Atmosphere. *Nano Lett.* **2014**, *14* (10), 6010–6015.
- (39) Crisp, R. W.; Kroupa, D. M.; Marshall, A. R.; Miller, E. M.; Zhang, J.; Beard, M. C.; Luther, J. M. Metal Halide Solid-State Surface Treatment for High Efficiency PbS and PbSe QD Solar Cells. *Sci. Rep.* 2015, *5*.
- (40) Zhang, J.; Gao, J.; Miller, E. M.; Luther, J. M.; Beard, M. C. Diffusion-Controlled Synthesis of PbS and PbSe Quantum Dots with in Situ Halide Passivation for Quantum Dot Solar Cells. ACS Nano 2014, 8 (1), 614–622.
- (41) Guyot-Sionnest, P. Electrical Transport in Colloidal Quantum Dot Films. *J. Phys. Chem. Lett.* **2012**, *3* (9), 1169–1175.
- (42) Tang, J.; Kemp, K. W.; Hoogland, S.; Jeong, K. S.; Liu, H.; Levina, L.; Furukawa, M.; Wang, X.; Debnath, R.; Cha, D.; et al. Colloidal-Quantum-Dot Photovoltaics Using Atomic-Ligand Passivation. *Nature Mater.* **2011**, *10* (10), 765–771.
- (43) Ip, A. H.; Thon, S. M.; Hoogland, S.; Voznyy, O.; Zhitomirsky, D.; Debnath, R.; Levina, L.; Rollny, L. R.; Carey, G. H.; Fischer, A.; et al. Hybrid Passivated Colloidal Quantum Dot Solids. *Nature Nanotech.* **2012**, *7* (9), 577–582.
- (44) Ip, A. H.; Kiani, A.; Kramer, I. J.; Voznyy, O.; Movahed, H. F.; Levina, L.; Adachi, M. M.; Hoogland, S.; Sargent, E. H. Infrared Colloidal Quantum Dot Photovoltaics via Coupling Enhancement and Agglomeration Suppression. ACS Nano 2015.
- (45) Thon, S. M.; Ip, A. H.; Voznyy, O.; Levina, L.; Kemp, K. W.; Carey, G. H.; Masala, S.; Sargent, E. H. Role of Bond Adaptability in the Passivation of Colloidal Quantum Dot Solids. ACS Nano 2013, 7 (9), 7680–7688.
- (46) Bae, W. K.; Joo, J.; Padilha, L. A.; Won, J.; Lee, D. C.; Lin, Q.; Koh, W.; Luo, H.; Klimov, V. I.; Pietryga, J. M. Highly Effective Surface Passivation of PbSe Quantum Dots through Reaction with Molecular Chlorine. *J. Am. Chem. Soc.* **2012**, *134* (49), 20160–20168.
- (47) Weidman, M. C.; Beck, M. E.; Hoffman, R. S.; Prins, F.; Tisdale, W. A. Monodisperse, Air-Stable PbS Nanocrystals via Precursor Stoichiometry Control. ACS Nano 2014, 8 (6), 6363–6371.
- (48) Hendricks, M. P.; Campos, M. P.; Cleveland, G. T.; Plante, I. J.-L.; Owen, J. S. A Tunable Library of Substituted Thiourea Precursors to Metal Sulfide Nanocrystals. *Science* 2015, 348 (6240), 1226–1230.

- (49) Campos, M. P.; Hendricks, M. P.; Beecher, A. N.; Walravens, W.; Swain, R. A.; Cleveland, G. T.; Hens, Z.; Sfeir, M. Y.; Owen, J. S. A Library of Selenourea Precursors to PbSe Nanocrystals with Size Distributions near the Homogeneous Limit. *J. Am. Chem. Soc.* 2017, 139 (6), 2296–2305.
- (50) Anderson, N. C.; Hendricks, M. P.; Choi, J. J.; Owen, J. S. Ligand Exchange and the Stoichiometry of Metal Chalcogenide Nanocrystals: Spectroscopic Observation of Facile Metal-Carboxylate Displacement and Binding. *J. Am. Chem. Soc.* 2013, 135 (49), 18536–18548.
- (51) Owen, J. S.; Park, J.; Trudeau, P.-E.; Alivisatos, A. P. Reaction Chemistry and Ligand Exchange at Cadmium–Selenide Nanocrystal Surfaces. *J. Am. Chem. Soc.* 2008, 130 (37), 12279–12281.
- (52) Moreels, I.; Lambert, K.; De Muynck, D.; Vanhaecke, F.; Poelman, D.; Martins, J. C.; Allan, G.; Hens, Z. Composition and Size-Dependent Extinction Coefficient of Colloidal PbSe Quantum Dots. *Chem. Mater.* 2007, 19 (25), 6101–6106.
- (53) Moreels, I.; Fritzinger, B.; Martins, J. C.; Hens, Z. Surface Chemistry of Colloidal PbSe Nanocrystals. *J. Am. Chem. Soc.* **2008**, *130* (45), 15081–15086.
- Moreels, I.; Justo, Y.; De Geyter, B.; Haustraete, K.; Martins, J. C.; Hens, Z. Size-Tunable, Bright, and Stable PbS Quantum Dots: A Surface Chemistry Study. *ACS Nano* 2011, 5 (3), 2004–2012.
- (55) Cass, L. C.; Malicki, M.; Weiss, E. A. The Chemical Environments of Oleate Species within Samples of Oleate-Coated PbS Quantum Dots. *Anal. Chem.* **2013**, *85* (14), 6974–6979.
- (56) Morris-Cohen, A. J.; Malicki, M.; Peterson, M. D.; Slavin, J. W. J.; Weiss, E. A. Chemical, Structural, and Quantitative Analysis of the Ligand Shells of Colloidal Quantum Dots. *Chem. Mater.* **2013**, *25* (8), 1155–1165.
- (57) Dai, Q.; Wang, Y.; Li, X.; Zhang, Y.; Pellegrino, D. J.; Zhao, M.; Zou, B.; Seo, J.; Wang, Y.; Yu, W. W. Size-Dependent Composition and Molar Extinction Coefficient of PbSe Semiconductor Nanocrystals. *ACS Nano* **2009**, *3* (6), 1518–1524.
- (58) Kim, S.; Noh, J.; Choi, H.; Ha, H.; Song, J. H.; Shim, H. C.; Jang, J.; Beard, M. C.; Jeong, S. One-Step Deposition of Photovoltaic Layers Using Iodide Terminated PbS Quantum Dots. *J. Phys. Chem. Lett.* **2014**, *5* (22), 4002–4007.
- (59) Kagan, C. R.; Lifshitz, E.; Sargent, E. H.; Talapin, D. V. Building Devices from Colloidal Quantum Dots. *Science* **2016**, *353* (6302), aac5523.
- (60) Ning, Z.; Dong, H.; Zhang, Q.; Voznyy, O.; Sargent, E. H. Solar Cells Based on Inks of N-Type Colloidal Quantum Dots. ACS Nano 2014, 8 (10), 10321–10327.

- (61) Liu, M.; Voznyy, O.; Sabatini, R.; García de Arquer, F. P.; Munir, R.; Balawi, A. H.; Lan, X.; Fan, F.; Walters, G.; Kirmani, A. R.; et al. Hybrid Organic-Inorganic Inks Flatten the Energy Landscape in Colloidal Quantum Dot Solids. *Nat Mater* **2017**, *16* (2), 258–263.
- (62) Fischer, A.; Rollny, L.; Pan, J.; Carey, G. H.; Thon, S. M.; Hoogland, S.; Voznyy, O.; Zhitomirsky, D.; Kim, J. Y.; Bakr, O. M.; et al. Directly Deposited Quantum Dot Solids Using a Colloidally Stable Nanoparticle Ink. *Adv. Mater.* **2013**, *25* (40), 5742–5749.
- (63) Giansante, C.; Carbone, L.; Giannini, C.; Altamura, D.; Ameer, Z.; Maruccio, G.; Loiudice, A.; Belviso, M. R.; Cozzoli, P. D.; Rizzo, A.; et al. Colloidal Arenethiolate-Capped PbS Quantum Dots: Optoelectronic Properties, Self-Assembly, and Application in Solution-Cast Photovoltaics. *J. Phys. Chem. C* **2013**, *117* (25), 13305–13317.
- (64) Brown, P. R.; Kim, D.; Lunt, R. R.; Zhao, N.; Bawendi, M. G.; Grossman, J. C.; Bulović, V. Energy Level Modification in Lead Sulfide Quantum Dot Thin Films through Ligand Exchange. ACS Nano 2014, 8 (6), 5863–5872.
- (65) Debellis, D.; Gigli, G.; ten Brinck, S.; Infante, I.; Giansante, C. Quantum-Confined and Enhanced Optical Absorption of Colloidal PbS Quantum Dots at Wavelengths with Expected Bulk Behavior. *Nano Lett.* **2017**, *17* (2), 1248–1254.
- Luther, J. M.; Beard, M. C.; Song, Q.; Law, M.; Ellingson, R. J.; Nozik, A. J. Multiple Exciton Generation in Films of Electronically Coupled PbSe Quantum Dots. *Nano Lett.* 2007, 7 (6), 1779–1784.
- (67) Kim, H.-S.; Lee, C.-R.; Im, J.-H.; Lee, K.-B.; Moehl, T.; Marchioro, A.; Moon, S.-J.; Humphry-Baker, R.; Yum, J.-H.; Moser, J. E.; et al. Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%. *Scientific Reports* **2012**, *2*, 591.
- (68) Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J. Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. *Science* 2012, 338 (6107), 643–647.
- (69) Yang, W. S.; Noh, J. H.; Jeon, N. J.; Kim, Y. C.; Ryu, S.; Seo, J.; Seok, S. I. High-Performance Photovoltaic Perovskite Layers Fabricated through Intramolecular Exchange. *Science* 2015, 348 (6240), 1234–1237.
- (70) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D.; Levi, D. H.; Ho-Baillie, A. W. Y. Solar Cell Efficiency Tables (Version 49). *Prog. Photovolt: Res. Appl.* 2017, 25 (1), 3–13.
- (71) Solar Cell Efficiency. Wikipedia; 2017.
- (72) Green, M. A.; Jiang, Y.; Soufiani, A. M.; Ho-Baillie, A. Optical Properties of Photovoltaic Organic–Inorganic Lead Halide Perovskites. *J. Phys. Chem. Lett.* **2015**, 6 (23), 4774– 4785.

