INFRARED SENSITIVE SOLUTION-PROCESSED QUANTUM DOT
PHOTOVOLTAICS IN A NANOPOROUS ARCHITECTURE

by

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Abstract

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If solar energy is to be a significant component of our energy supply, technologies are required which produce high efficiency solar cells using inexpensive materials and versatile manufacturing processes. Solution-processed materials have been used to create low cost, easily fabricated devices, but have suffered from low power conversion efficiencies. A lack of infrared energy capture limits their efficiency.

In this work we develop solution-processed photovoltaic devices using lead sulphide quantum dots and high surface area porous oxide electrodes. The resultant devices have a spectral response from 400 to 1800 nm. In fabricating these devices we utilize crosslinking molecules. We explore the impact crosslinkers have on the mobility and morphology of quantum dot films using field effect transistors and transmission electron microscopy. We also explore a hybrid organic/inorganic route for controlling the net doping in quantum dot films. We investigate the chemical and compositional changes that lead sulphide quantum dots films undergo during crosslinker treatment and annealing. Using this information we optimize our charge separation efficiency and our open circuit voltage. The resulting devices have an infrared power conversion efficiency of 2%, four orders of magnitude higher than that in previously reported lead sulphide quantum dot devices.
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List of Acronyms

AM1.5  Air mass 1.5
BTPF  3(')-(3,5-Bis-trifluoromethylphenyl)-1(')-(4-itrophenyl)pyrazolino[60]fullerene
BTPF70  3(')-(3,5-Bis-trifluoromethylphenyl)-1(')-(4-itrophenyl)pyrazolino[70]fullerene
CELIV  carrier extraction by linearly increasing voltage
CQD  colloidal quantum dot
C-V  capacitance voltage
EdT  ethanedithiol
EDX  energy dispersive x-ray analysis
EQE  external quantum efficiency
FET  field effect transistor
FTIR  fourier transform infrared spectroscopy
HS-GCSM  head-space gas chromatography mass spectrometry
ITO  indium tin oxide
Isc  short circuit current
IV  current-voltage
J-V  current density – voltage
<table>
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<th>Abbreviation</th>
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<tbody>
<tr>
<td>MEH-PPV</td>
<td>poly[2-methoxy-5-(2'-ethylhexyloxy-p-phenylenevinylene)]</td>
</tr>
<tr>
<td>OD</td>
<td>optical density</td>
</tr>
<tr>
<td>P3HT</td>
<td>poly-3(hexylthiophene)</td>
</tr>
<tr>
<td>P3OT</td>
<td>poly 3-octyl-thiophene</td>
</tr>
<tr>
<td>PLQE</td>
<td>photoluminescent quantum efficiency</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>TMS</td>
<td>bis(trimethylsilyl)sulfide (C$<em>6$H$</em>{18}$S$_2$Si)</td>
</tr>
<tr>
<td>Voc</td>
<td>open circuit voltage</td>
</tr>
<tr>
<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
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Chapter 1

Introduction

1.1. Why infrared sensitive photovoltaics?

There exists an urgent need to develop economically-sustainable clean energy technologies. This need motivates research into new materials and devices for future generations of clean energy technology. The world is overwhelmingly dependent on non-renewable fossil fuels such as oil, natural gas, and coal [1]. As can be seen in Figure 1.1 approximately 80% of the world’s energy comes from non-renewable sources.

There are a host of problems caused by our dependence on non-renewable energy sources. Burning fossil fuels causes pollution and the location of global reserves has led to growing concerns about energy security. The price of non-renewables continues to rise. As less economic reserves are sought and developed the costs associated with exploration and extraction will increase, pushing prices even higher [1].
The sun is an enormous renewable energy source [2]. Furthermore, carbon-neutral electricity from photovoltaic technologies addresses concerns about global warming. Currently the global solar market is growing at more than 30% per year [3]. Despite this growth, solar energy still only represents about 0.5% of our energy supply. If photovoltaics are going to compete with current methods of electricity generation, their manufacturing costs will have to come down [2, 4].

Widespread solar adoption requires cheap, efficient solar cells made from easy to manufacture materials. Achieving these requirements simultaneously has proven difficult. Although the world record photovoltaic power conversion efficiency is an impressive 40.7%, it was set by a triple-junction cell with a reported cost of $75,000/m² [5, 6]. On the other hand, silicon solar cells are produced from an abundant material and have shown efficiencies as high as 24.7%. Module costs, however, are about $300/m², in part due to manufacturing and processing requirements [2, 5]. Work on a future generation of photovoltaics must focus on technologies that are cheap and easy to manufacture.
Solution-processed materials such as semiconducting polymers and colloidal quantum dots are excellent candidates for next-generation photovoltaic devices. They are straightforward to manufacture and lend themselves to a variety of high-throughput manufacturing methods. Even when manufactured in small quantities, without the benefits of economies of scale, the PbS quantum dots can be produced for about $11/m^2$ (this figure is the raw material cost required to produce a 1 μm thick film) [7]. The challenge facing solution-processed solar cells is efficiency. The best solid-state solution-processed solar cells only have power conversion efficiencies in the range of 1-5% [8, 9].

Most solution-processed solar cells do not absorb wavelengths beyond 700 nm [8]. Half of the sun’s power that reaches the earth lies beyond 700 nm, and one third beyond 1000 nm. A plot of the air mass 1.5 (AM1.5) spectrum (the standard reference spectrum used for testing terrestrial-based solar cells) is shown in Figure 1.2 [10, 11]. In it one can see the energy contained in the infrared portion of the solar spectrum. This energy is lost by most solution-processed materials. A lack of infrared energy capture limits the efficiency of solution-processed solar cells.

Building tandem or multi-junction solar cells can increase the efficiency of solution-processed solar cells [12]. Although the optimum bandgap for a single junction device lies at about 1100 nm, the optimum bandgaps for a two junction cell are 760 nm and 1320 nm, and for a three junction cell are 1750 nm, 1070 nm, and 680 nm [13]. As the number of junctions increases in a solar cell, so does the maximum power conversion efficiency, increasing from 32.5% to 49.7% under unconcentrated illumination as one progresses from a single junction to a triple junction cell.
Figure 1.2 AM1.5 solar spectrum showing the spectral distribution of the terrestrial solar irradiance. Also shown are the bandgap of silicon and the energy captured by a typical crystalline solar cell [10, 11].

1.2. Why quantum dot photovoltaics?

Solution-synthesized colloidal quantum dots (also known as semiconductor nanocrystals) show an excellent potential for photovoltaic applications due to their size-tunable spectral response, their inexpensive fabrication, and their ready application to large-area devices.

PbS semiconductor nanocrystals are of interest in the creation of infrared-sensitive photovoltaics. As a result of the quantum size effect their bandgap can be tuned from 900 – 2000 nm [14, 15]. PbS nanocrystals can be synthesized with a diameter ranging from 3 to 8 nm by varying the thermal and chemical conditions present during synthesis.
Quantum confined materials also have an electron affinity and ionization potential shifted from that found in their bulk counterparts. This allows one to influence the type of heterojunction formed when nanocrystals are brought into contact with other semiconductors. Additionally, chemical synthesis of quantum dots means they are solution processable and soluble in organic solvents. This allows PbS nanocrystals to be processed like organic semiconducting polymers through spin coating, dip coating, spraying, and ink-jet printing.

1.3. **Thesis objectives and contributions of this work**

The first infrared-sensitive solution-processed solar cell with a spectral response beyond 1 μm was reported in 2005 [16]. It had an infrared power conversion efficiency of 0.00008%. Made using PbS quantum dots it begged the question: Could this material even be useful? A massive divide existed between the performance of this device and the level required for commercial applications.

The first demonstration of a photovoltaic effect from PbS quantum dots utilized a nanocrystal/polymer blend. In this architecture infrared light was absorbed by the PbS nanocrystals, excitons were separated at the nanocrystal/polymer interface, holes were transported out through the polymer, and electrons were transported out by hopping from dot to dot. To improve the performance of devices made from PbS quantum dots significant challenges needed to be addressed. These challenges included:

1. Low optical absorption in very thin devices.
2. Poor dot to dot charge transport resulting from the interdot spacing found in a blended device.
3. No observable conductivity in PbS thin films.
4. A lack of control of the electronic properties of quantum dots.
5. Indications of high trap state densities that would impede the efficiency of charge separation and carrier extraction

A new approach was needed to overcome these challenges and increase the power conversion efficiency. This was the primary research objective of this doctoral project. We set out to investigate, build and characterize a solid-state, solution-processed, infrared sensitive photovoltaic devices with 1% infrared power conversion efficiency, representing a significant step forward on the road toward commercial viability.

Over the course of this project we explored a novel device architecture through the use of high surface area porous electrodes infiltrated with colloidal quantum dots. We also developed an understanding of techniques and processes to influence the chemical, morphological, and electronic properties of PbS colloidal quantum dot films. The choice of device architecture, materials, processing techniques, and the material characterization that allowed us to build and optimize this device represents new work in the field of quantum dot photovoltaics.

The results of this research have led to a number of peer reviewed journal publications, invention disclosures, and patents. A complete list of these contributions can be seen in Chapter 9. These contributions can be summarized as follows:

1. The use of cross-linking ethanedithiol molecules for the assembly of smooth nanocrystal films on rough, high surface area electrodes.
2. Evaluation of the changes in mobility, conductivity, and carrier concentration in PbS colloidal quantum films when treated with ethanedithiol molecules and post-film deposition annealing.
3. Development of an understanding of the chemical and material changes underlying the changes electronic properties as a result of ethanedithiol treatment and inert and ambient atmosphere conditions.
We were able to bring these findings together in the fabrication of photovoltaic devices with 2% infrared power conversion efficiency. This power conversion efficiency is over four orders of magnitude greater than that of previously reported solution-processed infrared photovoltaic devices.

1.4. Thesis organization

The remainder of the thesis is organized as follows. Chapter 2 contains a survey of past relevant research in solution-processed quantum dot photovoltaics, high surface area porous metal oxide photovoltaics and IR sensitive photovoltaics. Areas and opportunities to improve over prior work are identified and placed in the context of this project. Chapter 2 also contains a brief background on the quantum size effect.

In Chapter 3 we present details of the strategy used in the development of our IR sensitive, solution-processed photovoltaic devices. Chapter 4 turns to the specifics of the synthesis of the PbS quantum dots used in this work and discusses the fabrication of the porous oxide substrate. In Chapter 4 we also discuss the methods used for infiltrating the porous oxide with quantum dots and introduce the use of cross-linking molecules for the fabrication of smooth nanocrystal films on high surface area electrodes.

In Chapter 5 we explore the changes in electronic properties and film morphologies seen as a result of the fabrication methodologies presented in Chapter 4 and demonstrate methods for altering the mobility and carrier concentration of the colloidal quantum dot thin films.

Chapter 6 contains an analysis of the morphological and compositional changes resulting from the fabrication methods and post processing used in Chapter 4 and Chapter 5. In Chapter 7 we bring everything together in the fabrication and optimization of photovoltaic devices.
Chapter 8 presents a brief discussion of the findings of this work and future opportunities and Chapter 9 details the list of publication and other contributions arising from it.

We show in Figure 1.3 a visual guide relating the chapters of this thesis to the development of the porous oxide/quantum dot devices fabricated in this project.

**Figure 1.3** A guide relating the chapters of this thesis to the development and optimization of the porous oxide/quantum dot devices fabricated in this work.
Chapter 2

Background and Literature Review

Given the intense interest in the development of solution-processed photovoltaics there exists an extensive body of literature covering a diversity of material systems and device architectures. The work contained in this thesis incorporates features from a subset of this larger field. As such we present in this chapter a review of the literature pertaining to this subset. In particular, we will discuss areas germane to the fabrication of infrared sensitive photovoltaic devices using colloidal quantum dots and porous metal oxides which we will then cover in detail in the remainder of this thesis.

We will first review research that has been carried out utilizing high surface area porous metal oxides in photovoltaic devices. These devices are also known as Gratzel cells, owing to the pioneering work of Michael Gratzel. As colloidal quantum dots were central to our research we will then present a brief background on the physics of quantum confinement. From there we will turn our attention to previous work utilizing quantum dots in photovoltaic devices. Finally we will look at the development of infrared sensitive photovoltaic devices made from solution-processed materials. These topics set the context and form the foundation of the photovoltaic device development detailed in the remainder of this thesis. Figure 2.1
shows the how sections of this chapter relate to the major components of our photovoltaic devices.

![Diagram](image.png)

**Figure 2.1** A depiction of a nanoporous oxide/quantum dot device and how the sections of this chapter relate to its major components.

### 2.1. Gratzel cells

Dye-sensitized heterojunction solar cells have been an area of active research since early work by Michael Gratzel in the 1990s [17]. In their earliest form they were fabricated from a porous wide bandgap semiconducting oxide, such as TiO$_2$, with a light absorbing dye adsorbed onto its surface. This oxide is then infiltrated with a liquid electrolyte and capped with a contact. Electron-hole pairs excited in the dye are separated at the interface between the oxide and the dye. Here the TiO$_2$ acts as an electron acceptor and also serves as the electron transport medium. Once an electron has been transferred to the TiO$_2$ it is transported out to a thin transparent conducting oxide which serves as the second contact [18]. Holes are transferred from the dye to the electrolyte and are then transported to the opposite contact through this electrolyte. A schematic of this device can be seen in Figure 2.2.
Figure 2.2 Schematic of a dye sensitized solar cell. The white circles represent the TiO₂ covered by an approximate monolayer of the sensitizing dye which is represented by the red circles [19].

One advantage of devices built with these structures is that they have high internal surface area and a distributed heterojunction between the dye and the TiO₂. This provides a large effective active region for increased incident light absorption and charge separation [20]. A measure of the physical surface area per unit of the projected area is called the roughness factor, RF [20, 21]. The roughness factor found in porous oxides used in these devices can be as high as 1000 in 10 μm thick films of randomly oriented particles [22]. There has also been work using semi-organized porous TiO₂ films and arrays of ZnO nanowires which serve to reduce device thickness and improve charge transport properties [21, 22].

Much additional work on these structures has focused on removing the liquid electrolyte and replacing it with a solid state hole conducting layer. This is seen as a major barrier to be overcome in order for widespread implementation to occur.
2.1.1. Solid state Gratzel cells

Similar to liquid electrolyte based Gratzel cells, solid-state dye-sensitized solar cells are based on a network of interpenetrating junctions formed by inorganic oxides, a monolayer of dye attached to the oxide, and an organic hole transport layer overcoating the dye [23]. To date most demonstrations of solid-state Gratzel cells have resulted in lower efficiency devices (4% power conversion efficiency in the solid state as opposed to 11% in solution-based devices) [18]. Efforts to improve the performance of these devices have focused on improving the transport characteristics of the solid-state hole transport medium and increasing the lifetime of the photoexcited charge carries by altering the sensitizing dyes [19, 24, 25].

An example of research modifying the sensitizing dyes can be seen in the spectra shown in Figure 2.3 [23].

![Figure 2.3](image)

**Figure 2.3** Incoming photon to current conversion efficiency (IPCE) for the dyes with different hydrocarbon chain lengths [23].
In Figure 2.3 it is interesting to note that there is no appreciable current generation for wavelengths to the red of 750 nm. It is in this spectral region that our work utilizing PbS quantum dots in lieu of organic dyes can help improve the performance of porous oxide based devices.

The hole transport layer that has been used in solid-state dye-sensitized devices with the highest reported efficiency (4% A.M 1.5 power conversion efficiency) is called spiro-MeOTAD and is typically deposited via spin coating from an organic solvent such as toluene [25]. Its hole mobility is reported to be $1 \times 10^{-4}$ cm$^2$ as measured by time-of-flight measurements and it has a work function of approximately 4.9 eV [19]. The amount of research into Gratzel cells provides an indication of the anticipated application of this device structure.

### 2.2. Quantum confinement and nanocrystals

Semiconductor particles with radii less than 10 nm - often referred to as nanocrystal quantum dots - have been the focus of considerable research in the past fifteen years. Nanocrystals have the characteristic of confining carrier motion in three dimensions while preserving the crystal structure of the bulk material of which they are composed. It is the combination of these two factors that make nanocrystals such an attractive material system.

At the heart of the array of physical phenomena that manifest themselves in these materials is quantum confinement. When a semiconducting crystal, such as CdSe, which has often been the prototypical nanocrystal material, is reduced in size to the point where the electron (and/or hole) wave functions begin to be squeezed into a region smaller than their characteristic Bohr radius, their allowed eigen energies increase in energy from that of the bulk [14].
In a bulk semiconductor the energy levels in the valence and conduction bands are closely spaced such that they form a nearly continuous density of states. However, as the volume of the semiconductor reduces, charge carriers within the semiconductor become confined to a smaller and smaller space. The result of this spatial confinement is that a carrier acquires increased kinetic energy and the bulk energy bands begin to separate into discrete levels [14, 26]. An illustration of this contrast in the density of states between the bulk and size-quantized semiconductor confined in three dimensions (i.e. a quantum dot) can be seen in Figure 2.4.

![Figure 2.4 Distribution of electron density of states in a bulk and size-quantized semiconductor [14].](image)

The separation of energy levels is most pronounced at the top of the valence band and the bottom of the conduction band. When the separation is greater than the thermal energy, changes in a material’s optical and electronic properties occur. One of the most useful changes is the increase in bandgap energy as the size decreases. The extent to which the bandgap energy can be changed is quite pronounced. For example, in CdSe quantum dots the bandgap energy has been varied from 3.1 eV to 1.8 eV (corresponding to a shift from 400 nm to 700 nm), a dramatic change considering the bulk bandgap energy of CdSe is 1.73 eV [27].
Figure 2.5 shows the shift in the absorption spectrum as the CdSe nanocrystal size decreases from 11.5 nm to 1.2 nm in diameter [27].

![Absorption Spectrum](image)

**Figure 2.5** Room temperature absorption spectra of CdSe nanocrystals ranging in size from 11.5 nm to 1.2 nm [27].

For charge carriers to feel confined the size of the crystal particle must be on the order (or less) than the Bohr radius of an electron-hole pair (referred to as an exciton), as would be found in the bulk solid.

The Bohr radii of excitons varies widely from semiconductor to semiconductor. For example, InSb has an exciton radius of 54 nm while CdSe has 6 nm. The excitonic Bohr radius of PbS is approximately ~18 nm [28]. The extent of quantum confinement is determined by the size of the crystallite relative to the size of the excitonic Bohr radius.
The earliest theoretical treatment used to explain the blue shift in the bandgap of crystallites with decreasing size utilized a particle in a sphere model and the effective mass approximation [29]. The consequence of the assumption of a spherical box with infinite confining potential is a set of solutions describing the energy levels of the electron \((e)\) and hole \((h)\) of the with the form [30]:

\[
E_{n,l}^{e,h} = \frac{\hbar^2 \phi_{n,l}^2}{2m_{e,h} a^2}
\]

Where \(m_{e,h}\) is the electron and hole effective mass respectively, \(a\) is the crystal radius, \(\Phi_{l,n}\) is the \(n\)th root of the spherical Bessel function of order \(l\). The use of this solution predicts an increase in energy levels with an inverse square dependence on radius. This is approximately true for most confinement regimes and is appropriate as a first order estimate of energy levels. It is useful for understanding the origin of the increase in bandgap and the discretization of energy level which arises as a consequence of the solution set of spherical Bessel functions.

Because the bandgap of a nanocrystal begins with that of the bulk material and subsequently shifts up in energy, certain semiconductors are more suitable to specific applications than others. As mentioned above CdSe (and CdS) can be tuned across the entire visible spectrum, making it a potential material for display applications. On the other hand PbS has a bulk bandgap of 0.41 eV (3100 nm) and can be tuned across the spectral region of 800-2000 nm. This makes it suitable for near-IR emitters, detectors, modulators, and photovoltaics [16, 31-34].

In work with quantum dots the effective bandgap is referred to as the first excitonic transition. A typical absorption spectrum of PbS nanocrystals with a first excitonic transition at about 1335 nm is shown in Figure 2.6 along with an illustration contrasting the bandgap of bulk PbS with the first and second excitonic transition of quantum confined PbS.
2.3. Nanocrystal photovoltaics

Owing to the inexpensive synthesis, diverse device fabrication routes, and wide material choices available in semiconductor nanocrystals there has been a great deal of interest in utilizing these materials for solar energy generation. Initial efforts to demonstrate a photovoltaic effect using solution-processed quantum dots focused on the well established material system of Cd(Se,S,Te).

The earliest demonstration of a photovoltaic effect used CdSe nanocrystals in a semiconducting polymer blend in 1997. In this work by Greenham et al., devices were made by mixing CdSe with MEH-PPV which then was spun onto ITO coated glass and capped with evaporated Al contacts [35]. In this structure charge separation occurs at the interface between the CdSe and MEH-PPV due to the Type II heterojunction formed between the two materials. The CdSe acted as a transport medium for electrons which had to tunnel from
nanocrystal to nanocrystal to be extracted at a contact. The authors carried out a study showing that the efficiency of charge extraction increased with nanocrystal loading. An optimum external quantum efficiency of 12% was found for mixtures with 90% nanocrystals (by weight). This was measured at a wavelength of 512 nm at an intensity of 5 W/m². As both CdSe and MEH-PPV are absorbing in the visible there was no spectral response beyond about 650 nm.

From this point forward research efforts focused on improving upon this initial result. Some of the most dramatic increases in device efficiency came using devices which incorporated CdSe nanorods in another semiconducting polymer, P3HT [36-38]. In this work nanorods (see Figure 2.7) exhibited improved performance over dots as they allow electron conduction along their length and require fewer “hops,” improving the charge transport within an ensemble of nanocrystals [37].

![Figure 2.7 CdSe Nanorods of varying aspect ratios. A) Dots: 7x7 nm, B) Rods: 7x30 nm, C) Rods: 7x60. The longer dots shown in (C) resulted in PV devices with the highest efficiency [37].](image)

Another compelling aspect of this device architecture is that by altering synthetic conditions the length of the nanorods can be tailored to match the thickness of the device. One of the limitations of this process was that as the length of the rods increased beyond 60
nm, they became less soluble and tended to aggregate within the polymer, decreasing the efficiency of charge separation.

The performance and spectral response of polymer/nanorod devices can be seen in Figure 2.8. Under monochromatic illumination of 0.084 mW/cm² at 515 nm it exhibited a monochromatic power conversion efficiency of 6.9%. The open circuit voltage under these conditions was found to be 0.5 V. Under A.M. 1.5 conditions the authors reported a power conversion efficiency of 1.7% and an open-circuit voltage of 0.7 V. It should be noted that these results were all obtained in a flowing Argon atmosphere to avoid oxidation of polymers and contacts.

![Figure 2.8](image)

**Figure 2.8** A) EQEs of 7-nm-diameter nanorods with lengths 7, 30, and 60 nm. The intensity is at 0.084 mW/cm² at 515 nm. (B) The current-voltage characteristics of the 7 nm by 60 nm nanorod device under illumination of 0.084 mW/cm² at 515 nm [37].

A further advancement in the performance of visible-light absorbing cadmium chalcogenide nanorod devices came about in 2005 when Gur et al. published results using CdSe and CdTe nanorods [8]. In these devices a bilayer heterojunction was formed between two spin coated layers of CdSe and CdTe. Power conversion efficiencies under AM 1.5 illumination of 2.9 % were reported. Similar to the CdSe/Polymer devices reported earlier
these devices were most sensitive to the visible spectral region with no reported response beyond about 750 nm.

2.3.1. Gratzel cells using quantum dots

Quantum dots have also been used in lieu of dyes as the sensitizing agent in the fabrication of Gratzel cells. This work falls into two categories; one where nanocrystals are fabricated in situ directly onto the oxide via chemical bath deposition [39, 40], and the second where nanocrystals are fabricated separately through organometallic synthetic methods (which will be discussed in detail in Chapter 4) and then deposited onto the oxide substrate [41, 42].

In devices made with nanocrystals fabricated via chemical bath deposition a wide variety of semiconducting materials and porous oxides have been explored. These include work using CdS, Bi$_2$S$_3$, Sb$_2$S$_3$, PbS grown on TiO$_2$ and ZnO [40]. Nanocrystals synthesized by this method had an optical bandgap shifted from that of the bulk and thus exhibited quantum confinement. However, due to the nature of the synthetic method, there was a minimal ability to control the particle size and as a result all of the materials reported had their absorption peak in the visible spectral region. The best reported performance for these type of devices was a power conversion efficiency of 0.49% under simulated solar conditions of 0.1 mW/cm$^2$ [39].

Previous reports of porous oxide devices infiltrated with separately fabricated nanocrystals include work by Yu et al. in fabricating TiO$_2$ oxide/InAs nanocrystal Gratzel cells and work by Robel et al. fabricating TiO$_2$/CdSe Gratzel cells [41, 43]. Yu et al. showed the benefit of the quantum size effect by fabricating a series of devices with different size InAs and hence different spectral response. The best reported power conversion they obtained was 0.3% under AM 1.5 illumination. Their best devices used InAs quantum dots with a first
excitonic transition of 800 nm which did not have significant absorption beyond about 850 nm.

Although prior research has been carried out using a quantum dot/porous oxide device architecture similar to that used in this thesis, there are important differences between this work and prior work. These differences include the fact that prior research used liquid electrolytes and visible wavelength sensitive nanocrystals, whereas our devices are solid-state and sensitive beyond the visible into the infrared.

2.4. Solution-processed infrared photovoltaics

Previous research on solution-processed infrared photovoltaic devices has been based on two different material systems. In one system devices were fabricated from blends of semiconducting polymers and fullerene-derivatives. In the other, devices were made from semiconducting polymers and PbS nanocrystals.

2.4.1. Performance metric

We will compare the performance of solution-processed infrared photovoltaic devices using their monochromatic power conversion efficiency at \( \sim 1000 \) nm. Our reason for doing so is two-fold. First, the assembly of solar cells having multiple junctions is considered essential in generating electricity at prices competitive with traditional methods [2, 44]. In a multiple junction cells each junction in a device stack must efficiently capture the energy of a portion of the solar spectrum. In a triple junction cell the optimum band-gaps needed are approximately 700, 1000, and 1800 nm. Second, using 1000 nm power conversion efficiency allows us to compare the performance of devices made using different materials and architectures.
2.4.2. Polymer/fullerene devices

Polymer/fullerene-derivative devices are composed of blends of a low bandgap polymer (called APFO-Green1) which acts as a hole acceptor and a functionalized C70 molecule (called BTPF70) which serves as an electron acceptor [45]. Functionalized fullerenes (BTPF) have also been used in these devices but it was found that C70 has better performance due to its optical bandgap of about 700 nm as compared to C60’s bandgap of 600 nm [46]. The best reported infrared performance from the fullerene/polymer photovoltaic devices show power conversion efficiencies of 0.3% under 1000 nm illumination [45]. These device’s spectral response can be seen in Figure 2.9.