- (73) Li, Z.; Yang, M.; Park, J.-S.; Wei, S.-H.; Berry, J. J.; Zhu, K. Stabilizing Perovskite Structures by Tuning Tolerance Factor: Formation of Formamidinium and Cesium Lead Iodide Solid-State Alloys. *Chem. Mater.* **2016**, *28* (1), 284–292.
- (74) Schmidt, L. C.; Pertegás, A.; González-Carrero, S.; Malinkiewicz, O.; Agouram, S.; Mínguez Espallargas, G.; Bolink, H. J.; Galian, R. E.; Pérez-Prieto, J. Nontemplate Synthesis of CH3NH3PbBr3 Perovskite Nanoparticles. *J. Am. Chem. Soc.* 2014, 136 (3), 850–853.
- (75) Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V. Nanocrystals of Cesium Lead Halide Perovskites (CsPbX3, X = Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15* (6), 3692–3696.
- (76) Swarnkar, A.; Chulliyil, R.; Ravi, V. K.; Irfanullah, M.; Chowdhury, A.; Nag, A. Colloidal CsPbBr3 Perovskite Nanocrystals: Luminescence beyond Traditional Quantum Dots. *Angew. Chem. Int. Ed.* **2015**, *54* (51), 15424–15428.
- (77) Bai, S.; Yuan, Z.; Gao, F. Colloidal Metal Halide Perovskite Nanocrystals: Synthesis, Characterization, and Applications. *J. Mater. Chem. C* **2016**, *4* (18), 3898–3904.
- (78) Wang, Y.; Li, X.; Song, J.; Xiao, L.; Zeng, H.; Sun, H. All-Inorganic Colloidal Perovskite Quantum Dots: A New Class of Lasing Materials with Favorable Characteristics. *Adv. Mater.* **2015**, *27* (44), 7101–7108.
- (79) Xu, Y.; Chen, Q.; Zhang, C.; Wang, R.; Wu, H.; Zhang, X.; Xing, G.; Yu, W. W.; Wang, X.; Zhang, Y.; et al. Two-Photon-Pumped Perovskite Semiconductor Nanocrystal Lasers. *J. Am. Chem. Soc.* **2016**, *138* (11), 3761–3768.
- (80) Hu, F.; Zhang, H.; Sun, C.; Yin, C.; Lv, B.; Zhang, C.; Yu, W. W.; Wang, X.; Zhang, Y.; Xiao, M. Superior Optical Properties of Perovskite Nanocrystals as Single Photon Emitters. *ACS Nano* **2015**, *9* (12), 12410–12416.
- (81) Yakunin, S.; Protesescu, L.; Krieg, F.; Bodnarchuk, M. I.; Nedelcu, G.; Humer, M.; Luca, G. D.; Fiebig, M.; Heiss, W.; Kovalenko, M. V. Low-Threshold Amplified Spontaneous Emission and Lasing from Colloidal Nanocrystals of Caesium Lead Halide Perovskites. *Nature Communications* **2015**, *6*, 8056.
- (82) E. Eperon, G.; M. Paternò, G.; J. Sutton, R.; Zampetti, A.; Abbas Haghighirad, A.; Cacialli, F.; J. Snaith, H. Inorganic Caesium Lead Iodide Perovskite Solar Cells. *Journal of Materials Chemistry A* 2015, *3* (39), 19688–19695.
- (83) Sutton, R. J.; Eperon, G. E.; Miranda, L.; Parrott, E. S.; Kamino, B. A.; Patel, J. B.; Hörantner, M. T.; Johnston, M. B.; Haghighirad, A. A.; Moore, D. T.; et al. Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells. *Adv. Energy Mater.* **2016**, *6* (8), n/a-n/a.

- (84) Tolbert, S. H.; Alivisatos, A. P. Size Dependence of a First Order Solid-Solid Phase Transition: The Wurtzite to Rock Salt Transformation in CdSe Nanocrystals. *Science* **1994**, *265* (5170), 373–376.
- (85) Alivisatos, A. P. Semiconductor Clusters, Nanocrystals, and Quantum Dots. *Science* **1996**, *271* (5251), 933–937.
- (86) Nenon, D. P.; Christians, J. A.; Wheeler, L. M.; Blackburn, J. L.; Sanehira, E. M.; Dou, B.; Olsen, M. L.; Zhu, K.; Berry, J. J.; Luther, J. M. Structural and Chemical Evolution of Methylammonium Lead Halide Perovskites during Thermal Processing from Solution. *Energy Environ. Sci.* **2016**, *9* (6), 2072–2082.
- (87) Akbulatov, A. F.; Luchkin, S. Y.; Frolova, L. A.; Dremova, N. N.; Gerasimov, K. L.; Zhidkov, I. S.; Anokhin, D. V.; Kurmaev, E. Z.; Stevenson, K. J.; Troshin, P. A. Probing the Intrinsic Thermal and Photochemical Stability of Hybrid and Inorganic Lead Halide Perovskites. *J. Phys. Chem. Lett.* **2017**, 1211–1218.
- (88) De Roo, J.; Ibáñez, M.; Geiregat, P.; Nedelcu, G.; Walravens, W.; Maes, J.; Martins, J. C.; Van Driessche, I.; Kovalenko, M. V.; Hens, Z. Highly Dynamic Ligand Binding and Light Absorption Coefficient of Cesium Lead Bromide Perovskite Nanocrystals. *ACS Nano* 2016, 10 (2), 2071–2081.
- (89) Pan, A.; He, B.; Fan, X.; Liu, Z.; Urban, J. J.; Alivisatos, A. P.; He, L.; Liu, Y. Insight into the Ligand-Mediated Synthesis of Colloidal CsPbBr3 Perovskite Nanocrystals: The Role of Organic Acid, Base, and Cesium Precursors. ACS Nano 2016, 10 (8), 7943–7954.
- (90) Parobek, D.; Dong, Y.; Qiao, T.; Rossi, D.; Son, D. H. Photoinduced Anion Exchange in Cesium Lead Halide Perovskite Nanocrystals. *J. Am. Chem. Soc.* **2017**.
- (91) Nedelcu, G.; Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Grotevent, M. J.; Kovalenko, M. V. Fast Anion-Exchange in Highly Luminescent Nanocrystals of Cesium Lead Halide Perovskites (CsPbX3, X = Cl, Br, I). *Nano Lett.* **2015**, *15* (8), 5635–5640.
- (92) Akkerman, Q. A.; D'Innocenzo, V.; Accornero, S.; Scarpellini, A.; Petrozza, A.; Prato, M.; Manna, L. Tuning the Optical Properties of Cesium Lead Halide Perovskite Nanocrystals by Anion Exchange Reactions. *J. Am. Chem. Soc.* 2015, 137 (32), 10276– 10281.
- (93) Zhang, D.; Yang, Y.; Bekenstein, Y.; Yu, Y.; Gibson, N. A.; Wong, A. B.; Eaton, S. W.; Kornienko, N.; Kong, Q.; Lai, M.; et al. Synthesis of Composition Tunable and Highly Luminescent Cesium Lead Halide Nanowires through Anion-Exchange Reactions. *J. Am. Chem. Soc.* **2016**, *138* (23), 7236–7239.
- (94) Bekenstein, Y.; Koscher, B. A.; Eaton, S. W.; Yang, P.; Alivisatos, A. P. Highly Luminescent Colloidal Nanoplates of Perovskite Cesium Lead Halide and Their Oriented Assemblies. *J. Am. Chem. Soc.* **2015**, *137* (51), 16008–16011.