![Figure 2.9 EQE of APFO-Green1:BTPF70 blend solar cells (solid circles) and APFO-Green1:BTPF (open circles as well as the absorption of APFO-Green1 (solid line) [45].]
2.4.3. Polymer/PbS quantum dot device

The other significant approach to fabricating infrared-sensitive solution-processed photovoltaics is by using PbS quantum dots. The first reported demonstration of this material system was in 2005 by McDonald et.al. [16]. In this work devices were fabricated using a blend of PbS and the semiconducting polymer MEH-PPV. Although significant for its novelty, this work produced devices that had an infrared power conversion efficiency of 0.00008% at 975 nm. Further improvements in efficiency first came by post fabrication annealing of devices which modified the ligand barrier between the quantum dots and the polymer and resulted in a power conversion efficiency of 0.001% at 975 nm [47].

In work by Maria et al. a bilayer device architecture was fabricated consisting of a layer of PbS nanocrystals spin coated on top of a layer of the semiconducting polymer P3OT [48]. The best reported power conversion efficiency obtained from this bilayer device at 975 nm was 0.025%. A plot of the spectral EQE is shown in Figure 2.10 for a series of these devices demonstrating that this material system is sensitive to light beyond 1000 nm. It is interesting to note that in these devices the internal quantum efficiency (that is, the ratio of the absorbed photons to the extracted electrons) was almost 10%, indicating that performance gains could be gained by increasing the optical density.

These initial results using PbS nanocrystals show that this material is capable of being used in solution-processed photovoltaics sensitive to wavelengths well beyond the 1000 nm accessible by polymer/C70 devices. These results also showed that there was an opportunity to increase the performance by pursuing alternative device structures with higher inherent optical densities and by developing and understanding an ability to control the factors influencing the electronic properties of PbS quantum dot composites.
Figure 2.10 External quantum efficiency as a function of wavelength for a series of devices having four different thicknesses nanocrystal layers ranging in thickness from 80 nm to 160 nm. The inset shows the absorption spectrum of P3OT [48].

2.5. Performance summary

We present in Figure 2.11 a summary of the results obtained from solution-processed solid state photovoltaic devices. For devices only sensitive to visible wavelengths we report power conversion efficiencies under broadband (AM1.5) illumination. For devices sensitive to the infrared we report power conversion efficiencies at ~1000 nm.
Figure 2.11 Progress of the power conversion efficiency of solution-processed photovoltaics. The devices only sensitive to visible light have their efficiencies reported for broadband illumination. The devices sensitive to infrared light have their efficiencies reported for illumination at ~1000 nm. Also indicated on this chart is the 1% IR power conversion efficiency goal of this research project.

In this chapter we have reviewed a subset of device architectures and materials used in the fabrication of solution-processed photovoltaics. Specifically, we have discussed Gratzel cells, quantum dot devices, and polymer/fullerene devices. These devices encompass the features most relevant to the work contained in this thesis. Through examining this prior work we have been able to identify opportunities for improving solution-processed infrared photovoltaics which we pursue in the remainder of this thesis.
Chapter 3

Device Fabrication Strategy

There are three fundamental requirements of making a photovoltaic device with 1% infrared power conversion efficiency utilizing solution-processed materials:

1. Absorb the incident light
2. Separate excited electron-hole pairs
3. Transport electrons and holes to their respective contacts

The goal of this research project was to fabricate infrared sensitive, solution-processed photovoltaic devices using PbS quantum dots which exceeded the performance of previous IR sensitive solution-processed devices. This goal required a device of sufficient optical density to absorb a significant fraction of the incident light. It required a material system in which the electron-hole pair could be extracted from the PbS quantum dots. It also required materials with electronic transport properties that allowed for low losses when the carriers were being transported out of the device. These losses included both resistive losses and recombination losses.

As we were working with quantum dots that inherently have a high surface to volume ratio, a means of passivating trap states and increasing mobility was also desired. A
A fabrication strategy for producing a solid state device which did not incorporate liquid electrolytes found in traditional Gratzel cells was a further requirement.

In this chapter we outline how the requirements for achieving good photovoltaic efficiencies informed our choice of device architecture, materials, and processing techniques. We also outline targets for electronic properties of our materials that allow us to fabricate high efficiency devices. Figure 3.1 outlines the major sections of this chapter in the context of the project as a whole.

**Figure 3.1** Image showing major sections of the fabrication strategy discussed in this chapter.
3.1. Optical density targets

One of the drawbacks of earlier work using PbS quantum dots in photovoltaic devices was that the thin PbS layers used resulted in low optical density. As discussed in Chapter 2, the highest reported PbS quantum dot device efficiency prior to this work was obtained with bilayer PbS/P3OT solar cells. In these devices spin coated PbS films 160 nm thick resulted in devices with EQEs of 0.4% at the first excitonic peak of 1260 nm [48]. However, due to the device thickness the optical density at 1260 nm was only 0.028, which meant that only 7% of the incident light was being absorbed (neglecting reflective losses). As such, a primary requirement of this project was to work with an architecture that resulted in devices with much higher absorption.

The target we set for this project was 90% light absorption at 975 nm, which meant devices with an optical density of 1. The measured absorption coefficient of PbS quantum dot films is about 1.1 x 10^4 cm⁻¹. Using the Beer-Lambert law and assuming reflective losses are minimal this means that to achieve an optical density of 1 our target film thickness was at least 2 μm.

3.2. Charge separation

One of the constraints in any photovoltaic device built using nanocrystal quantum dots arises from the fact that photoexcited electron-hole pairs have a higher binding energy than that found in bulk semiconductors. Any such photoexcited exciton must be dissociated (i.e. charge separated) before the electron and hole can be transported out to their respective contacts. In a photovoltaic device this charge separation typically occurs at junction between two materials (a heterojunction) or a junction between two differently doped regions of a single material (for example a p-n junction).
If an exciton is generated away from a junction then it must first be transported to it before the carriers recombine (either radiatively or nonradiatively). If an exciton recombines before charge separation occurs then the quantum efficiency of the device drops accordingly.

Exciton transport between quantum dots occurs primarily through Förster energy transfer. Förster transfer is a dipole-dipole interaction whereby an exciton in one nanocrystal induces an exciton in a second nanocrystal having a lower available energy state than the first [49]. Measurements of Förster transfer lengths in quantum dot films have ranged from about 2 nm to about 15 nm [49-51].

The implication that a short exciton transport length has for building photovoltaic devices using PbS quantum dots is that if a thick device is required for light absorption then an architecture is required which allows any photoexcited exciton to be no farther than about 15 nm from a region of charge separation. This requirement brings us to consider the use of a Gratzel cell-like architecture infiltrated with PbS quantum dots. One of the features of this architecture is that in a high surface area porous oxide any PbS quantum dot will be in close proximity to an oxide interface. This proximity will be determined by the average pore size of the material. Another feature of this architecture is that films in the 2-10 μm thickness range needed for a sufficiently high optical density, are routinely formed for porous oxides by spin coating or blade casting.

3.3. Choosing a porous oxide

Although TiO₂ is most commonly used in Gratzel cell work there were a number of other oxides available to us capable of forming high surface area electrodes. Many of these are commercially available and have average particle sizes on the order of 50 nm. As particle size and film annealing temperature determine pore size in an aggregate film, particle size becomes a factor in the selection of our material [52]. Another important factor in oxide
selection is whether the interface between a given oxide and the PbS quantum dots is suitable for exciton dissociation. Most Gratzel cell architectures use insulating, wide band-gap oxides. In these systems charge separation occurs as a result of the potential energy difference between the electron in the light absorber and that of the oxide [53]. In this donor-acceptor model the relative positions of conduction and valence bands in two materials determines whether charge separation will occur.

There is another possible mechanism for charge separation owing to the existence of highly doped, conductive oxides such as indium tin oxide (ITO). Although ITO is a doped wide-band gap metal-oxide (indium oxide, doped with tin) it is used as a transparent conductor and typically treated like a metal with a work function [54]. This raises the possibility of another mechanism for charge separation, the formation of a Schottky junction at the interface between a doped metal oxide and our PbS nanocrystals. This Schottky barrier will result in a depletion region and an associated electric field that can serve to separate photogenerated electrons [55, 56].

3.3.1. Photoluminescence quenching

There is a great deal of variation in the reported values of the ionization potential, electron affinity, and work function for many of the porous oxides of interest. As such we started with a list of potential candidates and sought a straightforward experiment to provide us with a means of determining the potential for charge separation to occur at the interface between PbS and a given oxide. Photoluminescence quenching provides a means of determining if charge separation is occurring at an interface [35]. At interfaces with rapid, efficient charge separation, the photoluminescence from optically pumped PbS quantum dots will be much lower than at interfaces with poor charge separation.
In this study PbS quantum dots with a first excitonic transition of 1500 nm were deposited onto a series of porous oxides of different compositions. The photoluminescent quantum efficiency (PLQE) of the PbS was the measured and compared between oxides. The oxides tested were: ZnO, ZrO$_2$, SnO$_2$, ITO, WO$_3$, In$_2$O$_3$, and TiO$_2$. Table 3.1 shows the results of this study.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>PLQE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS (no oxide)</td>
<td>0.50</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.40</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>0.23</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.11</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>0.10</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>0.017</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>0.0069</td>
</tr>
<tr>
<td>ITO</td>
<td>0.0016</td>
</tr>
</tbody>
</table>

**Table 3.1** Measured PbS PLQE when combined with different porous oxides. (Data acquired by Emanuel Istrate and Shannon Boettcher)

From this study we can see that ITO and WO$_3$ appear to be good starting candidates for further device development in a porous oxide/PbS architecture. PbS that is in contact with these oxides has a PLQE that is more than 100 times lower than ZnO.

Porous ITO film work done by other research groups has also shown that ITO films can be fabricated with low resistivities (less than 0.5 Ωcm) [57]. A low resistance electrode is desirable as this will aid in the reduction of resistive losses in completed photovoltaic devices. ITO is also available commercially with average particle sizes of about 30 – 50 nm, a particle size well suited for our needs. There is also a body of work modifying the work function of ITO which presents a useful lever in optimizing the performance of devices made with ITO [58, 59]. For these reasons we chose ITO as the porous oxide for the device work that followed.
3.4. Charge separating junctions

Schottky junctions form between semiconductors and metals and have been used in the fabrication of photovoltaic devices [60, 61]. As we have chosen to work with a highly doped porous oxide electrode it is expected that a Schottky junction will form between our PbS film and our ITO. We will also expect to have a Schottky barrier form between the top metal contact and the PbS in a completed device. As such we will briefly describe the Schottky junction and discuss some of the electronic properties we set out to control in our devices in order to understand and improve their performance.

3.4.1. Operation of Schottky PV devices

In the fabrication of Schottky barrier photovoltaic devices a metal with a work function $\Phi_m$, is deposited onto a semiconductor with a Fermi level $E_{FS}$. If $\Phi_m$ is not equal to $E_{FS}$ band-band bending occurs as charge carriers redistribute until the energy level reaches equilibrium (i.e. the local Fermi-level is flat throughout the junction) [62]. An image of a junction at equilibrium for an ideal metal-semiconductor interface is shown below in Figure 3.2.

![Band diagram of a metal-semiconductor contact](image)

**Figure 3.2** Band diagram of a metal-semiconductor contact
The barrier height, $\Phi_b$, that is formed at a Schottky junction is given by:

$$\phi_b = \phi_m - \chi_s \quad \text{Equation 3.1}$$

Where $\chi_s$ is the electron affinity of the semiconductor.

The built-in potential, $V_{bi}$, which arises from the amount of band-bending within the semiconductor is given by:

$$qV_{bi} = \phi_m - E_{FS} \quad \text{Equation 3.2}$$

Where $q$ is the electron charge.

In most metal-semiconductor contacts this ideal situation is never reached due to the presence of interface states. These interface states resulting in a pinning of the Fermi level at the surface of the semiconductor, reducing the height of the barrier $\Phi_b$ [62]. Nonetheless, this represents an upper bound for the built-in potential (and barrier height).

Another result of a Schottky junction is the formation of a depletion or accumulation region that forms within the semiconductor at the interface between it and the metal. This region has a fixed width, $w$, and within this region there is distribution of charge carriers different from that away from the interface. In the case of a depletion region these charges are either fixed donors or acceptors, or in the case of an accumulation region these charges are mobile majority carriers.

For the purposes of understanding the application of a Schottky junction in a photovoltaic device it is useful to understand the origin and strength of the electric field that
exists within this depletion region. Using the depletion approximation one can calculate the maximum electric field strength ($F_{\text{max}}$):

$$|F_{\text{max}}|^2 = \frac{2V_a q N_a}{\varepsilon}$$  \hspace{1cm} \text{Equation 3.3}

Where $N_a$ is the acceptor density and $\varepsilon$ is the permittivity of the semiconductor.

The electric field strength is of particular interest in the context of our devices because for charge separation to occur the field strength within a depletion region must be sufficient to disassociate a photogenerated exciton within a nanocrystal.

Within nanocrystals an upper bound for the exciton binding energy, $E_b$, is the Stokes shift [63]. The Stokes shift is the spectral difference between first excitonic absorption peak and the photoluminescence peak. A typical Stokes shift observed in our PbS nanocrystals is about 0.1 eV. Exciton dissociation in the presence of an electric field can be broken down into that occurring under high field conditions and under intermediate field conditions [64]. Under high field conditions exciton dissociation is rapid and efficient and it is in this regime we would like to operate our devices. This regime occurs when the following condition is true [64]:

$$F > F^* = \frac{E_b}{a}$$  \hspace{1cm} \text{Equation 3.4}

Where $F$ is the electric field and $a$ is the exciton radius. Using an average quantum dot size diameter of 5 nm and a binding energy of 0.1 eV, one calculates that $F^*$ is equal to $9 \times 10^4$ V/cm. This analysis shows us that to achieve efficient charge separation one must be able to control the strength of the electric field seen in the depletion region of the device.
Looking back at the Equation 3.3 one can see that the two parameters which can be influenced to alter $F_{\text{max}}$ are the acceptor density, $N_a$, and the built in voltage $V_{bi}$. However, the built in voltage can only change by a few tenths of a volt as this is set by a combination of the Fermi level in our PbS and the work function of our ITO. On the other hand $N_a$ can potentially be changed by orders of magnitude if we can impact the doping level of our PbS films.

### 3.5. Controlling doping levels in quantum dot nanocrystals

As discussed above, controlling the doping level within our ensemble of colloidal quantum dots will be an important tool in improving the efficiency of our photovoltaic devices. As such we will first present a brief review of doping nanocrystals.

There have been a number of techniques used to change the carrier density in colloidal quantum dot solids. One of these methods is an electrochemical method called charge-transfer doping. Charge transfer doping has shown strong net doping changes over multiple orders of magnitude but has unfortunately lacked convenient long-term stability. While electrochemistry has been shown to be a very effective means of populating charge carriers in cross-linked CdSe nanocrystals [65], to keep the doping level constant in time it was necessary to cool samples to -73 °C. More recently, charge transfer doping in ensembles of Au nanoparticles was used to control Schottky barrier heights between Au nanoparticle ensembles and bulk InP [66]. While a degree of stability was conferred due to ions from the electrolyte solution intercalating around the ligand shell of the nanoparticles, it was noted that the electrical characteristics of the charged devices change considerably over a period of hours to days.

Other colloidal quantum dot doping methods have sought to incorporate dopants into the bulk of the nanoparticles either during nanoparticle synthesis or through post-processing
of films. Evaporating potassium in high vacuum led initially intrinsic CdSe colloidal quantum dot solids to become n-type; however, the limited depth of diffusion of the dopant into the film resulted in the doping of only about six monolayers of nanoparticles [65]. Inclusion of atomic dopants in nanoparticles has also been pursued during synthesis via the addition of impurity dopants during growth of the nanoparticles. The variability of this method has led to the hypothesis that nanoparticles self-purify during growth [67].

Recently, a hybrid organic-inorganic route to doping nanoparticles was demonstrated through the use of hydrazine [68]. Non-conducting PbSe colloidal quantum dot solids were doped n-type by soaking in hydrazine and were employed in thin-film field effect transistors (FET). The devices were then switched to p-channel FETs by vacuum treatment or low temperature heating (100 °C) which served to remove the hydrazine from the film. Hydrazine was reported to desorb, even under modest temperatures of 40 °C, over the course of a few hours.

In PbS quantum dots there may exist another doping method which avoids the self-purification and stability problems seen in previous methods. This method exploits the fact that oxygen is known to be effective in the formation of acceptor states in naturally-occurring galena and in synthesized microcrystalline PbS films[69, 70]. Bulk n-type PbS and PbTe can be doped to p-type behaviour by annealing in air or O₂. This conversion is stable and effective in creating photosensitive films useful in infrared photodetection [71, 72]. This has led to the use of oxygen as a dopant in commercial infrared PbS photodector devices which operate stably at up to 70 °C over years. Indeed in many binary metal/non-metal semiconductor systems such as Pb(S,Se,Te), Ga(As,P), Cd(S,Se,Te) and Zn(S,Te) this same doping route exists [73-77].

We explored the formation of surface oxides in PbS quantum dots as a route for producing doping changes in our devices. Thermal and chemical treatments were pursued as
a practical method for controlling carrier density in our PbS films. This was done with the aim of altering the maximum electric field strength in our devices in order to allow for complete ionization of photogenerated excitons.

3.6. Charge transport – the importance of mobility

Charge transport in semiconductors occurs as a result of an electric field (i.e. drift) or as a result of a carrier concentration gradient (i.e. diffusion). Once charges are separated in our photovoltaic device they need to be transported out to opposite contacts. In a semiconductor the diffusion length is as follows:

\[ L_{\text{diff}} = \sqrt{\frac{\mu \tau k T}{2}} \]  

Equation 3.5

Where \( \tau \) is the carrier lifetime and \( \mu \) is the mobility, \( k \) is Boltzmann’s constant and \( T \) is the temperature.

The drift length is given by:

\[ L_{\text{drift}} = \sqrt{\frac{\mu \tau F_{\text{max}}}{2}} \]  

Equation 3.6

To maximize the charge transport length in our devices it is clear that a means of controlling mobility was needed. This would allow us to increase the efficiency of charge transport. Mobility in ensembles of colloidal quantum dots is heavily dependant on inter-dot spacing. As such means of controlling this spacing was explored through the course of device processing.

3.7. Passivation

Passivation of nanocrystal surfaces was expected to have an influence on the open circuit voltage with a photovoltaic device and on the efficiency of charge transport. The maximum theoretical open circuit voltage (that is the voltage generated by an illuminated
photovoltaic device under open circuit conditions) generated in a Schottky barrier device is determined by the built-in voltage of the barrier [78]. In practice this is an upper limit that is rarely reached due to the presence of interface states [62]. Pinning of the Fermi level at the metal-semiconductor influence typically lowers the built in potential seen at this interface. In order to improve the open circuit voltage of our devices, annealing techniques were explored in an effort to improve the surface passivation of our semiconductor nanocrystals. Improved surface passivation is also likely to decrease the distribution of scattering centres and recombination sites, further improving transport efficiency and charge separation.

3.8. Summary

In this chapter we looked at the requirements for building an efficient solar cell using solution-processed colloidal quantum dots. We have presented a solid-state architecture with a high optical density and surface area. We have also presented a material set that results in high light absorption and efficient charge separation. To ensure efficient charge separation we sought to develop techniques that allowed us to increase the doping levels, and hence the electric field strength present in the depletion region of our devices. To effectively extract charge carriers once charge separation has occurred, we developed techniques and processes that allowed us in increase (and measure) mobility. Finally, we set out to explore the impact that annealing has on improving the open circuit voltage of our devices. Taken together these guidelines and techniques allowed us to build solution-processed, infrared sensitive photovoltaics with an efficiency greatly exceeding that which preceded this work.
Chapter 4

Quantum Dot Synthesis and the Fabrication and Infiltration of Porous ITO

In this chapter we discuss the fabrication routes used in the synthesis of colloidal quantum dots and how these synthetic routes influence their optical and electronic properties. We also discuss post-synthesis modification of the ligands passivating the nanocrystal surface. Modifying the ligand type is a common technique used to enhance nanocrystal charge transport properties in solid state devices.

We then turn to the fabrication of the second major constituent of our devices, the porous metal oxide. We present the specifics of our oxide fabrication procedure and show SEM images of the structures obtained by these techniques.

Finally, we turn to the challenges associated with infiltrating the porous oxide and report on EDX measurements that we used for infiltration confirmation. We also introduced a chemical cross-linking procedure employed to deposit a continuous, crack free, pin-hole free nanocrystal film covering the top surface of the porous oxide. Figure 4.1 outlines the major sections of this chapter in the context of the project as a whole.
4.1 Nanocystal Synthesis

There are two primary methods for preparing nanocrystals, synthesis in confined matrices, and solution-based colloidal synthesis utilizing a metal-organic reaction [79]. Matrix-based non-solution techniques have the advantage of creating environmentally stable nanocrystals, but typically results in quantum dots permanently trapped in the matrix they were synthesized in. An additional disadvantage is the relatively large size distribution, typically 20%, which leads to spectral broadening, mitigating the effects of concentrated oscillator strength seen in individual dots [26]. On the other hand, organometallic synthesis has the advantage of producing much narrower size distributions, on the order of 5%, and provides excellent control over size [27].
Most early nanocrystal quantum dot synthesis used non-solution based techniques. However solution based processing is now well developed and can produce nanocrystals from a wide variety of materials. The solution-based synthetic techniques presented here are used to make the PbS nanocrystals used in this work.

4.1.1. Solution based synthesis

Organometallic synthesis was first used in 1983 to produce CdS nanocrystals and the technique has been further developed to produce high quality, monodispersed particles of a variety of materials [80]. Organometallic synthesis also has the flexibility to allow surface modification through exchange of the passivation layer, and can be used to create core-shell heterostructures [81, 82]. The resultant nanocrystals can also be incorporated into polymer and sol-gel hosts for use in emission, detection, and modulation device architectures [83, 84].

4.1.2. Chemical precursors

There are typically two primary precursors (which can be liquid or solid) each containing one of the elemental components of the desired nanocrystals. For example in the first reported preparation of high quality CdSe fabricated via the organometallic method, the precursors used were Me₂Cd - a metal alkyl – and TOPSe (tri-n-octylphosphine selenide) – a chalcogen source [27].

In the PbS synthesis used for our work the Pb precursor is PbO and the sulphur precursor is bis(trimethylsilyl)sulfide (C₆H₁₈S₂Si), referred to as TMS. Both of these precursors are solids which are first dissolved in oleic acid (C₁₈H₃₄O₂) and octadecene (C₁₈H₃₆) respectively, creating liquid precursors.

A coordinating solvent is also needed during synthesis which consists of a molecule that will passivate the nanocrystal surface, preventing aggregation upon completion of
synthesis. These molecules are typically long chain organic hydrocarbons and are referred to as ligands. One can see in Figure 4.2 a graphic depicting a single quantum dot surrounded by a shell of capping ligands. TOPO (tri-\textit{n}-octylphosphine oxide) and TOP are typically used in Cd(S,Se) synthesis. In our PbS synthesis the coordinating solvent and capping ligand is oleic acid.

![Figure 4.2 Graphic depicting a single nanocrystal and a shell of passivating ligands.](image)

4.1.3. Equipment

The following equipment is typically used during synthesis:

- Three Necked Flask: this method is often referred to as a “one-pot” reaction and it is in the flask that the reagents are combined
- Stirring Bar: a Teflon-coated magnetic bar that is used to stir the reactants
- Condenser: a doubled-walled glass tube by which gas enters the system and which re-condenses evaporated solvent from the reaction chamber
- Compressed Gas: an inert gas, typically Argon, which flushes oxygen out of the reaction chamber
- Rubber Septum: used to seal the un-used necks of the flask
- Heating Mantle, Temperature Probe, Temperature Controller: used to uniformly heat the reaction vessel to set temperatures over the course of the reaction.
4.1.4. Nucleation and growth dynamics

The general sequence of events describing nanocrystal growth begins with the two precursors being added to a coordinating solvent. An initial discrete nucleation event is followed by crystal growth, which in turn leads to Ostwald ripening. The mechanical, procedural and chemical details will be considered in the section below.

Rapid injection of the precursors into the coordinating solvent lowers solution temperature, creating a supersaturated environment. This condition causes the precursor elements (for example Pb and S) to form nuclei and begin growing a lattice structure. The coordinating ligands immediately begin to bond to the nanocrystal, passivating the surface [15, 79]. The process of nucleation reduces the concentration of reagents in solution, dropping it out of supersaturation. Growth continues to occur by maintaining the solution temperature whereby precursor elements can continue to displace surface ligands which are in turn replaced by ligands from solution. Growth rates are controlled by varying the temperature of the solution.

Ostwald ripening occurs after the initial growth stage. It is a process that occurs when the precursor elements are depleted from the solution. This causes smaller nanocrystals to dissolve in order to feed the growth of the larger crystals. It is often undesirable as it reduces the number of smaller sized nanocrystals. To prevent Ostwald ripening the temperature of the reaction vessel is lowered to room temperature. Figure 4.3 shows the timeline for each of the stages of growth.
4.1.5. Procedural and chemical details

The original method of organometallic synthesis provided a synthetic route to produce high quality CdS, CdSe, and CeTe nanocrystals with diameters 1.2 – 11.5 nm in size, capped with TOP or TOPO passivating ligands [27]. Through the use of size selective precipitation very narrow size distributions (less than 5% variation in diameter) have been obtained, which leads to sharp absorption features and photoluminescence at the band edge.

The method of organometallic synthesis employed in the fabrication of the PbS quantum dots used in this work is a variation of the original method used to fabricate Cd(S,Se,Te) nanocrystals. The primary differences between these two methods is the use of oleic acid as the passivating ligand (and coordinating solvent) and the omission of size selective precipitation during the synthesis of our PbS nanocrystals.

The procedure and chemical reagents used in the synthesis are as follows:
1. 0.90 g of PbO is dissolved in 18 g of oleic acid which is heated at 80 °C under vacuum for 12 hours to remove the water created when these chemicals are mixed.

2. 0.36 g of TMS is dissolved in 10 ml of octadecene which has been degassed by heating at 80 °C under vacuum for 48 hours.

3. The PbO/oleic acid mixture is heated and rapidly stirred in a three-necked flask to temperature of 150 °C. This mixture is held under Ar atmosphere for the duration of the synthesis.

4. The room temperature TMS/octadecene mixture is then injected through a rubber septum into the flask and the temperature drops to approximately 120 °C.