- (95) Luther, J. M.; Law, M.; Beard, M. C.; Song, Q.; Reese, M. O.; Ellingson, R. J.; Nozik, A. J. Schottky Solar Cells Based on Colloidal Nanocrystal Films. *Nano Lett.* **2008**, *8* (10), 3488–3492.
- (96) Pattantyus-Abraham, A. G.; Kramer, I. J.; Barkhouse, A. R.; Wang, X.; Konstantatos, G.; Debnath, R.; Levina, L.; Raabe, I.; Nazeeruddin, M. K.; Grätzel, M.; et al. Depleted-Heterojunction Colloidal Quantum Dot Solar Cells. *ACS Nano* **2010**, *4* (6), 3374–3380.
- (97) Chuang, C.-H. M.; Brown, P. R.; Bulović, V.; Bawendi, M. G. Improved Performance and Stability in Quantum Dot Solar Cells through Band Alignment Engineering. *Nature Mater.* **2014**, *13* (8), 796–801.
- (98) Chernomordik, B. D.; Marshall, A. R.; Pach, G. F.; Luther, J. M.; Beard, M. C. Quantum Dot Solar Cell Fabrication Protocols. *Chem. Mater.* **2017**, *29* (1), 189–198.
- (99) Lan, X.; Voznyy, O.; Kiani, A.; García de Arquer, F. P.; Abbas, A. S.; Kim, G.-H.; Liu, M.; Yang, Z.; Walters, G.; Xu, J.; et al. Passivation Using Molecular Halides Increases Quantum Dot Solar Cell Performance. *Adv. Mater.* **2015**, n/a-n/a.
- (100) Chuang, C.-H. M.; Maurano, A.; Brandt, R. E.; Hwang, G. W.; Jean, J.; Buonassisi, T.; Bulović, V.; Bawendi, M. G. Open-Circuit Voltage Deficit, Radiative Sub-Bandgap States, and Prospects in Quantum Dot Solar Cells. *Nano Lett.* **2015**, *15* (5), 3286– 3294.
- (101) Kiani, A.; Brandon R. Sutherland; Younghoon Kim; Olivier Ouellette; Larissa Levina; Grant Walters; Cao-Thang Dinh; Mengxia Liu; Oleksandr Voznyy; Xinzheng Lan; et al. Single-Step Colloidal Quantum Dot Films for Infrared Solar Harvesting. *Appl. Phys. Lett.* **2016**, *109* (18), 183105.
- (102) Kim, S.; Marshall, A. R.; Kroupa, D. M.; Miller, E. M.; Luther, J. M.; Jeong, S.; Beard, M. C. Air-Stable and Efficient PbSe Quantum-Dot Solar Cells Based upon ZnSe to PbSe Cation-Exchanged Quantum Dots. *ACS Nano* **2015**, *9* (8), 8157–8164.
- (103) Marshall, A. R.; Beard, M. C.; Johnson, J. C. Nongeminate Radiative Recombination of Free Charges in Cation-Exchanged PbS Quantum Dot Films. *Chemical Physics* 2016, 471, 75–80.
- (104) Zhitomirsky, D.; Furukawa, M.; Tang, J.; Stadler, P.; Hoogland, S.; Voznyy, O.; Liu, H.; Sargent, E. H. N-Type Colloidal-Quantum-Dot Solids for Photovoltaics. *Adv. Mater.* 2012, *24* (46), 6181–6185.
- (105) Ning, Z.; Voznyy, O.; Pan, J.; Hoogland, S.; Adinolfi, V.; Xu, J.; Li, M.; Kirmani, A. R.; Sun, J.-P.; Minor, J.; et al. Air-Stable N-Type Colloidal Quantum Dot Solids. *Nature Mater.* 2014, *13* (8), 822–828.
- (106) Oh, S. J.; Uswachoke, C.; Zhao, T.; Choi, J.-H.; Diroll, B. T.; Murray, C. B.; Kagan, C. R. Selective P- and N-Doping of Colloidal PbSe Nanowires To Construct Electronic and Optoelectronic Devices. *ACS Nano* **2015**, *9* (7), 7536–7544.
- (107) Oh, S. J.; Berry, N. E.; Choi, J.-H.; Gaulding, E. A.; Lin, H.; Paik, T.; Diroll, B. T.; Muramoto, S.; Murray, C. B.; Kagan, C. R. Designing High-Performance PbS and PbSe Nanocrystal Electronic Devices through Stepwise, Post-Synthesis, Colloidal Atomic Layer Deposition. *Nano Lett.* **2014**, *14* (3), 1559–1566.
- (108) Brown, P. R.; Kim, D.; Lunt, R. R.; Zhao, N.; Bawendi, M. G.; Grossman, J. C.; Bulovi, V. Energy Level Modification in Lead Sulfide Quantum Dot Thin Films through Ligand Exchange. *ACS Nano* **2014**, *8* (6), 5863–5872.
- (109) Goodwin, E. D.; Straus, D. B.; Gaulding, E. A.; Murray, C. B.; Kagan, C. R. The Effects of Inorganic Surface Treatments on Photogenerated Carrier Mobility and Lifetime in PbSe Quantum Dot Thin Films. *Chemical Physics* **2015**, *471*, 32–36.
- (110) Klimov, V. I.; Baker, T. A.; Lim, J.; Velizhanin, K. A.; McDaniel, H. Quality Factor of Luminescent Solar Concentrators and Practical Concentration Limits Attainable with Semiconductor Quantum Dots. *ACS Photonics* **2016**, *3* (6), 1138–1148.
- (111) Ellingson, R. J.; Beard, M. C.; Johnson, J. C.; Yu, P.; Micic, O. I.; Nozik, A. J.; Shabaev, A.; Efros, A. L. Highly Efficient Multiple Exciton Generation in Colloidal PbSe and PbS Quantum Dots. *Nano Letters* **2005**, *5* (5), 865–871.
- (112) Lee, D. C.; Robel, I.; Pietryga, J. M.; Klimov, V. I. Infrared-Active Heterostructured Nanocrystals with Ultralong Carrier Lifetimes. *Journal of the American Chemical Society* **2010**, *132* (29), 9960–9962.
- (113) Cirloganu, C. M.; Padilha, L. a; Lin, Q.; Makarov, N. S.; Velizhanin, K. a; Luo, H.; Robel, I.; Pietryga, J. M.; Klimov, V. I. Enhanced Carrier Multiplication in Engineered Quasi-Type-II Quantum Dots. *Nature Communications* **2014**, *5*, 4148.
- (114) Brown, P. R.; Kim, D.; Lunt, R. R.; Zhao, N.; Bawendi, M. G.; Grossman, J. C.; Bulovic, V. Energy Level Modification in Lead Sulfide Quantum Dot Thin Films Through Ligand Exchange. ACS nano 2014, 8 (6), 5863–5872.
- (115) Supran, G. J.; Shirasaki, Y.; Song, K. W.; Caruge, J.-M.; Kazlas, P. T.; Coe-Sullivan, S.; Andrew, T. L.; Bawendi, M. G.; Bulović, V. QLEDs for Displays and Solid-State Lighting. *MRS Bulletin* **2013**, *38* (9), 703–711.
- (116) Konstantatos, G.; Badioli, M.; Gaudreau, L.; Osmond, J.; Bernechea, M.; de Arquer, F. P. G.; Gatti, F.; Koppens, F. H. L. Hybrid graphene–Quantum Dot Phototransistors with Ultrahigh Gain. *Nature Nanotechnology* **2012**, *7* (6), 363–368.
- (117) Kim, S.; Lim, Y. T.; Soltesz, E. G.; De Grand, A. M.; Lee, J.; Nakayama, A.; Parker, J. A.; Mihaljevic, T.; Laurence, R. G.; Dor, D. M.; et al. Near-Infrared Fluorescent Type II

Quantum Dots for Sentinel Lymph Node Mapping. *Nature biotechnology* **2004**, *22* (1), 93–97.

- (118) Lan, X.; Voznyy, O.; García de Arquer, F. P.; Liu, M.; Xu, J.; Proppe, A. H.; Walters, G.; Fan, F.; Tan, H.; Liu, M.; et al. 10.6% Certified Colloidal Quantum Dot Solar Cells via Solvent-Polarity-Engineered Halide Passivation. *Nano Letters* 2016, *16* (7), 4630– 4634.
- (119) Wang, H.; Pei, Y.; Lalonde, A. D.; Snyder, G. J. Heavily Doped P-Type PbSe with High Thermoelectric Performance: An Alternative for PbTe. *Advanced Materials* 2011, *23* (11), 1366–1370.
- (120) Supran, G. J.; Song, K. W.; Hwang, G. W.; Correa, R. E.; Scherer, J.; Dauler, E. a; Shirasaki, Y.; Bawendi, M. G.; Bulović, V. High-Performance Shortwave-Infrared Light-Emitting Devices Using Core–Shell (PbS–CdS) Colloidal Quantum Dots. *Advanced Materials* 2015, 1437–1442.
- (121) Mashford, B.; Stevenson, M.; Popovic, Z. High-Efficiency Quantum-Dot Light-Emitting Devices with Enhanced Charge Injection. *Nature Photonics* **2013**, *7*, 407–412.
- (122) Hanna, M. C.; Nozik, a. J. Solar Conversion Efficiency of Photovoltaic and Photoelectrolysis Cells with Carrier Multiplication Absorbers. *Journal of Applied Physics* **2006**, *100* (7), 74510.
- (123) Semonin, O. E.; Luther, J. M.; Choi, S.; Chen, H.-Y.; Gao, J.; Nozik, a. J.; Beard, M. C. Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell. *Science* **2011**, *334* (6062), 1530–1533.
- (124) Davis, N. J. L. K.; Böhm, M. L.; Tabachnyk, M.; Wisnivesky-Rocca-Rivarola, F.; Jellicoe, T. C.; Ducati, C.; Ehrler, B.; Greenham, N. C. Multiple-Exciton Generation in Lead Selenide Nanorod Solar Cells with External Quantum Efficiencies Exceeding 120%. *Nature Communications* 2015, 6, 8259.
- (125) Böhm, M. L.; Jellicoe, T. C.; Tabachnyk, M.; Davis, N. J. L. K.; Wisnivesky Rocca Rivarola, F.; Ducati, C.; Ehrler, B.; Bakulin, A. a.; Greenham, N. C. Lead Telluride Quantum Dot Solar Cells Displaying External Quantum Efficiencies Exceeding 120%. *Nano Letters* **2015**, *15* (12), 7987–7993.
- (126) Cunningham, P. D.; Boercker, J. E.; Foos, E. E.; Lumb, M. P.; Smith, A. R.; Tischler, J. G.; Melinger, J. S. Enhanced Multiple Exciton Generation in Quasi-One-Dimensional Semiconductors. *Nano Letters* **2011**, *11* (8), 3476–3481.
- (127) Yang, Y.; Ostrowski, D. P.; France, R. M.; Zhu, K.; van de Lagemaat, J.; Luther, J. M.; Beard, M. C. Observation of a Hot-Phonon Bottleneck in Lead-Iodide Perovskites. *Nature Photonics* **2016**, *10*, 53–59.