5. The heating mantle is then removed and the flask is allowed to cool to room temperature.

6. Once cooled the PbS nanocrystals need are isolated from the residual reaction products through a process of repeated precipitation and re-dispersion. A 10 ml mixture of 1:1 ethyl acetate and methanol is added to reaction product which causes the PbS nanocrystals to precipitate from the solution. The solution is centrifuged and the precipitate (the PbS) is collected and is then re-dispersed in 5 ml of toluene.

7. To remove additional impurities the solution of PbS goes through another round of precipitation and re-dispersal. This time 10 ml of methanol is added to the solution which causes the nanocrystals to precipitate out of solution, leaving the undesired impurities in the supernatant. This mixture is then centrifuged and the precipitate is collected and re-dispersed in toluene.
This synthetic approach is able to produce PbS nanocrystals with an absorption edge ranging from about 800 nm to 2000 nm [15]. Figure 4.4(a) shows the band edge tuning that can be achieved with PbS nanocrystals and Figure 4.4(b) shows band edge absorption and photoluminescence peaks for a sample of ~6.5 nm diameter nanocrystals.

![Absorption Spectra of PbS nanocrystals. (b) Absorption and emission spectrum of 6.5 nm diameter PbS nanocrystals [15].](image)

**Figure 4.4** (a) Absorption Spectra of PbS nanocrystals. (b) Absorption and emission spectrum of 6.5 nm diameter PbS nanocrystals [15].

The width of the emission peak and clear first excitonic absorption peak seen in Figure 4.4(b) indicates that this synthetic method is capable of producing quantum dots with a narrow size distribution. It is for this reason that size selective distribution is not commonly used as part of this synthesis. A TEM image of an ensemble of PbS nanocrystals and an individual nanocrystal resulting from this synthesis are presented in Figure 4.5.
4.2. Surface passivation – ligand exchange

As mentioned previously, ligands are the functional groups that coordinate to the surface of nanocrystals. They play an important role in the functionality, photoluminescence quantum efficiency, and stability of the nanocrystal. This is due to the fact that surface atoms make up one-third to one-half of the atoms in small nanocrystal [81].

Ligands serve multiple purposes, among which include prevention of aggregation during synthesis and processing. They also determine the solubility of the nanocrystals and they stabilize surface atoms by passivating dangling bonds, minimizing charge carrier trap states.

As synthesized, the PbS nanocrystals are capped with ~2.5 nm long oleic acid ligands. These impede charge transport, producing insulating thin films. To create conductive nanocrystals films, we used a solution-phase ligand exchange to replace oleic ligands with ~0.6 nm long butylamine (CH₃(CH₂)₃NH₂) ligands. Following ligand exchange, the butylamine capped nanocrystals exhibited linear current-voltage characteristics [86].
4.2.1. Ligand exchange procedure

All PbS quantum dots used in this work undergo a butylamine ligand exchange before being used in devices or other measurements. Octylamine was also used for the exchange but quantum dot films made from butylamine exchanged nanocrystals were seen to be more conductive. The ligand exchange procedure is carried out in an inert N₂ atmosphere glove box. All solvents used in the procedure are anhydrous and the butylamine used has been distilled prior to use to remove impurities. A typical starting sample size is 5 ml of a solution of PbS dispersed in toluene with a concentration of 100 mg/ml. The exchange procedure is as follows:

1. As-synthesized PbS nanocrystals dispersed in toluene are precipitated out of solution using 20 ml of methanol.
2. The mixture is centrifuged for about 2 min and the supernatant is discarded.
3. The precipitate is dried under vacuum for about 5 min to remove excess solvent. The resultant PbS solid is weighed.
4. A volume of butylamine necessary to obtain a concentration of 100 mg/ml is then added to the PbS which is readily re-dispersed in the new ligand.
5. The solution of PbS in butylamine is left to exchange for three days. Over this time the oleic acid ligands are exchanged for butylamine ligands.
6. To finish the exchange the PbS nanocrystals are isolated by precipitating them out of solution using about 15 ml of 2-propanol.
7. The mixture is centrifuged and the supernatant is discarded.
8. The PbS solid is re-dispersed in octane or chloroform to a concentration of 150 mg/ml which is then filtered through a 0.1 μm polytetrafluoroethylene syringe filter.
4.3. Porous ITO fabrication

The next major material piece in our photovoltaic devices is the high surface area, porous oxide film into which we infiltrate ligand-exchanged PbS quantum dots. We fabricated the ITO phase of our photovoltaic devices by spin coating a slurry of ITO particles, suspended in water, onto a glass substrate. The ITO is a powder purchased commercially from Nanotek or Alfa Aesar. The slurry is made by mixing 4 g of ITO into 4 ml of distilled water. To this suspension, approximately 0.02 ml of Triton-X surfactant (Aldrich) was added drop wise and stirred overnight. This surfactant is used to break up clumps of ITO particles. 100 μL of the slurry was then spin coated (800 rpm, 60 sec) onto a 1” square glass slide. The film was then baked in air at 310 °C for 30 minutes in a tube furnace, resulting in 2-5 μm thick films with resistivities on the order of 0.5 Ω-cm. Film resistivities were measured using four-probe measurement. Figure 4.6 and Figure 4.7 show the resulting high surface area film.
Figure 4.6 SEM image of the cross section of a typical porous high surface area ITO electrode used in photovoltaic devices.
Figure 4.7 High magnification SEM image taken of a porous ITO film showing textured surface and sintered particles

4.4. Oxide infiltration and coverage

We first tried spin coating a layer of nanocrystals onto the porous ITO. When we deposited top metal contacts (Mg, 100 nm thick, 300 μm in diameter) capped by a layer of silver (100 nm thick) via thermal evaporation we found that almost all of the devices fabricated using this method resulted in short circuits when current-voltage (IV) curves were taken.

When we examined the devices using SEM we found that spin coating resulted in non-uniform nanocrystal films that caused direct ITO to Mg shorting. A typical image of the surface one of these devices can be seen Figure 4.8. In it one can see exposed regions of ITO.
Spin coating multiple layers sequentially helped reduce the number of voids but led to cracking of the nanocrystal overcoating.

Figure 4.8 SEM image of the surface of a device made by spin coating PbS nanocrystals on porous ITO. The voids in the top nanocrystal film show exposed ITO.

When cross-sections of our spin coated devices were examined under SEM further problems were seen. Spin coating resulted in poor infiltration of the porous oxide. An example of this can be seen in Figure 4.6. In it one can see the contrast between the spin coated top nanocrystal layer and the oxide underneath. It appears that only minor amounts of PbS had infiltrated below the surface of the oxide.
We then tried infiltrating our porous ITO through a dip-coating methodology. We soaked the ITO-coated substrate in a 5 mg/ml solution of butylamine-capped PbS quantum dots in chloroform for 10 minutes. Absorption spectra of these devices showed a nanocrystal spectral absorption characteristic. Subsequent deposition iterations were employed until a saturation was observed in the growth of the nanocrystal absorption feature. This typically occurred after 3-5 cycles of dip coating and resulted in films having an optical density of 0.8 at the first excitonic peak. This corresponds to an absorption of about 85%. Examination of a cross section of a device showed that much better infiltration was occurring through this fabrication route. Infiltration was confirmed thorough the use of EDX and the results are presented in detail later in the chapter.

Figure 4.9 SEM image of a cross section of a PbS nanocrystal film spin coated onto a porous ITO substrate. One can see that the PbS has poorly infiltrated the porous ITO.
Metal contacts were deposited and once again we found that the majority of the devices fabricated using this method resulted in short circuits. When we examined the devices using SEM we found that this deposition method also resulted in films with poor nanocrystal coverage and exposed areas of ITO. Figure 4.10 shows a magnification of an area of an ITO-PbS quantum dot device before metal contacts were evaporated.

![Figure 4.10](image)

**Figure 4.10** SEM image of the surface of a PbS nanocrystal/porous ITO device where the nanocrystals have been deposited by dip coating.

### 4.5. Nanocrystal cross-linking

We needed to find a nanocrystal deposition method that formed a smooth, continuous film on a rough substrate. To do so we turned to the use of linker molecules to aid in film formation. We first used mercaptoacetic acid which we expected would attach at one end to
the ITO via its carboxylic group, and at the other end attach to PbS via a thiol group. Bifunctional linker molecules of a similar type had been used previously in the attachment of monolayers of visible-sensitive quantum dots sensitizers in liquid electrolyte Gratzel cells [41]. Interestingly, we found this method, too, to lead to short circuits.

We therefore sought not to link the PbS quantum dots directly to the ITO; but instead to link PbS nanoparticles to one another. We hoped that this would lead to lateral growth of the PbS film in such a way as to overgrow the faceted ITO. This approach involved the use of a bridging molecule to facilitate interparticle-linking. Although bridging molecules have been used for monolayer deposition of semiconductor nanoparticles on metal electrodes [87], we used them instead to direct multilayer particle assembly in both lateral and vertical directions towards the realization of a planarized film on a rough substrate.

We selected ethanedithiol for two reasons. First, thiols possess a strong affinity for Pb atoms, leading to effective competition with the existing amines for ligand-binding sites. Second, ethanedithiol is short (~ 0.7 nm) enough that any thiols remaining after subsequent device processing would not significantly impede charge transport. Due to the dual role of our quantum dots as both light absorber and charge transport medium our use of a cross-linker molecule additionally coincided with a desire to improve electrical transport properties. Previously the charge transport mobility in thin film transistors [68] and conducting nanoparticle solids [65] has benefited by the use of hydrazine and 1,4 pheynlenediamine as cross-linking molecules.

We fabricated devices using this cross-linker strategy by treating ITO in a 4% by volume solution of ethanedithiol in acetonitrile for 30 min. Acetonitrile was selected as it is a polar non-solvent for the nanocrystals. The ITO was then soaked in a nanocrystal solution for 10 min. This procedure was repeated three times.
We show in Figure 4.11 a comparison of bare ITO, nanocrystals deposited onto ITO without the use of ethanedithiol, and nanocrystals deposited onto ITO with the use of ethanedithiol. In Figure 4.11(c) one can see an area of exposed ITO in a device made without the use of ethanedithiol. Figure 4.11(d) shows a higher magnification image of the exposed bare ITO. Here individual PbS nanoparticles can be seen clustered in the crevices formed between ITO particles. Figure 4.11(e) and Figure 4.11(f) show the smooth, continuous films produced when ethanedithiol was used during fabrication. We also made devices using ethanedithiol dispersed in toluene and chloroform but found that the resulting nanocrystal film morphology was not as smooth as that using acetonitrile.

We found that once top metal contacts had been deposited these devices produced short-free IV characteristics.
Figure 4.11 SEM images of the surface of a textured ITO substrate before nanocrystal deposition and the surface of a ITO substrate after nanocrystal deposition with and without the use of cross-linking molecules. a-b, Bare textured ITO substrate. c-d, textured ITO after nanocrystal deposition without cross-linker showing the exposed ITO which leads to short-circuited devices. Individual nanocrystals can be seen clustered in the crevices between sintered ITO particles. e-f, Surface of functional devices after nanocrystal deposition utilizing cross-linkers to obtain a continuous nanocrystal over-coating.
4.6. Confirmation of infiltration via EDX

To confirm that our fabrication method resulted in porous ITO films that have been well infiltrated with PbS quantum dots we looked at cross sections of our devices using an SEM with an EDX (energy dispersive x-ray analysis) accessory.

EDX is an analytical technique used in the identification of atomic species within a sample [88]. In this measurement the high energy beam of electrons in an SEM are focused on a sample causing inner shell electrons to be ejected from the atoms within sample. When this occurs an electron from a higher energy shell decays to this empty lower energy state which in turn causes a photon (i.e. an x-ray) to be emitted. These x-rays are collected and the energy of the emitted photon is analyzed by an energy dispersive spectrometer. The energy of these emitted x-rays is dependant on the difference between the energy levels of the atomic core levels which in turn is dependant on the structure of the atomic species. By analyzing the quantity (i.e. the count) and the energy of the emitted x-rays and mapping this information spatially to an SEM image, one can determine the distribution of atomic species within a sample [88].

We used this technique to examine the distribution of Pb, S, In, Sn, Ga, and As in a cross section of our samples. In these samples we used GaAs as a substrate because it cleaves readily, creating smooth, clean cross sections. One can see an example of an EDX measurement in Figure 4.12. Here the coloured lines each represent a separate element present in the sample. The EDX measurement was set-up to scan vertically along the thick yellow line. A different representation of this EDX data is shown in Figure 4.13. Here each of the atomic species is plotted individually as a function of the distance from the top of the sample. One can see an overcoating of PbS is present at the top of the sample, a fairly constant level of PbS as the scan progresses through the ITO, and finally a reduction of the PbS signal at the bottom of the ITO where the GaAs substrate signal picks-up.
It is important to point out that we sought to keep the thickness of the PbS overcoating seen in these cross-sectional images as small as possible. Any PbS material that is more than an exciton diffusion length from an interface does not contribute to the extracted photocurrent. Furthermore, this PbS overcoating also presents a series resistance to charge carriers that are extracted through the top metal contact, contributing to device losses.