- (128) Du, J.; Du, Z.; Hu, J.-S.; Pan, Z.; Shen, Q.; Sun, J.; Long, D.; Dong, H.; Sun, L.; Zhong, X.; et al. Zn-Cu-In-Se Quantum Dot Solar Cells with a Certified Power Conversion Efficiency of 11.6. *Journal of the American Chemical Society* **2016**, *138* (12), 4201–4209.
- (129) Zhang, J.; Chernomordik, B. D.; Crisp, R. W.; Kroupa, D. M.; Luther, J. M.; Miller, E. M.; Gao, J.; Beard, M. C. Preparation of Cd/Pb Chalcogenide Heterostructured Janus Particles via Controllable Cation Exchange. ACS Nano 2015, 9 (7), 7151–7163.
- (130) Zhang, J.; Gao, J.; Church, C. P.; Miller, E. M.; Luther, J. M.; Klimov, V. I.; Beard, M. C. PbSe Quantum Dot Solar Cells with More than 6% Efficiency Fabricated in Ambient Atmosphere. *Nano letters* **2014**, *14* (10), 6010–6015.
- (131) Hu, Y.; Diao, X.; Wang, C.; Hao, W.; Wang, T. Effects of Heat Treatment on Properties of ITO Films Prepared by Rf Magnetron Sputtering. *Vacuum* **2004**, *75* (2), 183–188.
- (132) Church, C. P.; Muthuswamy, E.; Zhai, G.; Kauzlarich, S. M.; Carter, S. A. Quantum Dot Ge/TiO2 Heterojunction Photoconductor Fabrication and Performance. *Applied Physics Letters* **2013**, *103* (22), 223506.
- (133) Gao, J.; Jeong, S.; Lin, F.; Erslev, P. T.; Semonin, O. E.; Luther, J. M.; Beard, M. C. Improvement in Carrier Transport Properties by Mild Thermal Annealing of PbS Quantum Dot Solar Cells. *Applied Physics Letters* **2013**, *102* (4), 43506.
- (134) Emery, K. Measurement and Characterization of Solar Cells and Modules. In *Handbook of Photovoltaic Science and Engineering*; 2011; pp 797–840.
- (135) Snaith, H. J. How Should You Measure Your Excitonic Solar Cells? *Energy & Environmental Science* **2012**, *5*, 6513–6520.
- (136) Law, M.; Beard, M. C.; Choi, S.; Luther, J. M.; Hanna, M. C.; Nozik, A. J. Determining the Internal Quantum Efficiency of PbSe Nanocrystal Solar Cells with the Aid of an Optical Model. *Nano Letters* 2008, *8* (11), 3904–3910.
- (137) Sites, J. R.; Tavakolian, H.; Sasala, R. A. Analysis of Apparent Quantum Efficiency. *Solar Cells* **1990**, *29* (1), 39–48.
- (138) Hegedus, S. S.; Shafarman, W. N. Thin-Film Solar Cells: Device Measurements and Analysis. Progress in Photovoltaics: Research and Applications 2004, 12 (2–3), 155– 176.
- (139) Zhang, H.; Hyun, B. R.; Wise, F. W.; Robinson, R. D. A Generic Method for Rational Scalable Synthesis of Monodisperse Metal Sulfide Nanocrystals. *Nano Letters* 2012, *12*, 5856–5860.
- (140) Pu, C.; Zhou, J.; Lai, R.; Niu, Y.; Nan, W.; Peng, X. Highly Reactive, Flexible yet Green Se Precursor for Metal Selenide Nanocrystals: Se-Octadecene Suspension (Se-SUS). *Nano Research* **2013**, *6* (9), 652–670.

- (141) Luther, J. M.; Law, M.; Beard, M. C.; Song, Q.; Reese, M. O.; Ellingson, R. J.; Nozik, A. J. Schottky Solar Cells Based on Colloidal Nanocrystal Films. *Nano Letters* 2008, 8 (10), 3488–3492.
- (142) NREL. Best Research-Cell Efficiencies http://www.nrel.gov/ncpv/images/efficiency_chart.jpg (accessed Jul 17, 2016).
- (143) Leschkies, K. S.; Beatty, T. J.; Kang, M. S.; Norris, D. J.; Aydil, E. S. Solar Cells Based on Junctions between Colloidal PbSe Nanocrystals and Thin ZnO Films. ACS nano 2009, 3 (11), 3638–3648.
- (144) Pattantyus-Abraham, A. G.; Kramer, I. J.; Barkhouse, A. R.; Wang, X.; Konstantatos, G.; Debnath, R.; Levina, L.; Raabe, I.; Nazeeruddin, M. K.; Grätzel, M.; et al. Depleted-Heterojunction Colloidal Quantum Dot Solar Cells. *ACS nano* **2010**, *4* (6), 3374–3380.
- (145) Gao, J.; Luther, J. M.; Semonin, O. E.; Ellingson, R. J.; Nozik, A. J.; Beard, M. C. Quantum Dot Size Dependent J-V Characteristics in Heterojunction ZnO/PbS Quantum Dot Solar Cells. *Nano letters* **2011**, *11* (3), 1002–1008.
- (146) Gao, J.; Perkins, C. L.; Luther, J.; Hanna, M.; Chen, H.; Semonin, O.; Nozik, A.; Ellingson, R. J.; Beard, M. N-Type Transition Metal Oxide as a Hole Extraction Layer in PbS Quantum Dot Solar Cells. *Nano Letters* 2011, *11* (8), 3263–3266.
- (147) Semonin, O. E.; Luther, J. M.; Choi, S.; Chen, H.-Y.; Gao, J.; Nozik, a. J.; Beard, M. C. Peak External Photocurrent Quantum Efficiency Exceeding 100% via MEG in a Quantum Dot Solar Cell. *Science* **2011**, *334* (6062), 1530–1533.
- (148) Chuang, C.-H. M.; Brown, P. R.; Bulović, V.; Bawendi, M. G. Improved Performance and Stability in Quantum Dot Solar Cells through Band Alignment Engineering. *Nature Materials* **2014**, *13*, 796–801.
- (149) Oh, S. J.; Berry, N. E.; Choi, J. H.; Gaulding, E. A.; Paik, T.; Hong, S. H.; Murray, C. B.; Kagan, C. R. Stoichiometric Control of Lead Chalcogenide Nanocrystal Solids to Enhance Their Electronic and Optoelectronic Device Performance. *ACS Nano* 2013, 7 (3), 2413–2421.
- (150) Crisp, R. W.; Kroupa, D. M.; Marshall, A. R.; Miller, E. M.; Zhang, J.; Beard, M. C.; Luther, J. M. Metal Halide Solid-State Surface Treatment for High Efficiency PbS and PbSe QD Solar Cells. *Scientific Reports* **2015**, *5*, 9945.
- (151) Marshall, A. R.; Young, M. R.; Nozik, A. J.; Beard, M. C.; Luther, J. M. Exploration of Metal Chloride Uptake for Improved Performance Characteristics of PbSe Quantum Dot Solar Cells. *The Journal of Physical Chemistry Letters* **2015**, *6* (15), 2892–2899.
- (152) Gao, J.; Johnson, J. C. Charge Trapping in Bright and Dark States of Coupled PbS Quantum Dot Films. *ACS Nano* **2012**, *6* (4), 3292–3303.

- (153) Tang, J.; Kemp, K. W.; Hoogland, S.; Jeong, K. S.; Liu, H.; Levina, L.; Furukawa, M.; Wang, X.; Debnath, R.; Cha, D.; et al. Colloidal-Quantum-Dot Photovoltaics Using Atomic-Ligand Passivation. *Nature Materials* **2011**, *10* (10), 765–771.
- (154) Ip, A. H.; Thon, S. M.; Hoogland, S.; Voznyy, O.; Zhitomirsky, D.; Debnath, R.; Levina, L.; Rollny, L. R.; Carey, G. H.; Fischer, A.; et al. Hybrid Passivated Colloidal Quantum Dot Solids. *Nature Nanotechnology* **2012**, *7*, 577–582.
- (155) Marshall, A. R.; Beard, M. C.; Johnson, J. C. Nongeminate Radiative Recombination of Free Charges in Cation-Exchanged PbS Quantum Dot Films. *Chemical Physics* 2016, 471, 75–80.
- (156) Kim, S.; Marshall, A. R.; Kroupa, D. M.; Miller, E. M.; Luther, J. M.; Jeong, S.; Beard, M. C. Air-Stable and Efficient PbSe Quantum-Dot Solar Cells Based upon Quantum Dots. ACS Nano 2015, 9 (8), 8157–8164.
- (157) Moreels, I.; Fritzinger, B.; Martins, J. C.; Hens, Z. Surface Chemistry of Colloidal PbSe Nanocrystals. *Journal of the American Chemical Society* **2008**, *130* (45), 15081– 15086.
- (158) Zhang, J.; Gao, J.; Miller, E. M.; Luther, J. M.; Beard, M. C. Diffusion-Controlled Synthesis of PbS and PbSe Quantum Dots with in Situ Halide Passivation for Quantum Dot Solar Cells. *ACS nano* **2014**, *8* (1), 614–622.
- (159) Selinsky, R. S.; Ding, Q.; Faber, M. S.; Wright, J. C.; Jin, S. Quantum Dot Nanoscale Heterostructures for Solar Energy Conversion. *Chem. Soc. Rev.* 2013, 42 (7), 2963– 2985.
- (160) Sitt, A.; Hadar, I.; Banin, U. Band-Gap Engineering, Optoelectronic Properties and Applications of Colloidal Heterostructured Semiconductor Nanorods. *Nano Today* 2013, 8 (5), 494–513.
- (161) Hanna, M. C.; Beard, M. C.; Nozik, A. J. Effect of Solar Concentration on the Thermodynamic Power Conversion Efficiency of Quantum-Dot Solar Cells Exhibiting Multiple Exciton Generation. *Journal of Physical Chemistry Letters* **2012**, *3* (19), 2857–2862.
- (162) Schaller, R. D.; Klimov, V. I. High Efficiency Carrier Multiplication in PbSe Nanocrystals: Implications for Solar Energy Conversion. *Physical Review Letters* 2004, 92 (18), 186601.
- (163) Nozik, A. J. Multiple Exciton Generation in Semiconductor Quantum Dots. *Chemical Physics Letters* **2008**, *457*, 3–11.
- (164) Kim, D.; Kim, D.-H.; Lee, J.-H.; Grossman, J. C. Impact of Stoichiometry on the Electronic Structure of PbS Quantum Dots. *Phys. Rev. Lett.* **2013**, *110* (19), 196802.