Figure 4.12 An SEM image of the cross section of a porous ITO film, infiltrated with PbS nanocrystals. This image is overlayed with the results of an EDX analysis showing the presences of Pb (red line), S (yellow line), In (magenta line), Sn (green line), Ga (teal line) and As (blue line). GaAs was used as the sample substrate.
Figure 4.13 The results of an EDX scan of the cross section of a sample consisting of a porous ITO film infiltrated with PbS nanocrystals. This sample was prepared on a GaAs substrate. The scan maps the signal strength of Pb, S, Sn, Ga, As, and In through the cross section of the film. It shows that there is a PbS overcoating at the top of the sample and then a good distribution of PbS infiltrated into the ITO film. Both the PbS and the ITO signals decline to a noise level when the scan transitions from the ITO to the GaAs.
4.7. Summary

In this chapter we have outlined the synthesis and fabrication techniques used to make our PbS quantum dot, porous ITO photovoltaics. We have described the synthetic procedures we employed to synthesize nanocrystals and the ligand exchange procedure we employ to decrease interparticle spacing. We also outline the fabrication of our porous ITO and have introduced the use of ethanedithiol cross-linking molecules which allow us to fabricate smooth, continuous PbS films on the rough surface of the ITO. We show via EDX measurements that we have good infiltration of our PbS into the porous ITO.
Chapter 5

Electronic Properties and Morphology

We now discuss the measured electronic properties of the colloidal quantum dot films that are used in the fabrication of our solar cells. We examine the impact chemical and thermal treatments have on the conductivity, mobility and carrier concentration of nanocrystal ensembles.

The capacity to modify the electronic properties of nanocrystal ensembles is an important step in the rational design and optimization of colloidal quantum dots for use in practical electronic devices.

The chemical application of cross-linker molecules during fabrication of nanocrystal-infiltrated porous oxide devices is expected to have a morphological impact on the structure of our quantum dot ensembles. During the application of ethanedithiol (EdT), existing ligands may be displaced and multiple quantum dots may be linked together. This will likely change the interparticle spacing and lead to changes in the mobility of a quantum dot ensemble. In this chapter we examine the impact on interparticle spacing through the use of TEM and measure the changes in mobility associated with this treatment.
Another important treatment we examine is the impact of annealing on the carrier concentration and mobility. Changes in mobility are likely to arise due to the removal of organic ligands during heating. Changes in carrier concentration may arise during heating in air as oxygen has been known to form acceptor states in naturally-occurring galena (PbS) and microcrystalline lead sulphide films [69, 70]. We use thin film FET measurements to obtain mobility and with this information extract carrier concentration from conductivity measurements. Figure 5.1 outlines the major sections of this chapter in the context of the project as a whole.

![Figure 5.1](image.png)

**Figure 5.1** An image displaying the topics on electronic properties and film morphology that are discussed in this chapter. The impact that ethanedithiol and air annealing may have on quantum dot ensembles is also depicted.
5.1. Cross-linking molecules - background

In the previous chapter we showed that ethanedithiol was useful in assisting the formation of continuous films during the fabrication of porous oxide devices infiltrated with PbS nanocrystals.

Electrical and optical devices based on non-PbS nanoparticle thin-film solids have been seen to benefit from the use of short-chain organic cross-linking molecules [65, 66, 68, 89]. The role ascribed to the cross-linking molecules in these devices has included improving charge transport properties and altering the charge carrier concentration of the quantum dot film. In work published by Talapin et al. thin-film field effect transistors fabricated from PbSe nanocrystals were treated with hydrazine (a bidentate ligand possessing amine end groups) in order to alter the charge carrier concentration and improve transport. In other work Boettcher et al. fabricated Schottky barrier devices using Au nanoparticles on bulk InP and treated their films with 1,9-nonandithiol before employing charge transfer doping to control Schottky contact barrier heights [66]. In addition, Yu et al. fabricated conducting nanocrystal solids from CdSe nanocrystals that were treated with hexanediamine which was found to improve the film conductivity [65].

5.2. Interparticle spacing – TEM study

To further our understanding of the interaction between PbS nanocrystals and ethanedithiol we set out to examine the impact of ethanedithiol treatment on interparticle spacing, conductivity, mobility and carrier concentration. Interparticle spacing was first investigated using transmission electron microscopy (TEM).
5.2.1. Sample preparation and TEM results

Butylamine ligand-exchanged PbS nanocrystals with a first excitonic transition of 1400 nm were drop-cast from solution onto Formvar overcoated copper grids.

TEM images (taken with a Hitachi HD-2000 STEM) of untreated nanocrystals and ethanedithiol treated nanocrystals can be seen in Figure 5.2.

Figure 5.2 TEM images of PbS Nanocrystals before (A) and after (B) EDT treatment. Scale bar is 50 nm in both images. Interparticle spacing initially is approximately 4 nm and reduces to 1.6 nm as a result of EDT treatment. The reduction in interparticle spacing contributes to the measured increase in mobility of thin solid films treated in this manner.
The ethanedithiol treatment consisted of soaking the CQD film in a 4% by volume solution of ethanedithiol in acetonitrile for 5 minutes. Examining the images one can see that the PbS nanocrystals films treated with ethanedithiol have a higher packing fraction than those without ethanedithiol treatment. Centre-to-centre spacing for the untreated nanocrystals was about 9 nm. After ethanedithiol treatment, centre-to-centre spacing decreased to about 6.6 nm. With an average nanocrystal diameter of 5 nm, this centre-to-centre spacing corresponds to a distance between individual nanocrystals of 4 nm in the case of the untreated films and a distance of 1.6 nm in the ethanedithiol treated films.

5.3. Absorption spectra

Absorption spectra of quantum dot films were taken as-exchanged, after ethanedithiol treatment, and after ethanedithiol treatment followed by air annealing. These spectra are shown in Figure 5.3. Samples were prepared by drop casting quantum dots from an octane solution onto a glass substrate. One can see in all three spectra that the absorption peak associated with the first excitonic transition is still present at 1400 nm, indicating that quantum confinement remains. This indicates that the nanocrystals have not been sintered into a polycrystalline PbS film. The spectral absorption measurements were carried out with a Cary 200 Spectrophotometer operating in transmission mode with glass slide used as a baseline absorption reference.
Figure 5.3 Absorption spectra of PbS nanocrystal films. **A** shows the nanocrystal absorption before treatment. **B** shows the nanocrystal absorption after treatment with 4% ethanedithiol in acetonitrile for 5 minutes and **C** shows absorption after both ethanedithiol treatment and air heating at 130 °C for three hours. The presence of an excitonic absorption feature at 1400 nm indicates that the quantum confinement is still occurring the quantum dot ensemble and that the nanocrystals have not been sintered into and amorphous or multicrystalline film.
5.4. FET devices and conductivity measurements

To understand the impact of ethanedithiol treatment and air annealing on the electronic properties of our CQD films we fabricated thin film field-effect transistor (FET) devices. Thin film FETs have been used extensively to determine the electronic properties of semiconducting polymers [90, 91], thin film amorphous semiconductors [92, 93] and other types of colloidal quantum dot thin films [68, 94].

Here we used FET measurements to find the majority carrier type and mobility and we used this information in conjunction with measurements of conductivity to extract the majority carrier concentration of our films.

5.4.1. FET fabrication

The FET devices consisted of a highly doped Si substrate with 100 nm thick SiO$_2$ thermal gate oxide and Au source and drain electrodes 5 µm in width, 3 mm long, separated by a 14 µm gap. The doped Si substrate serves as the gate contact for the FET devices. PbS nanocrystal films 20 nm thick (as confirmed by AFM) were spin-coated onto the substrates. A device schematic is shown in Figure 5.4 along with an AFM image taken of a section of a typical device.
Figure 5.4 FET Device Schematic and AFM image of a typical device. Source and drain electrodes are gold and are 14 µm apart. The gate electrode is highly doped silicon and the thermal gate oxide is approximately 100 nm thick. PbS nanocrystals are spin cast onto the substrate with a thickness of approximately 20 nm as measured by AFM. In the AFM image the z (height) scale is 150 nm/div and the x and y scale are 10 µm/div.

Application of a gate voltage to the back of the substrate modulates the current through the nanocrystal film creating a FET [93]. The majority carrier type can be determined by examining the FET gate voltage (Vgs) versus drain current (Ids) transfer curve. Figure 5.5 shows that as the applied gate voltage becomes more negative, the drain-source current increases in magnitude. This is characteristic of p-FET operation and indicates that the CQD film is p-type with holes as the majority carrier. The slope of the transfer curve in the linear region yields a value for the field effect hole mobility.
Figure 5.5 PbS nanocrystal thin film FET for a device at the initial stage of treatment. The Vgs vs Ids transfer curve of the device before any EDT or heating treatments indicates that it behaves as a p-FET with p-type conduction and majority hole carriers in the nanocrystal thin film.

5.4.2. FET data analysis

Calculation of the majority carrier field-effect mobility ($\mu$) is carried out in the linear operating region where Ids increases linearly with Vds [93]. Here $\mu$ is calculated from the slope (i.e. the transconductance, $g_m$) of the Vgs vs Ids transfer curve with fixed Vds:

$$
\mu = \frac{WC_i V_{ds}}{L} \cdot \frac{g_m}{\mu}, \quad \text{Equation 5.1}
$$

Where W is the transistor width (3 mm), $C_i$ is the gate oxide capacitance and L is the transistor length (14 $\mu$m).

As-deposited the partially oxidized nanocrystals have a measured conductance of $4 \times 10^{-7}$ S cm$^{-1}$. The field-effect hole mobility ($\mu$) calculated from the transfer characteristic of
the p-FET is $3 \times 10^{-5}$ cm$^2$V$^{-1}$s$^{-1}$. The following relationship between conductance ($\sigma$), mobility ($\mu$) and carrier density is used to calculate the hole density ($p$):

$$\sigma = pe\mu,$$

Equation 5.2

Where $e$ is $1.602 \times 10^{-19}$ coulombs.

The majority carrier density for the initially untreated PbS CQD film was found to be $8 \times 10^{16}$ cm$^{-3}$. These results are summarized in Table 5.1.

To observe the impact of ethanedithiol on the electronic properties of the CQD solid the same FET was then treated with 4% ethanedithiol in acetonitrile for 5 minutes at 90 °C. It was then removed from the ethanedithiol treatment and rinsed in a clean acetonitrile bath. The FET transfer characteristics and film conductivity were measured again and it was found that the conductivity and the mobility increased. Specifically, conductivity increased to $6 \times 10^{-7}$ S cm$^{-1}$ and mobility increased to $1 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$. On the other hand, the hole concentration was found to decrease to $2 \times 10^{16}$ cm$^{-3}$.

<table>
<thead>
<tr>
<th>Stage of Treatment</th>
<th>Conductivity (S cm$^{-1}$)</th>
<th>Mobility (cm$^2$/Vs)</th>
<th>Hole Density (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>$4 \times 10^{-7}$</td>
<td>$3 \times 10^{-5}$</td>
<td>$8 \times 10^{16}$</td>
</tr>
<tr>
<td>Ethanedithiol treated</td>
<td>$6 \times 10^{-7}$</td>
<td>$1 \times 10^{-4}$</td>
<td>$2 \times 10^{16}$</td>
</tr>
<tr>
<td>Air Heated</td>
<td>$4 \times 10^{-6}$</td>
<td>$2.5 \times 10^{-4}$</td>
<td>$1 \times 10^{17}$</td>
</tr>
</tbody>
</table>

**Table 5.1** Summary of electronic properties of a CQD PbS thin film at progressive stages of treatment.

5.4.3. Consequences of Ethanedithiol treatment

These FET measurements indicate that while ethanedithiol has increased the mobility of a CQD film by about an order of magnitude it has simultaneously decreased the doping level in the film. This observation has important implications in the application of ethanedithiol in fabricating practical devices. Control over doping levels is a crucial
determinant of device properties ranging from transistor gain and photodetector sensitivity to the built-in voltage in junction devices. Indeed in a recent report on p-type doping in binary nanoparticle superlattices, control of the doping level was motivated by the potential application of this material system to thermoelectric generation [95]. In Schottky barrier photovoltaic devices, the offset between the semiconductor Fermi level and the metal contact work function is a key determinant of the open circuit voltage \( V_{oc} \) [78]. In light of the important role doping plays in making high performance nanoparticle-based devices an understanding of the nature of the interaction between ethanedithiol and doping is needed. For ethanedithiol treatment to be of practical use a means of re-introducing dopants into the CQD film is clearly desired.

These findings raised the following question: Are high mobility and strong doping quantities that must be traded off against one another? Or can a materials processing strategy be devised that achieves mobility and doping simultaneously?

We sought to bring back the doping density by lightly oxidizing our FET devices in an effort to re-dope the CQD film. The same FET device used in Figure 5.5 was heated in air in order to re-oxidize the CQD film. The transfer curve obtained for this device can be seen in Figure 5.6.
Chapter 5.

The maximum conductivity was measured after three minutes of air heating and was found to be $4 \times 10^{-6}$ S cm$^{-1}$. The mobility after this initial heating was found to be $2 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$, a slight increase over the initial gain in mobility brought about by ethanedithiol treatment. It was also found that air annealing brought up the hole concentration to $1 \times 10^{17}$ cm$^{-3}$, representing almost an order of magnitude increase over that measured after ethanedithiol treatment. A summary of these results can be seen in Table 5.1. The FET $I_d$ vs $V_d$ curves for varying $V_g$ are shown in Figure 5.7 for a device after air annealing.
Figure 5.7 FET Ids vs Vds curves for varying Vgs. FET characteristics are taken after air annealing.

5.4.4. Varying mobility and conductivity

We then measured the change in mobility and conductivity with increased heating to gain some insight into the mechanism underlying these changes. A FET device was fabricated and a transfer curve was measured at each processing step and during heating at increasing time intervals. On the same device conductivity measurements were also carried out at equivalent steps. The change in mobility can be seen in Figure 5.8 and the changes in conductivity can be seen in Figure 5.9.
Figure 5.8 Changes in mobility observed in a single FET device during treatment and heating as-spun EDT treated 1 min heat 2 min heat 3 min heat 5 min heat 15 min heat 30 min heat 60 min heat

Figure 5.9 Changes in film conductivity observed during treatment and heating of a nanocrystal thin film.

These measurements indicated that there is an optimal amount of air annealing after which the mobility and conductivity began to decrease. After about 90 minutes of heating the
mobility had gone down by about an order of magnitude, reversing the gains achieved through ethanedithiol treatment. This reduction in mobility is attributed to an over-oxidation of the nanocrystals. Over-oxidation likely led to the growth of an oxide barrier sufficient enough to impede effective dot-to-dot charge transport in the colloidal quantum dot film.

While thin film FET measurements are a readily accessible way of measuring a number of important electronic properties in solution processed materials it is important to comment on the accuracy of this measurement technique. There are a number of sources of error in these measurements including errors associated with the physical dimensions of the devices, errors associated with noise in the electrical measurements, and errors associated with the assumption of ideal FET behaviour during the analysis of the data. Although we haven’t quantified the exact error bars that should be applied to our FET measurements, in Section 5.6 we compare our mobility results to those measured by different techniques and find that our values are within about a factor of 5 those obtained by other means. That being the case, we see FET measurements as a useful tool for gauging the overall trend of the changes in the electronic properties of our materials, and for obtaining absolute values that are accurate to within an order of magnitude.

5.5. Thermal voltage measurements

A thermoelectric measurement was carried out to provide confirmation that the PbS films had majority p-type carriers. A nanocrystal film was spin-coated onto a glass substrate which was then mounted on two hot plates using thermal paste. Electrical contacts were made to the film using Au electrodes 3.2 cm apart. A diagram depicting this measurement setup can be seen in Figure 5.10. Au contacts were used as Au has been seen to form an ohmic junction with PbS nanocrystals [86]. The small difference between the work function of the metal and the Fermi level of the nanocrystals reduces the contribution of this junction to the observed thermal voltage.
Figure 5.10 Thermal voltage measurement set-up and sample configuration.

A thermal gradient was applied by heating one hotplate and keeping the other at room temperature. The voltage potential between the hot and cold probes was measured using a Kiethley 6517A Electrometer. Majority carriers diffuse away from the hot probe and the polarity of the measured voltage indicates the sign of the majority carriers. A graph showing measured thermal voltage for increasing temperature differential is show in the inset of Figure 5.11. The polarity of the voltage confirms that the film has majority p-type carriers.

Figure 5.11 Thermal voltage measurement results indicating that the majority carriers in the PbS quantum dot film were holes.

As a control the same measurement was carried out with the positive and negative leads reversed, resulting in a reversal of the sign of the thermal voltage. Additional controls consisted of measuring bare glass (with no observable thermal voltage) and the measurement of p-type Si, which produced the same polarity thermal voltage as that observed for PbS nanocrystals. A graph showing the results of this measurement can be seen in Figure 5.12.
5.6. Additional methods of extracting electronic properties of nanocrystal thin films

In addition to FET measurements other methods of determining the majority carrier mobility and carrier density of PbS quantum dot thin films have been utilized by other researchers. These methods include time of flight measurements, carrier extraction by linearly increasing voltage (CELIV) and capacitance-voltage measurements. To provide confirmation that the mobility extracted with our measurement apparatus and analysis was accurate we compare our FET results with those of other methods.

In work examining the carrier transport properties of thin film diodes fabricated with PbS nanocrystals, CELIV was employed to extract the hole mobility of the quantum dot films [96, 97]. A linearly increasing voltage was applied to Schottky diodes in reverse bias and the transient dynamics of the current response of the devices were used to extract the mobility. A value of $2 \times 10^{-4} \text{cm}^2/\text{Vs}$ was obtained from this measurement which is somewhat higher than the $3 \times 10^{-5} \text{cm}^2/\text{Vs}$ obtained from our untreated devices but is similar to the $2.5 \times 10^{-4}$
cm$^2$/Vs obtained after air annealing. This similar range of mobilities measured by a different measurement method provides confidence in the FET techniques used in this chapter.

In other work examining the Schottky barrier in PbS/Al devices used for photodetectors the hole density was found through the use of capacitance-voltage (C-V) measurements [56]. In these measurements the capacitance of a diode is measured at different applied voltages. When the diode is held at different biases the variation of the depletion width exposes additional acceptor states, changing the capacitance of the device [62]. Using this data the hole density of PbS colloidal quantum dot films was found to range from $2 \times 10^{16}$ cm$^{-3}$ to $7 \times 10^{16}$ cm$^{-3}$. These values compare to a range of $2.2 \times 10^{16}$ cm$^{-3}$ to $1.2 \times 10^{17}$ cm$^{-3}$ obtained from our use of FET mobility and conductivity to obtain hole concentration in this chapter.

The overlap in the range of mobility and carrier concentrations obtained through independent measurement techniques gives confidence to the results presented here.

5.7. Discussion

Here we have shown that ethanedithiol treatment of PbS CQD films results in nearly a 10-fold increase in mobility but is accompanied by a reduction in the p-type doping of the film. The loss of doping is thought to result from a reduction of the surface oxides in the nanocrystal film by ethanedithiol. It has been found that by heating in air one can reintroduce oxide content and increase the carrier concentration without sacrificing gains in mobility. This results in nearly a 10-fold increase in hole density over that observed after ethanedithiol treatment. This finding represents a practical organic-inorganic route to doping control in nanocrystal films.

In the next chapter we will analyze the material changes in PbS films which underpin the modification of the changes in electronic properties observed here.
Chapter 6

Material and Chemical Changes

During device processing the PbS nanocrystals undergo a number of chemical and thermal treatments that alter the composition and structure of the colloidal quantum dot ensembles. These treatments include exposure to ethanediithiol as well as thermal annealing in vacuum, air and nitrogen atmospheres. This chapter examines the changes these treatments impart on PbS films using Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), Head Space Gas Chromatography/Mass Spectroscopy (HS-GCMS), and X-ray Photoelectron Spectroscopy (XPS). We will use the results of these studies to help provide some understanding of the changes observed in the electronic properties of the nanocrystal thin films and to inform the processing steps taken in fabricating photovoltaic devices. Figure 6.1 outlines the major sections of this chapter and depicts two of the potential results annealing will have on PbS nanocrystals.
6.1. Why annealing?

Annealing has been successfully used to improve the performance of a number of nanocrystal-based devices [8, 89, 95]. A recent report on binary nanoparticle superlattices found that the maximum p-type conductivity came about after heating in air to 150 °C [95]. Similarly, a report on CdSe/CdTe nanorod heterojunction devices noted that long exposure to air increased the open circuit voltage [8].

We also expect that annealing will have an impact on the ligands coordinated to the nanocrystal surfaces. For example heating significantly above the boiling point of a ligand will likely remove weakly-bound or excess ligands, potentially impacting film conductivity.

In bulk and microcrystalline semiconductor devices annealing and oxide growth have been shown to be useful in influencing device performance by altering the energy distribution...
and density of interface-induced mid-gap states. For devices based on semiconductor heterojunctions, such as microcrystalline CdS/CdTe solar cells, control of the interface states is a primary determinant in device power conversion efficiencies [98]. In Schottky-junction devices the interface induced gap states are the fundamental mechanism that determines the barrier heights of the Schottky contact [99]. Furthermore, in bulk and microcrystalline Schottky junction photovoltaic devices, altering the composition and extent of the interface layer between the metal and the semiconductor is seen as a key factor influencing the open circuit voltage of the solar cell [78, 100, 101].

6.2. Thermogravimetric analysis of PbS quantum dots

We first examined the impact of heating PbS colloidal quantum dots using thermogravimetric analysis. Butyl-amine exchanged nanocrystals were studied during heating in air and in nitrogen.

6.2.1. Thermogravimetric analysis

Thermogravimetric analysis (TGA) is performed by heating a solid sample using a known temperature profile and measuring the change in mass as the temperature profile progresses. TGA data is typically presented as a plot of mass vs. temperature. Examining the results of this measurement one locates temperature points where there is an increase or decrease in the slope of the plot. These temperatures are called onset points as they indicate the onset of a change in the material composition. For example, in the measurement of our PbS quantum dots we expected to see that at approximately 78 °C there will be an onset point corresponding to the boiling point of butylamine.
6.2.2. Sample preparation

Samples for TGA were prepared by drop casting quantum dots from solutions of octane onto glass slides. To achieve approximately 10 mg sample sizes 0.1 ml of solution with a concentration of 100 mg/ml was used to prepare each sample. We examined both as-exchanged nanocrystals and nanocrystals treated with ethanedithiol. Ethanedithiol treatment was carried out by soaking the drop-cast nanocrystal films in a solution of 4% ethanedithiol in acetonitrile for approximately 10 minutes. Once removed the films were rinsed with acetonitrile to remove the excess unbound ethanedithiol and were then dried with nitrogen. The films were then scraped off the glass slide and transferred to platinum crucibles used for the TGA. Due to some sample loss during transfer sample sizes varied from 8.6 mg to 9.7 mg.

6.2.3. TGA measurement results

TGA measurements were carried out in both air and in nitrogen on both untreated and ethanedithiol treated quantum dots. A Perkins-Elmer TGA Q500 was used for the measurement. Samples were heated at a rate of 10 °C/min from room temperature to 300 °C. The TGA results can be seen in Figure 6.2. Initially all four samples had a gradual decrease in mass which is attributed to the loss of residual solvent. At above ~100 °C the ethanedithiol treated and untreated samples heated in air started to diverge from those not heated in air. The air heated samples had an increase in mass relative to the nitrogen heated samples. This mass increase is attributed to the formation of oxidation products. This hypothesis is further explored through the use of XPS and FTIR measurements presented later in this chapter. It is interesting to note that the ethanedithiol treated samples show a further increase in mass between 130 °C and 150 °C. We also observe a reduction in mass starting at ~85 °C which we attribute to the loss of butylamine ligands as they have a boiling point of 78 °C. This ligand
loss appears to be present in all four samples. To confirm the hypothesis of ligand loss we turn to HS-GCMS.

Figure 6.2 TGA of a PbS nanocrystals in air (magenta) and nitrogen (maroon) before ethanedithiol treatment. TGA is also shown for PbS after treatment with ethanedithiol and was done in air (green) and in nitrogen (blue). Evidence of oxidation is shown by the weight increase that occurs for both the air heated samples. The ethanedithiol treated samples were rinsed in acetonitrile before TGA was performed in order to reduce the content of thiols that are not coordinated to the nanocrystal surface. The onset point seen at about 85 °C in the ethanedithiol treated samples in both air and nitrogen likely corresponds to the removal of butylamine as butylamine has a boiling point of 78 °C.

6.3. Gas chromatography/mass spectroscopy

To provide information about the composition of the chemical species coming off of the quantum dot samples during heating HS-GCMS was employed on both ethanedithiol treated and untreated PbS nanocrystals.
6.3.1. HS-GCMS

In head space gas chromatograph/mass spectroscopy a solid or solution phase sample is heated at a controlled rate in a sealed system. The gasses collected from the chamber above the sample holder (called the head-space) are separated in a gas chromatography column and then analyzed in a mass spectrometer [102]. The data this measurement generates consists of a list of chemical species that corresponds to the mass spectroscopy signatures measured by the instrument. As the temperature of the sample is increased different chemical species are detected at their respective decomposition temperatures.

6.3.2. HS-GCMS Findings

Samples were prepared in a similar manner as used in Section 6.2.2. A Perkins-Elmer Autosystem GC was used for the measurement. Samples were heated from 50 °C to 300 °C at a linear rate of 15 °C/min. In both the untreated nanocrystals and the ethanedithiol treated nanocrystals amine species were detected at the 80 °C range and the 125 °C range. This confirms that one of the results of heating is the removal of butylamine ligands from the PbS surface. In the ethanedithiol treated samples, sulphur species were not detected until about the 200 °C temperature range, indicating that the thiol-nanocrystal coordination is much stronger than that between PbS and the amine-terminated ligands.

To summarize: TGA and HS GCMS have shown that oxidation is occurring in the CQD films during annealing in air and that butylamine ligands are being removed during annealing in both air and inert atmospheres.
6.4. FTIR measurements

To further explore the nature of the compositional changes that occur in PbS colloidal quantum dot solids during ethanedithiol treatment and annealing we turned to Fourier transform infrared spectroscopy (FTIR). We used FTIR to identify chemical species present in our samples at different stages in processing. In an FTIR measurement the absorption spectrum of a sample is taken over a large range of IR wavelengths (a range of 4000 to 400 cm\(^{-1}\) was typically used in our measurements). Information about the material content of the sample is obtained by examining the intensity and spectral location of the observed absorption peaks. An infrared absorption spectra results from transitions between vibrational energy states within a molecule. These molecular vibrational states can arise from a range of molecular structures. A simple example of one such state is the motion of two atoms in a diatomic molecule [103]. Each molecule has a slightly different vibrational mode from other molecules. This allows one to use the infrared spectrum to identify that molecule. Comparing absorption spectra of a sample to a known reference spectrum enables the identification of the molecules present in a sample.