- (165) Voznyy, O.; Thon, S. M.; Ip, A. H.; Sargent, E. H. Dynamic Trap Formation and Elimination in Colloidal Quantum Dots. *J. Phys. Chem. Lett.* **2013**, *4* (6), 987–992.
- (166) Lifshitz, E.; Glozman, A.; Litvin, I. D.; Porteanu, H. Optically Detected Magnetic Resonance Studies of the Surface/Interface Properties of II–VI Semiconductor Quantum Dots. *J. Phys. Chem. B* **2000**, *104* (45), 10449–10461.
- (167) Nagpal, P.; Klimov, V. I. Role of Mid-Gap States in Charge Transport and Photoconductivity in Semiconductor Nanocrystal Films. *Nature Communications* 2011, 2, 486.
- (168) Bozyigit, D.; Yazdani, N.; Yarema, M.; Yarema, O.; Lin, W. M. M.; Volk, S.; Vuttivorakulchai, K.; Luisier, M.; Juranyi, F.; Wood, V. Soft Surfaces of Nanomaterials Enable Strong Phonon Interactions. *Nature* **2016**, *531* (7596), 618–622.
- (169) Nelson, C. A.; Zhu, X.-Y. Reversible Surface Electronic Traps in PbS Quantum Dot Solids Induced by an Order–Disorder Phase Transition in Capping Molecules. *J. Am. Chem. Soc.* 2012, *134* (18), 7592–7595.
- (170) Bozyigit, D.; Volk, S.; Yarema, O.; Wood, V. Quantification of Deep Traps in Nanocrystal Solids, Their Electronic Properties, and Their Influence on Device Behavior. *Nano Lett.* **2013**, *13* (11), 5284–5288.
- (171) Konstantatos, G.; Sargent, E. H. PbS Colloidal Quantum Dot Photoconductive Photodetectors: Transport, Traps, and Gain. *Appl. Phys. Lett.* **2007**, *91* (17), 173505.
- (172) Wanger, D. D.; Correa, R. E.; Dauler, E. A.; Bawendi, M. G. The Dominant Role of Exciton Quenching in PbS Quantum-Dot-Based Photovoltaic Devices. *Nano Lett.* 2013, *13* (12), 5907–5912.
- (173) Zhitomirsky, D.; Kramer, I. J.; Labelle, A. J.; Fischer, A.; Debnath, R.; Pan, J.; Bakr, O. M.; Sargent, E. H. Colloidal Quantum Dot Photovoltaics: The Effect of Polydispersity. *Nano Lett.* **2012**, *12* (2), 1007–1012.
- (174) Jeong, K. S.; Tang, J.; Liu, H.; Kim, J.; Schaefer, A. W.; Kemp, K.; Levina, L.; Wang, X.; Hoogland, S.; Debnath, R.; et al. Enhanced Mobility-Lifetime Products in PbS Colloidal Quantum Dot Photovoltaics. *ACS Nano* **2012**, *6* (1), 89–99.
- (175) Marshall, A. R.; Young, M. R.; Nozik, A. J.; Beard, M. C.; Luther, J. M. Exploration of Metal Chloride Uptake for Improved Performance Characteristics of PbSe Quantum Dot Solar Cells. *J. Phys. Chem. Lett.* **2015**, 2892–2899.
- (176) Moreels, I.; Lambert, K.; Smeets, D.; De Muynck, D.; Nollet, T.; Martins, J. C.; Vanhaecke, F.; Vantomme, A.; Delerue, C.; Allan, G.; et al. Size-Dependent Optical Properties of Colloidal PbS Quantum Dots. *ACS Nano* **2009**, *3* (10), 3023–3030.

- (177) Baumgardner, W. J.; Whitham, K.; Hanrath, T. Confined-but-Connected Quantum Solids via Controlled Ligand Displacement. *Nano Lett.* **2013**, *13* (7), 3225–3231.
- (178) Gao, J.; Johnson, J. C. Charge Trapping in Bright and Dark States of Coupled PbS Quantum Dot Films. *ACS Nano* **2012**, *6* (4), 3292–3303.
- (179) Zhang, J.; Tolentino, J.; Smith, E. R.; Zhang, J.; Beard, M. C.; Nozik, A. J.; Johnson, J. C. Carrier Transport in PbS and PbSe QD Films Measured by Photoluminescence Quenching. *J. Phys. Chem. C* **2014**, *118* (29), 16228–16235.
- (180) Chappell, H. E.; Hughes, B. K.; Beard, M. C.; Nozik, A. J.; Johnson, J. C. Emission Quenching in PbSe Quantum Dot Arrays by Short-Term Air Exposure. *J. Phys. Chem. Lett.* **2011**, *2* (8), 889–893.
- (181) Hughes, B. K.; Ruddy, D. A.; Blackburn, J. L.; Smith, D. K.; Bergren, M. R.; Nozik, A. J.; Johnson, J. C.; Beard, M. C. Control of PbSe Quantum Dot Surface Chemistry and Photophysics Using an Alkylselenide Ligand. *ACS Nano* **2012**, *6* (6), 5498–5506.
- (182) Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29* (9), 2176–2179.
- (183) Miller, O. D.; Yablonovitch, E.; Kurtz, S. R. Strong Internal and External Luminescence as Solar Cells Approach the Shockley-Queisser Limit. *IEEE J. Photovolt.* **2012**, *2* (3), 303–311.
- (184) Smestad, G.; Ries, H. Luminescence and Current-Voltage Characteristics of Solar Cells and Optoelectronic Devices. *Sol. Energ. Mat. Sol. Cells* **1992**, *25* (1–2), 51–71.
- (185) Gao, J.; Zhang, J.; van de Lagemaat, J.; Johnson, J. C.; Beard, M. C. Charge Generation in PbS Quantum Dot Solar Cells Characterized by Temperature-Dependent Steady-State Photoluminescence. ACS Nano 2014, 8 (12), 12814–12825.
- (186) Solar cell efficiency http://en.wikipedia.org/wiki/Solar_cell_efficiency (accessed Apr 8, 2015).
- (187) Labelle, A. J.; Thon, S. M.; Masala, S.; Adachi, M. M.; Dong, H.; Farahani, M.; Ip, A. H.; Fratalocchi, A.; Sargent, E. H. Colloidal Quantum Dot Solar Cells Exploiting Hierarchical Structuring. *Nano Lett.* **2015**, *15* (2), 1101–1108.
- (188) Barkhouse, D. A. R.; Pattantyus-Abraham, A. G.; Levina, L.; Sargent, E. H. Thiols Passivate Recombination Centers in Colloidal Quantum Dots Leading to Enhanced Photovoltaic Device Efficiency. *ACS Nano* **2008**, *2* (11), 2356–2362.

- (189) Crisp, R. W.; Kroupa, D. M.; Marshall, A. R.; Miller, E. M.; Zhang, J.; Beard, M. C.; Luther, J. M. Metal Halide Solid-State Surface Treatment for High Efficiency PbS and PbSe QD Solar Cells. *Sci. Rep.* **2015**, *5*, 9945.
- (190) Speirs, M. J.; Balazs, D. M.; Fang, H.-H.; Lai, L.-H.; Protesescu, L.; Kovalenko, M. V.; Loi, M. A. Origin of the Increased Open Circuit Voltage in PbS–CdS Core–shell Quantum Dot Solar Cells. *J. Mater. Chem. A* **2014**.
- (191) Woo, J. Y.; Ko, J.-H.; Song, J. H.; Kim, K.; Choi, H.; Kim, Y.-H.; Lee, D. C.; Jeong, S. Ultrastable PbSe Nanocrystal Quantum Dots via in Situ Formation of Atomically Thin Halide Adlayers on PbSe(100). *J. Am. Chem. Soc.* **2014**, *136* (25), 8883–8886.
- (192) Jähnig, F.; Bozyigit, D.; Yarema, O.; Wood, V. Research Update: Comparison of Saltand Molecular-Based Iodine Treatments of PbS Nanocrystal Solids for Solar Cells. *APL Mat.* **2015**, *3* (2), 20701.
- (193) Klimov, V. I.; Mikhailovsky, A. A.; McBranch, D. W.; Leatherdale, C. A.; Bawendi, M. G. Quantization of Multiparticle Auger Rates in Semiconductor Quantum Dots. *Science* 2000, 287 (5455), 1011–1013.
- (194) Beard, M. C.; Ellingson, R. J. Multiple Exciton Generation in Semiconductor Nanocrystals: Toward Efficient Solar Energy Conversion. *Laser & Photon. Rev.* 2008, 2 (5), 377–399.
- (195) Beard, M. C.; Midgett, A. G.; Law, M.; Semonin, O. E.; Ellingson, R. J.; Nozik, A. J. Variations in the Quantum Efficiency of Multiple Exciton Generation for a Series of Chemically Treated PbSe Nanocrystal Films. *Nano Lett.* **2009**, *9* (2), 836–845.
- (196) Guglietta, G. W.; Diroll, B. T.; Gaulding, E. A.; Fordham, J. L.; Li, S.; Murray, C. B.; Baxter, J. B. Lifetime, Mobility, and Diffusion of Photoexcited Carriers in Ligand-Exchanged Lead Selenide Nanocrystal Films Measured by Time-Resolved Terahertz Spectroscopy. ACS Nano 2015, 9 (2), 1820–1828.
- (197) Turk, M. E.; Vora, P. M.; Fafarman, A. T.; Diroll, B. T.; Murray, C. B.; Kagan, C. R.; Kikkawa, J. M. Ultrafast Electron Trapping in Ligand-Exchanged Quantum Dot Assemblies. *ACS Nano* **2015**, *9* (2), 1440–1447.
- (198) Ghanassi, M.; Schanne-Klein, M. C.; Hache, F.; Ekimov, A. I.; Ricard, D.; Flytzanis, C. Time-resolved Measurements of Carrier Recombination in Experimental Semiconductor-doped Glasses: Confirmation of the Role of Auger Recombination. *Appl. Phys. Lett.* **1993**, *62* (1), 78–80.
- (199) Yamada, Y.; Nakamura, T.; Endo, M.; Wakamiya, A.; Kanemitsu, Y. Photocarrier Recombination Dynamics in Perovskite CH3NH3PbI3 for Solar Cell Applications. *J. Am. Chem. Soc.* **2014**, *136* (33), 11610–11613.

- (200) Lakhwani, G.; Rao, A.; Friend, R. H. Bimolecular Recombination in Organic Photovoltaics. *Annu. Rev. Phys. Chem.* **2014**, *65* (1), 557–581.
- (201) Poulikakos, L. V.; Prins, F.; Tisdale, W. A. Transition from Thermodynamic to Kinetic-Limited Excitonic Energy Migration in Colloidal Quantum Dot Solids. *J. Phys. Chem. C* 2014, *118* (15), 7894–7900.
- (202) Werner, J.; Peisl, M. Exponential Band Tails in Polycrystalline Semiconductor Films. *Phys. Rev. B* **1985**, *31* (10), 6881–6883.
- (203) Erslev, P. T.; Chen, H.-Y.; Gao, J.; Beard, M. C.; Frank, A. J.; van de Lagemaat, J.; Johnson, J. C.; Luther, J. M. Sharp Exponential Band Tails in Highly Disordered Lead Sulfide Quantum Dot Arrays. *Phys. Rev. B* **2012**, *86* (15), 155313.
- (204) Osedach, T. P.; Zhao, N.; Andrew, T. L.; Brown, P. R.; Wanger, D. D.; Strasfeld, D. B.; Chang, L.-Y.; Bawendi, M. G.; Bulović, V. Bias-Stress Effect in 1,2-Ethanedithiol-Treated PbS Quantum Dot Field-Effect Transistors. *ACS Nano* 2012, 6 (4), 3121– 3127.
- (205) Liu, Y.; Gibbs, M.; Puthussery, J.; Gaik, S.; Ihly, R.; Hillhouse, H. W.; Law, M. Dependence of Carrier Mobility on Nanocrystal Size and Ligand Length in PbSe Nanocrystal Solids. *Nano Lett.* **2010**, *10* (5), 1960–1969.
- (206) Gao, Y.; Sandeep, C. S. S.; Schins, J. M.; Houtepen, A. J.; Siebbeles, L. D. A. Disorder Strongly Enhances Auger Recombination in Conductive Quantum-Dot Solids. *Nat. Commun.* **2013**, *4*.
- (207) Coe, S.; Woo, W.-K.; Bawendi, M.; Bulović, V. Electroluminescence from Single Monolayers of Nanocrystals in Molecular Organic Devices. *Nature* 2002, 420 (6917), 800–803.
- (208) Kim, S.; Kim, T.; Kang, M.; Kwak, S. K.; Yoo, T. W.; Park, L. S.; Yang, I.; Hwang, S.; Lee, J. E.; Kim, S. K.; et al. Highly Luminescent InP/GaP/ZnS Nanocrystals and Their Application to White Light-Emitting Diodes. *J. Am. Chem. Soc.* **2012**, *134* (8), 3804–3809.
- (209) Bharali, D. J.; Lucey, D. W.; Jayakumar, H.; Pudavar, H. E.; Prasad, P. N. Folate-Receptor-Mediated Delivery of InP Quantum Dots for Bioimaging Using Confocal and Two-Photon Microscopy. *J. Am. Chem. Soc.* **2005**, *127* (32), 11364–11371.
- (210) Talapin, D. V. PbSe Nanocrystal Solids for N- and P-Channel Thin Film Field-Effect Transistors. *Science* **2005**, *310* (5745), 86–89.
- (211) Kamat, P. V. Quantum Dot Solar Cells. Semiconductor Nanocrystals as Light Harvesters. *J. Phys. Chem. C* **2008**, *112* (48), 18737–18753.

- (212) Luther, J. M.; Law, M.; Song, Q.; Perkins, C. L.; Beard, M. C.; Nozik, A. J. Structural, Optical, and Electrical Properties of Self-Assembled Films of PbSe Nanocrystals Treated with 1,2-Ethanedithiol. *ACS Nano* **2008**, *2* (2), 271–280.
- (213) J. Peterson, J.; D. Krauss, T. Photobrightening and Photodarkening in PbS Quantum Dots. *Physical Chemistry Chemical Physics* **2006**, *8* (33), 3851–3856.
- (214) Stouwdam, J. W.; Shan, J.; van Veggel, F. C. J. M.; Pattantyus-Abraham, A. G.; Young, J. F.; Raudsepp, M. Photostability of Colloidal PbSe and PbSe/PbS Core/Shell Nanocrystals in Solution and in the Solid State. *J. Phys. Chem. C* 2007, *111* (3), 1086–1092.
- (215) Zhang, Y.; Dai, Q.; Li, X.; Liang, J.; Colvin, V. L.; Wang, Y.; Yu, W. W. PbSe/CdSe and PbSe/CdSe/ZnSe Hierarchical Nanocrystals and Their Photoluminescence. *Langmuir* 2011, 27 (15), 9583–9587.
- (216) Yanover, D.; Čapek, R. K.; Rubin-Brusilovski, A.; Vaxenburg, R.; Grumbach, N.; Maikov, G. I.; Solomeshch, O.; Sashchiuk, A.; Lifshitz, E. Small-Sized PbSe/PbS Core/Shell Colloidal Quantum Dots. *Chem. Mater.* **2012**, *24* (22), 4417–4423.
- (217) Nam, M.; Kim, S.; Kim, S.; Kim, S.-W.; Lee, K. Efficient Hybrid Solar Cells Using PbSxSe1-x Quantum Dots and Nanorods for Broad-Range Photon Absorption and Well-Assembled Charge Transfer Networks. *Nanoscale* **2013**, *5* (17), 8202–8209.
- (218) Fayette, M.; Robinson, R. D. Chemical Transformations of Nanomaterials for Energy Applications. *J. Mater. Chem. A* **2014**, *2* (17), 5965–5978.
- (219) Spanhel, L.; Haase, M.; Weller, H.; Henglein, A. Photochemistry of Colloidal Semiconductors. 20. Surface Modification and Stability of Strong Luminescing CdS Particles. J. Am. Chem. Soc. **1987**, 109 (19), 5649–5655.
- (220) Kim, S.; Park, J.; Kim, T.; Jang, E.; Jun, S.; Jang, H.; Kim, B.; Kim, S.-W. Reverse Type-I ZnSe/InP/ZnS Core/Shell/Shell Nanocrystals: Cadmium-Free Quantum Dots for Visible Luminescence. *Small* **2011**, 7 (1), 70–73.
- (221) Hines, M. A.; Guyot-Sionnest, P. Bright UV-Blue Luminescent Colloidal ZnSe Nanocrystals. *J. Phys. Chem. B* **1998**, *102* (19), 3655–3657.
- (222) Nikesh, V. V.; Amit D. Lad Siji Kimura; Shinji Nozaki Shailajo Mahamuni. Electron Energy Levels in ZnSe Quantum Dots. *Journal of Applied Physics* **2006**, *100* (11), 113520.
- (223) Smith, D. K.; Luther, J. M.; Semonin, O. E.; Nozik, A. J.; Beard, M. C. Tuning the Synthesis of Ternary Lead Chalcogenide Quantum Dots by Balancing Precursor Reactivity. ACS Nano 2011, 5 (1), 183–190.

- (224) Lee, S.; Lee, D. T.; Ko, J.-H.; Kim, W.-J.; Joo, J.; Jeong, S.; McGuire, J. A.; Kim, Y.-H.; Lee, D. C. Slow Colloidal Growth of PbSe Nanocrystals for Facile Morphology and Size Control. *RSC Adv.* **2014**, *4* (19), 9842–9850.
- (225) Perkins, C.; Hasoon, F. Surfactant-Assisted Growth of CdS Thin Films for Photovoltaic Applications. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **2006**, *24* (3), 497–504.
- (226) Beard, M. C.; Luther, J. M.; Nozik, A. J. The Promise and Challenge of Nanostructured Solar Cells. *Nature Nanotech.* **2014**, *9* (12), 951–954.
- (227) Hughes, B. K.; Luther, J. M.; Beard, M. C. The Subtle Chemistry of Colloidal, Quantum-Confined Semiconductor Nanostructures. *ACS Nano* **2012**, *6* (6), 4573–4579.
- (228) Padilha, L. A.; Stewart, J. T.; Sandberg, R. L.; Bae, W. K.; Koh, W.-K.; Pietryga, J. M.; Klimov, V. I. Carrier Multiplication in Semiconductor Nanocrystals: Influence of Size, Shape, and Composition. *Acc. Chem. Res.* **2013**, *46* (6), 1261–1269.
- (229) Trinh, M. T.; Houtepen, A. J.; Schins, J. M.; Hanrath, T.; Piris, J.; Knulst, W.; Goossens, A. P. L. M.; Siebbeles, L. D. A. In Spite of Recent Doubts Carrier Multiplication Does Occur in PbSe Nanocrystals. *Nano Lett.* **2008**, *8* (6), 1713–1718.
- (230) Ellingson, R. J.; Beard, M. C.; Johnson, J. C.; Yu, P.; Micic, O. I.; Nozik, A. J.; Shabaev, A.; Efros, A. L. Highly Efficient Multiple Exciton Generation in Colloidal PbSe and PbS Quantum Dots. *Nano Lett.* **2005**, *5* (5), 865–871.
- (231) Midgett, A. G.; Hillhouse, H. W.; Hughes, B. K.; Nozik, A. J.; Beard, M. C. Flowing versus Static Conditions for Measuring Multiple Exciton Generation in PbSe Quantum Dots. *J. Phys. Chem. C* **2010**, *114* (41), 17486–17500.
- (232) Shabaev, A.; Hellberg, C. S.; Efros, A. L. Efficiency of Multiexciton Generation in Colloidal Nanostructures. *Acc. Chem. Res.* **2013**, *46* (6), 1242–1251.
- (233) Midgett, A. G.; Luther, J. M.; Stewart, J. T.; Smith, D. K.; Padilha, L. A.; Klimov, V. I.; Nozik, A. J.; Beard, M. C. Size and Composition Dependent Multiple Exciton Generation Efficiency in PbS, PbSe, and PbSxSe1–x Alloyed Quantum Dots. *Nano Lett.* 2013, 13 (7), 3078–3085.
- (234) Wang, H.; Pei, Y.; LaLonde, A. D.; Snyder, G. J. Heavily Doped P-Type PbSe with High Thermoelectric Performance: An Alternative for PbTe. *Adv. Mater.* **2011**, *23* (11), 1366–1370.
- (235) Zhou, J.; Yang, R. Quantum and Classical Thermoelectric Transport in Quantum Dot Nanocomposites. *J. Appl. Phys.* **2011**, *110* (8), 84317.
- (236) Hetsch, F.; Zhao, N.; Kershaw, S. V.; Rogach, A. L. Quantum Dot Field Effect Transistors. *Mater. Today* **2013**, *16* (9), 312–325.

- (237) Leschkies, K. S.; Kang, M. S.; Aydil, E. S.; Norris, D. J. Influence of Atmospheric Gases on the Electrical Properties of PbSe Quantum-Dot Films. *J. Phys. Chem. C* 2010, *114* (21), 9988–9996.
- (238) Ma, W.; Swisher, S. L.; Ewers, T.; Engel, J.; Ferry, V. E.; Atwater, H. A.; Alivisatos, A. P. Photovoltaic Performance of Ultrasmall PbSe Quantum Dots. ACS Nano 2011, 5 (10), 8140–8147.
- (239) Hoye, R. L. Z.; Ehrler, B.; Böhm, M. L.; Muñoz-Rojas, D.; Altamimi, R. M.; Alyamani, A. Y.; Vaynzof, Y.; Sadhanala, A.; Ercolano, G.; Greenham, N. C.; et al. Improved Open-Circuit Voltage in ZnO–PbSe Quantum Dot Solar Cells by Understanding and Reducing Losses Arising from the ZnO Conduction Band Tail. *Adv. Energy Mater.* 2014, 4 (8), 1301544.
- (240) Ko, D.-K.; Brown, P. R.; Bawendi, M. G.; Bulović, V. P-I-N Heterojunction Solar Cells with a Colloidal Quantum-Dot Absorber Layer. *Adv. Mater.* **2014**, *26* (28), 4845–4850.
- (241) Kuo, C.-Y.; Su, M.-S.; Hsu, Y.-C.; Lin, H.-N.; Wei, K.-H. An Organic Hole Transport Layer Enhances the Performance of Colloidal PbSe Quantum Dot Photovoltaic Devices. *Adv. Funct. Mater.* **2010**, *20* (20), 3555–3560.
- (242) Kuo, C.-Y.; Su, M.-S.; Ku, C.-S.; Wang, S.-M.; Lee, H.-Y.; Wei, K.-H. Ligands Affect the Crystal Structure and Photovoltaic Performance of Thin Films of PbSe Quantum Dots. *J. Mater. Chem.* **2011**, *21* (31), 11605–11612.
- (243) Ma, W.; Luther, J. M.; Zheng, H.; Wu, Y.; Alivisatos, A. P. Photovoltaic Devices Employing Ternary PbSxSe1-X Nanocrystals. *Nano Lett.* **2009**, *9* (4), 1699–1703.
- (244) Ouyang, J.; Schuurmans, C.; Zhang, Y.; Nagelkerke, R.; Wu, X.; Kingston, D.; Wang, Z. Y.; Wilkinson, D.; Li, C.; Leek, D. M.; et al. Low-Temperature Approach to High-Yield and Reproducible Syntheses of High-Quality Small-Sized PbSe Colloidal Nanocrystals for Photovoltaic Applications. *ACS Appl. Mater. Interfaces* **2011**, *3* (2), 553–565.
- (245) Dai, Q.; Wang, Y.; Zhang, Y.; Li, X.; Li, R.; Zou, B.; Seo, J.; Wang, Y.; Liu, M.; Yu, W. W. Stability Study of PbSe Semiconductor Nanocrystals over Concentration, Size, Atmosphere, and Light Exposure. *Langmuir* **2009**, *25* (20), 12320–12324.
- (246) Liu, Y.; Gibbs, M.; Perkins, C. L.; Tolentino, J.; Zarghami, M. H.; Bustamante, J.; Law, M. Robust, Functional Nanocrystal Solids by Infilling with Atomic Layer Deposition. *Nano Lett.* **2011**, *11* (12), 5349–5355.
- (247) McDaniel, H.; Fuke, N.; Makarov, N. S.; Pietryga, J. M.; Klimov, V. I. An Integrated Approach to Realizing High-Performance Liquid-Junction Quantum Dot Sensitized Solar Cells. *Nat. Commun.* **2013**, *4*.

- (248) Shen, Q.; Kobayashi, J.; Diguna, L. J.; Toyoda, T. Effect of ZnS Coating on the Photovoltaic Properties of CdSe Quantum Dot-Sensitized Solar Cells. *J. Appl. Phys.* 2008, 103 (8), 84304.
- (249) Liu, C.; Mu, L.; Jia, J.; Zhou, X.; Lin, Y. Boosting the Cell Efficiency of CdSe Quantum Dot Sensitized Solar Cell via a Modified ZnS Post-Treatment. *Electrochim. Acta* 2013, *111*, 179–184.
- (250) Mora-Seró, I.; Giménez, S.; Fabregat-Santiago, F.; Gómez, R.; Shen, Q.; Toyoda, T.; Bisquert, J. Recombination in Quantum Dot Sensitized Solar Cells. *Acc. Chem. Res.* 2009, 42 (11), 1848–1857.
- (251) Ihly, R.; Tolentino, J.; Liu, Y.; Gibbs, M.; Law, M. The Photothermal Stability of PbS Quantum Dot Solids. *ACS Nano* **2011**, *5* (10), 8175–8186.
- (252) Liu, Y.; Tolentino, J.; Gibbs, M.; Ihly, R.; Perkins, C. L.; Liu, Y.; Crawford, N.; Hemminger, J. C.; Law, M. PbSe Quantum Dot Field-Effect Transistors with Air-Stable Electron Mobilities above 7 cm2 V–1 s–1. *Nano Lett.* **2013**, *13* (4), 1578–1587.
- (253) ten Cate, S.; Liu, Y.; Suchand Sandeep, C. S.; Kinge, S.; Houtepen, A. J.; Savenije, T. J.; Schins, J. M.; Law, M.; Siebbeles, L. D. A. Activating Carrier Multiplication in PbSe Quantum Dot Solids by Infilling with Atomic Layer Deposition. *J. Phys. Chem. Lett.* 2013, 4 (11), 1766–1770.
- (254) Peng, X.; Schlamp, M. C.; Kadavanich, A. V.; Alivisatos, A. P. Epitaxial Growth of Highly Luminescent CdSe/CdS Core/Shell Nanocrystals with Photostability and Electronic Accessibility. *J. Am. Chem. Soc.* **1997**, *119* (30), 7019–7029.
- (255) Cirloganu, C. M.; Padilha, L. A.; Lin, Q.; Makarov, N. S.; Velizhanin, K. A.; Luo, H.; Robel, I.; Pietryga, J. M.; Klimov, V. I. Enhanced Carrier Multiplication in Engineered Quasi-Type-II Quantum Dots. *Nat. Commun.* **2014**, *5*.
- (256) Zhang, Y.; Dai, Q.; Li, X.; Cui, Q.; Gu, Z.; Zou, B.; Wang, Y.; Yu, W. W. Formation of PbSe/CdSe Core/Shell Nanocrystals for Stable Near-Infrared High Photoluminescence Emission. *Nanoscale Res. Lett.* **2010**, *5* (8), 1279–1283.
- (257) Zhang, Z.; Liu, C.; Zhao, X. Utilizing Sn Precursor To Promote the Nucleation of PbSe Quantum Dots with in Situ Halide Passivation. *J. Phys. Chem. C* **2015**, *119* (10), 5626–5632.
- (258) Crisp, R. W.; Panthani, M. G.; Rance, W. L.; Duenow, J. N.; Parilla, P. A.; Callahan, R.; Dabney, M. S.; Berry, J. J.; Talapin, D. V.; Luther, J. M. Nanocrystal Grain Growth and Device Architectures for High-Efficiency CdTe Ink-Based Photovoltaics. *ACS Nano* 2014, 8 (9), 9063–9072.
- (259) Kovalenko, M. V.; Scheele, M.; Talapin, D. V. Colloidal Nanocrystals with Molecular Metal Chalcogenide Surface Ligands. *Science* **2009**, *324* (5933), 1417–1420.

- (260) Nag, A.; Chung, D. S.; Dolzhnikov, D. S.; Dimitrijevic, N. M.; Chattopadhyay, S.; Shibata, T.; Talapin, D. V. Effect of Metal Ions on Photoluminescence, Charge Transport, Magnetic and Catalytic Properties of All-Inorganic Colloidal Nanocrystals and Nanocrystal Solids. *J. Am. Chem. Soc.* **2012**, *134* (33), 13604–13615.
- (261) Talapin, D. V.; Lee, J.-S.; Kovalenko, M. V.; Shevchenko, E. V. Prospects of Colloidal Nanocrystals for Electronic and Optoelectronic Applications. *Chem. Rev.* 2010, *110* (1), 389–458.
- (262) Yoon, W.; Boercker, J. E.; Lumb, M. P.; Placencia, D.; Foos, E. E.; Tischler, J. G. Enhanced Open-Circuit Voltage of PbS Nanocrystal Quantum Dot Solar Cells. *Sci. Rep.* 2013, 3.
- (263) Liu, H.; Zhitomirsky, D.; Hoogland, S.; Tang, J.; Kramer, I. J.; Ning, Z.; Sargent, E. H. Systematic Optimization of Quantum Junction Colloidal Quantum Dot Solar Cells. *Appl. Phys. Lett.* **2012**, *101* (15), 151112.
- (264) Sahu, A.; Kang, M. S.; Kompch, A.; Notthoff, C.; Wills, A. W.; Deng, D.; Winterer, M.; Frisbie, C. D.; Norris, D. J. Electronic Impurity Doping in CdSe Nanocrystals. *Nano Lett.* **2012**, *12* (5), 2587–2594.
- (265) Stavrinadis, A.; Rath, A. K.; de Arquer, F. P. G.; Diedenhofen, S. L.; Magén, C.; Martinez, L.; So, D.; Konstantatos, G. Heterovalent Cation Substitutional Doping for Quantum Dot Homojunction Solar Cells. *Nat. Commun.* **2013**, *4*.
- (266) Choi, J.-H.; Fafarman, A. T.; Oh, S. J.; Ko, D.-K.; Kim, D. K.; Diroll, B. T.; Muramoto, S.; Gillen, J. G.; Murray, C. B.; Kagan, C. R. Bandlike Transport in Strongly Coupled and Doped Quantum Dot Solids: A Route to High-Performance Thin-Film Electronics. *Nano Lett.* **2012**, *12* (5), 2631–2638.
- (267) Luther, J. M.; Pietryga, J. M. Stoichiometry Control in Quantum Dots: A Viable Analog to Impurity Doping of Bulk Materials. *ACS Nano* **2013**, *7* (3), 1845–1849.
- (268) Bozyigit, D.; Lin, W. M. M.; Yazdani, N.; Yarema, O.; Wood, V. A Quantitative Model for Charge Carrier Transport, Trapping and Recombination in Nanocrystal-Based Solar Cells. *Nat. Commun.* 2015, *6*, 6180.
- (269) Greaney, M. J.; Couderc, E.; Zhao, J.; Nail, B. A.; Mecklenburg, M.; Thornbury, W.; Osterloh, F. E.; Bradforth, S. E.; Brutchey, R. L. Controlling the Trap State Landscape of Colloidal CdSe Nanocrystals with Cadmium Halide Ligands. *Chem. Mater.* 2015, *27* (3), 744–756.
- (270) Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc.* **2009**, *131* (17), 6050–6051.

- (271) Sharma, S.; Weiden, N.; Weiss, A. Phase Diagrams of Quasibinary Systems of the Type: ABX3 — A'BX3; ABX3 — AB'X3, and ABX3 — ABX'3; X = Halogen. *Zeitschrift für Physikalische Chemie* **1992**, *175* (1), 63–80.
- (272) Beal, R. E.; Slotcavage, D. J.; Leijtens, T.; Bowring, A. R.; Belisle, R. A.; Nguyen, W. H.; Burkhard, G. F.; Hoke, E. T.; McGehee, M. D. Cesium Lead Halide Perovskites with Improved Stability for Tandem Solar Cells. *J. Phys. Chem. Lett.* **2016**, *7* (5), 746–751.
- (273) Wang, F.; Han, Y.; Lim, C. S.; Lu, Y.; Wang, J.; Xu, J.; Chen, H.; Zhang, C.; Hong, M.; Liu, X. Simultaneous Phase and Size Control of Upconversion Nanocrystals through Lanthanide Doping. *Nature* **2010**, *463* (7284), 1061–1065.
- (274) Yang, C. C.; Li, S. Size-Dependent Phase Stability of Silver Nanocrystals. *J. Phys. Chem. C* **2008**, *112* (42), 16400–16404.
- (275) Schlag, S.; Eicke, H.-F. Size Driven Phase Transition in Nanocrystalline BaTiO3. *Solid State Commun.* **1994**, *91* (11), 883–887.
- (276) Zhang, F.; Zhong, H.; Chen, C.; Wu, X.; Hu, X.; Huang, H.; Han, J.; Zou, B.; Dong, Y. Brightly Luminescent and Color-Tunable Colloidal CH3NH3PbX3 (X = Br, I, Cl) Quantum Dots: Potential Alternatives for Display Technology. *ACS Nano* **2015**, *9* (4), 4533–4542.
- (277) Zhang, D.; Eaton, S. W.; Yu, Y.; Dou, L.; Yang, P. Solution-Phase Synthesis of Cesium Lead Halide Perovskite Nanowires. *J. Am. Chem. Soc.* **2015**, *137* (29), 9230–9233.
- (278) Huang, H.; Zhao, F.; Liu, L.; Zhang, F.; Wu, X.; Shi, L.; Zou, B.; Pei, Q.; Zhong, H. Emulsion Synthesis of Size-Tunable CH3NH3PbBr3 Quantum Dots: An Alternative Route toward Efficient Light-Emitting Diodes. *ACS Appl. Mater. Interfaces* 2015, 7 (51), 28128–28133.
- (279) Hassan, Y.; Song, Y.; Pensack, R. D.; Abdelrahman, A. I.; Kobayashi, Y.; Winnik, M. A.; Scholes, G. D. Structure-Tuned Lead Halide Perovskite Nanocrystals. *Adv. Mater.* 2016, *28* (3), 566–573.
- (280) Sun, S.; Yuan, D.; Xu, Y.; Wang, A.; Deng, Z. Ligand-Mediated Synthesis of Shape-Controlled Cesium Lead Halide Perovskite Nanocrystals via Reprecipitation Process at Room Temperature. *ACS Nano* **2016**, *10* (3), 3648–3657.
- (281) Jellicoe, T. C.; Richter, J. M.; Glass, H. F. J.; Tabachnyk, M.; Brady, R.; Dutton, S. E.; Rao, A.; Friend, R. H.; Credgington, D.; Greenham, N. C.; et al. Synthesis and Optical Properties of Lead-Free Cesium Tin Halide Perovskite Nanocrystals. *J. Am. Chem. Soc.* 2016, 138 (9), 2941–2944.
- (282) Akkerman, Q. A.; Motti, S. G.; Srimath Kandada, A. R.; Mosconi, E.; D'Innocenzo, V.; Bertoni, G.; Marras, S.; Kamino, B. A.; Miranda, L.; De Angelis, F.; et al. Solution

Synthesis Approach to Colloidal Cesium Lead Halide Perovskite Nanoplatelets with Monolayer-Level Thickness Control. *J. Am. Chem. Soc.* **2016**, *138* (3), 1010–1016.

- (283) Makarov, N. S.; Guo, S.; Isaienko, O.; Liu, W.; Robel, I.; Klimov, V. I. Spectral and Dynamical Properties of Single Excitons, Biexcitons, and Trions in Cesium–Lead-Halide Perovskite Quantum Dots. *Nano Lett.* **2016**, *16* (4), 2349–2362.
- (284) Park, Y.-S.; Guo, S.; Makarov, N. S.; Klimov, V. I. Room Temperature Single-Photon Emission from Individual Perovskite Quantum Dots. ACS Nano 2015, 9 (10), 10386– 10393.
- (285) Lin, C. C.; Meijerink, A.; Liu, R.-S. Critical Red Components for Next-Generation White LEDs. *J. Phys. Chem. Lett.* **2016**, *7* (3), 495–503.
- (286) Pearson, R. G. Hard and Soft Acids and Bases. J. Am. Chem. Soc. **1963**, 85 (22), 3533–3539.
- (287) Trots, D. M.; Myagkota, S. V. High-Temperature Structural Evolution of Caesium and Rubidium Triiodoplumbates. *Journal of Physics and Chemistry of Solids* **2008**, 69 (10), 2520–2526.
- (288) S. Tsunekawa; K. Ishikawa; Z.-Q. Li; Y. Kawazoe; A. Kasuya. Origin of Anamalous Lattice Expansion in Oxide Nanoparticles. *Phys. Rev. Lett.* **2000**, *85*, 3440.
- (289) Dastidar, S.; Egger, D. A.; Tan, L. Z.; Cromer, S. B.; Dillon, A. D.; Liu, S.; Kronik, L.; Rappe, A. M.; Fafarman, A. T. High Chloride Doping Levels Stabilize the Perovskite Phase of Cesium Lead Iodide. *Nano Lett.* **2016**, *16* (6), 3563–3570.
- (290) Yettapu, G. R.; Talukdar, D.; Sarkar, S.; Swarnkar, A.; Nag, A.; Ghosh, P.; Mandal, P. Terahertz Conductivity within Colloidal CsPbBr3 Perovskite Nanocrystals: Remarkably High Carrier Mobilities and Large Diffusion Lengths. *Nano Lett.* 2016, 16 (8), 4838–4848.
- (291) Yassitepe, E.; Yang, Z.; Voznyy, O.; Kim, Y.; Walters, G.; Castañeda, J. A.; Kanjanaboos, P.; Yuan, M.; Gong, X.; Fan, F.; et al. Amine-Free Synthesis of Cesium Lead Halide Perovskite Quantum Dots for Efficient Light-Emitting Diodes. *Adv. Funct. Mater.* n/an/a.
- (292) Wang, C.; R. Chesman, A. S.; J. Jasieniak, J. Stabilizing the Cubic Perovskite Phase of CsPbI 3 Nanocrystals by Using an Alkyl Phosphinic Acid. *Chemical Communications* 2017, 53 (1), 232–235.
- (293) Lutterotti, L.; Scardi, P.; Maistrelli, P. LSI a Computer Program for Simultaneous Refinement of Material Structure and Microstructure. *J Appl Cryst, J Appl Crystallogr* **1992**, *25* (3), 459–462.

Appendix

A1. FET Mobility Calculations

Field Effect Transistors (FETs) were used to determine the mobility in EDT treated PbS (from cation exchange of Cds) QD films. The output characteristics, shown in Figure 4.3a, is a graph of the current as a function of source-drain voltage at gate voltages ranging from 0 V to 80 V. The devices switch from linear mode to saturation mode between 10-15 V. The transfer characteristics are shown in Figure 4.3b, the current is graphed as a function of gate voltage at different source-drain voltages (from 0 V to 30 V as the traces increase). The slope of the line was used to determine the mobility, based on Equation A1.1 for source-drain voltages in the linear regime (0V to 15V).

$$I_{D} = \frac{W\mu_{n}C_{ox}}{L}(V_{GS} - V_{T})V_{DS}$$
(A1.1)

 I_D is the drain current, W is the width of the channel, μ_n is the mobility, C_{ox} is the areal capacitance of the oxide, L is the channel length, V_{GS} is the gate voltage, V_T is the threshold voltage, and V_{DS} is the source-drain voltage. The slope of the I_D vs V_{GS} graph therefore allows us to calculate μ_n , the mobility. In the saturation region, Equation A1.2 describes I_D as a function of V_{GS} .

$$\sqrt{I_D(sat)} = \sqrt{\frac{W\mu_n C_{ox}}{2L}} (V_{GS} - V_T)$$
(A1.2)

To solve for the mobility in the saturation regime, we look at Figure 4.3c which is the square root of I_D vs V_{GS} . The slopes of the lines for V_{DS} from 15 V to 30 V are used to calculate the mobility in the saturation regime. In Table 4.1 the mobility calculated from each trace is recorded, with the average being 3.8×10^{-3} cm²/Vs.

A2. NREL Certification of PbSe QD Solar Cell

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NREL

quantum dot

Sample: ARM356nE



This file is a composite of two QEs. Data up to and including 1103nm is from "HLBQE 150114-101448." The rest is from "FQE 150114-111511." The relative QE was scaled by 133.1 %

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NREL QD Cell



Kelvin at end of adapter wire

Efficiency = 5.90

A3. Tauc Plot Analysis of EQE Spectrum

The transmitted light (I_t) is given as a function of incident light (I_o) in Equation A3.1:

$$I_t = I_o * e^{-\alpha L} \tag{A3.1}$$

Where α is the absorption coefficient and *L* is the film thickness.

If we assume that all absorbed photons are extracted as current, then as shown in Equation A3.2, the EQE is equivalent to:

$$EQE = \frac{I_o - I_t}{I_o} = 1 - \frac{I_t}{I_o} = 1 - e^{-\alpha L}$$
(A3.2)

Where α in Equation A3.2 is shown in Equation A3.3:

$$\alpha = -\frac{\ln\left(1 - EQE\right)}{L} \tag{A3.3}$$

Since *L* is a constant, α is proportional to -ln(1-EQE). Using α calculated in this way,

a Tauc plot was constructed and the bandgap of each solar cell was determined.