6.4.1. Sample preparation

FTIR analysis was performed by drop-casting nanocrystals onto double-sided-polished undoped silicon substrates in a nitrogen filled glove box. A nitrogen glove box was used to present inert processing conditions, particularly with respect to the introduction of oxygen. Silicon substrates were used as they provide a reasonably flat absorption window over the range of wavelengths used in these measurements. PbS samples treated with thiols were soaked in a 4% ethanedithiol solution in acetonitrile for about 10 minutes. A Bruker Tensor 27 was used for all FTIR measurements.
6.4.2. FTIR Results

We first examined nanocrystals that had been stored in solution in inert (nitrogen glovebox) and ambient atmospheres. The FTIR spectra reveals the presence of PbO and PbSO$_4$ in our as-drop-cast films. Figure 6.3A shows the spectra of an untreated PbS sample stored in an inert atmosphere and a PbS sample store under ambient conditions. These spectra are accompanied by a reference spectrum of PbO powder. We focus our attention on the peak at 3437 cm$^{-1}$ which serves as a fingerprint for PbO and peaks at 1161 cm$^{-1}$ and 1033 cm$^{-1}$ which serve to identify PbSO$_4$ [104]. Figure 6.3A reveals that PbO and PbSO$_4$ are readily formed on nanoparticles under certain storage conditions. Only the strictest inert atmosphere and dry solvent processing led to nanocrystal films possessing no identifiable PbO or PbSO$_4$ content. Nanocrystals stored under ambient conditions readily oxidize.

As water has a strong absorption peak centred at about 3392 cm$^{-1}$, we also carried out a set of experiments tracking our PbO fingerprint feature in the presence of water. These experiments served to confirm that this feature is independent of water content. The results of these experiments can be seen in Appendix 1.

We then examined the FTIR spectra of nanocrystal films treated with ethanedithiol (Figure 6.3B) as compared to that without ethanedithiol treatment. The most pronounced result of this comparison is that the PbO feature is almost entirely absent after ethanedithiol treatment. In contrast to this observation the PbSO$_4$ feature is present before and after thiol treatment. PbS films were also treated with different length thiol-terminated ligands, including butanethiol and hexane-dithiol, both of which were shown to be effective in the removal of PbO in nanocrystal films.
Figure 6.3 A. FTIR spectra of untreated PbS nanocrystals, PbO reference spectrum and a PbS nanocrystal sample stored under ambient conditions for three days. The peak labelled at 3437 cm$^{-1}$ is used to identify the presence of PbO. The peaks labelled at 1161 cm$^{-1}$ and 1033 cm$^{-1}$ are associated with PbSO$_4$. The peaks labelled at 2924 and 2857 cm$^{-1}$ are associated with C-H bonds present in the butylamine ligands and in the remaining oleic acid ligands.[105] In thiol treated samples where these ligands are expected to be predominately displaced by thiol functionalized ligands, these features correspond to the C-H stretches in the new thiol
ligands. While the inert stored PbS does not show any observable spectral feature at 3437 cm$^{-1}$, after ambient storage the PbS film shows the emergence of the PbO spectral feature. B. FTIR spectra of untreated PbS films and films rinsed with solutions of 4% ethanedithiol in acetonitrile for 10 minutes. The lack of a discernable PbO feature indicates that the thiols have reduced the PbO content. C. FTIR spectra of PbS nanocrystals rinsed with 4% ethanedithiol in acetonitrile for 10 minutes followed by heating at 130°C for 2 hours in vacuum, nitrogen and air. The PbO peak at 3437 cm$^{-1}$ is re-introduced only in the sample heated in air. Note that all the data shown has been processed using a “Remove Offset” software function included with the Bruker FTIR software. This function subtracts a linear offset from the as-collected data. In two of the presented spectra T > 1 near 2300 cm$^{-1}$, this is attributed to this post-processing.

Table 6.1 shows a summary of the peaks labelled in the FTIR spectra shown in Figure 6.3.

<table>
<thead>
<tr>
<th>Peaks(s) (cm$^{-1}$)</th>
<th>Attributed Species</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1033, 1161</td>
<td>PbSO$_4$</td>
<td>104</td>
</tr>
<tr>
<td>2857, 2924</td>
<td>C-H bond in butylamine and oleic acid</td>
<td>105</td>
</tr>
<tr>
<td>3437</td>
<td>PbO</td>
<td>Measurement of PbO sample</td>
</tr>
</tbody>
</table>

Table 6.1 Summary of peaks labelled in FTIR spectra

To examine the impact of annealing on the composition of our PbS films we first look at the FTIR spectra of nanocrystals heated in air, nitrogen and vacuum (Figure 6.3C). As expected the PbO peak returns after air heating but does not show any growth after nitrogen or vacuum heating. The sulphate feature remains strong in our air annealed sample and does not show any significant change in our inert annealed samples.

To confirm our FTIR findings regarding PbO reduction vis-à-vis thiol treatment we turned to x-ray photoelectron spectroscopy (XPS) to examine the oxidation state of the elements present in our materials.

6.5. XPS measurements of PbS nanocrystals

XPS is an excellent tool for providing a more complete picture of the material composition of our samples than that gained thus far through the use of FTIR, TGA and
HSGC. We also turned to this measurement technique as an independent means of providing verification of the observation that thiols reduced the oxide content of our PbS films.

XPS is an analytical technique useful in the identification of atomic species and their chemical state [106]. In this measurement a sample is bombarded with high energy photons which excite core electrons, ejecting them from the atoms in the sample. Excited electrons are collected and the kinetic energy of the electrons is measured. The difference between the kinetic energy and the energy of the photons used for excitation is equal to the binding energy of the electron. By analyzing the energy of the emitted electrons one can find elemental composition and the chemical coordination of those elements in a sample. Quantitative information can also be obtained by examining the intensity of the collected signal for a given wavelength. By comparing the spectra collected from a sample to known reference spectra one can find its chemical composition [106].

In a typical XPS measurement a survey scan is first performed which identifies the energy peaks (corresponding to different elements) present in the sample. A detailed scan is then performed of each of these regions which provides greater resolution suitable for post-processing and analysis. In examining the results of the measurements of our samples, we paid particular attention to the oxygen signal and the sulphur signal. From these two signals we obtained the information about the evolution of the primary oxidation products identified by FTIR. Chemical species are identified by comparing the spectral location of emission peaks in the sample to that obtained from reference samples. In samples containing multiple chemical compounds (such as PbS and PbSO₄) the analysis of the raw XPS data is accomplished by fitting a series of energy signatures (corresponding to each compound) to the measured data.
6.5.1. XPS sample preparation

Samples for XPS analysis were prepared by drop-casting nanocrystals from octane onto double-sided-polished undoped silicon substrates. Samples that were treated with ethanediethiol were soaked in a 4% ethanediethiol solution in acetonitrile for about 10 minutes. The heated sample was heated at 130 °C for three hours in air. The samples were measured at using a PHI 5500 (XPS) Spectrometer.

6.5.2. Methods used for the XPS analysis

Before analysis the binding energy of all XPS spectra were referenced to the C1s hydrocarbon line at 285.0 eV. High resolution O1s spectra were used for examining the evolution of the PbO, PbSO\textsubscript{3} and PbSO\textsubscript{4} content in drop cast nanocrystal films. The S2p high resolution spectra were used for further confirmation of the PbSO\textsubscript{3} and PbSO\textsubscript{4} content.

The deconvolution of the O1s spectra was performed by fitting a sum of Gaussian-Lorentzian functions (always with greater than 80% Gaussian weighting) to the experimental data. PbO was identified using a peak centred at 529.3 eV [107, 108], PbSO\textsubscript{3} was identified using a peak centred at 530.8 eV [109], while PbSO\textsubscript{4} was centred at 531.8 eV [107] and SiO\textsubscript{2} (from the Si substrate) was centred at 533.3 eV.

The deconvolution of the S2p spectra was also performed by fitting a sum of Gaussian-Lorentzian functions to the experimental data. Each species was fit with a S2p doublet (due to the presence of S2p3/2 and S2p1/2 peaks) with a 2:1 area ratio and a splitting of 1.2 eV. PbSO\textsubscript{3} was identified using a S2p3/2 peak position of 166-166.6 eV [108, 110]. The PbSO\textsubscript{4} was identified using a peak position of 168-169 eV [108, 110] and PbS identified using a peak position of 160.7-160.8 eV [110, 111]. After treatment with ethanediethiol the samples also show the presence of metal-bound thiols which were identified using a S2p3/2 peak position of 161.9 eV [112] and unbound thiols at a peak position 163.5 eV [112].
6.5.3. **XPS results and analysis – O1s spectra**

The O1s spectrum was obtained for nanocrystals stored under ambient conditions. The measurement data and the results of the analysis of this data can be seen in Figure 6.4. In Figure 6.4 one can see the individual curves corresponding to the identified oxygen-containing chemical species in the sample. Comparing the sum of the individual curves to experimental data allows one to validate the analysis of this data. This XPS measurement shows the presence of PbO, PbSO$_3$, PbSO$_4$ and SiO$_2$ (from the Si substrate). While PbO and PbSO$_4$ have been identified by FTIR (and whose presence has now been confirmed by this measurement), PbSO$_3$ is an additional oxidation product not previously identified.

![XPS O1s Spectrum - Ambient Stored PbS Nanocrystals](image)

**Figure 6.4** XPS O1s spectrum of ambient stored PbS nanocrystals fit using a sum of four curves indicating the presence of PbO, PbSO$_3$, PbSO$_4$ and SiO$_2$. 
The same nanocrystal batch used in Figure 6.4 was drop cast onto a silicon substrate and then treated with ethanediithiol. The O1s spectrum along with the analysis of this spectrum can be seen in Figure 6.5. After ethanediithiol treatment one can see that the PbO content is substantially diminished, confirming the FTIR findings. The magnitude of the PbSO$_3$ has also been reduced as a result of the ethanediithiol treatment while the PbSO$_4$ content appears to be largely unaffected.

![XPS O1s Spectrum - Ethanediithiol Treated PbS Nanocrystals](image)

**Figure 6.5** XPS O1s spectrum of ambient stored PbS nanocrystals which have been treated with a 4% solution of ethanediithiol in acetonitrile. The spectrum has been fit using a sum of three curves indicating the presence of PbSO$_3$, PbSO$_4$ and SiO$_2$. The PbO peak position is indicated for reference but was not needed to provide an accurate fit.
We measured the O1s spectrum of a further nanocrystal sample which was first treated with ethanedithiol and then heated in air at 130 °C. The results of this measurement and the subsequent data analysis can be seen in Figure 6.6. We see in the O1s spectrum that the PbO content has indeed been re-introduced, confirming our FTIR findings. There has also been a growth in the PbSO₃ content.

![XPS O1s Spectrum](image)

**Figure 6.6** XPS O1s spectrum of an ethanedithiol treated PbS nanocrystal film heated in air at 130 °C. The spectrum has been fit using a sum of four curves indicating the presence of PbO, PbSO₃, PbSO₄ and SiO₂.

Another feature of the O1s spectra that should be discussed is the variation in the strength of the SiO₂ peak which arises from the surface oxide layer on the Si substrates used.
for the XPS samples. The drop-cast nanocrystal films used for XPS measurements were relatively thick (approximately 3 µm), especially when compared to those used for FET and TEM measurements. It was found that in these drop-cast samples the CQD films contained drying cracks and that ethanedithiol treatment lead to further cracking of the thick films. The distribution and extent of the cracks exposing the Si surface contributed to the variations observed in the intensity of the SiO$_2$ signal. It should be noted that nanocrystal layers thinner than 100 nm deposited via dip coating or spin coating did not exhibit the same drying cracks seen in thick films.

6.5.4. XPS results and analysis – S2p spectra

To gain additional information about the chemical changes occurring in the PbS films during ethanedithiol treatment and annealing we also examined the S2p spectra obtained from the same samples used in the analysis of the O1s spectra in Section 6.5.3. These spectra allow us to identify what sulphur-containing compounds are present in our samples.

The S2p spectrum and analysis of the untreated nanocrystals can be seen in Figure 6.7. It confirms the presence of sulphites (PbSO$_3$) and sulphates (PbSO$_4$) in our PbS sample. As discussed earlier each sulphur S2p compound is fit with a doublet due to the presence of the spin-orbit splitting [106]. This means that there are two curves present in each compound used in the deconvolution of the measured signal.
Figure 6.7 XPS S2p spectrum of ambient stored PbS nanocrystals. The spectrum has been fit using a sum of three S2p doublets with 2:1 area ratios and a splitting of 1.2 eV. The fit indicates the presence of PbSO₃, PbSO₄ and PbS. The broad hump seen in the energy spectrum between 156 eV and 164 eV is attributed to the Pb4f energy loss spectrum.

The S2p spectrum for the sample treated with ethanedithiol can be seen in Figure 6.8. This spectrum shows that in addition to PbSO₃ and PbSO₄, the sample also shows the presence of metal-bound thiols as well as unbound thiols [112]. The growth of the PbSO₄ peak in the S2p spectra after ethanedithiol treatment relative to the PbS peak suggests a mechanism whereby ethanedithiol reduces the PbO content of PbS nanocrystals by promoting the growth PbSO₄.
The S2p spectrum for an ethanedithiol treated sample which has then been heated in air can be seen in Figure 6.9. The S2p spectrum of air-heated samples shows that PbSO$_3$ content has also increased. The PbSO$_4$ content also remains present in the S2p spectrum after air heating but the deconvolution of the S2p spectrum before and after annealing (Figure 6.8 and Figure 6.9) indicates that the amount of PbSO$_4$ present relative to PbS has increased only slightly. Air annealing has in effect promoted the growth of PbO and PbSO$_3$, but not PbSO$_4$. As a further control we annealed PbS nanocrystals in nitrogen and as expected XPS showed no change in the content of any of our identified oxidation products.
Experimental Data

Peak Fitting Result

XPS S2p Spectrum
Ethanedithiol Treated then Air Heated Nanocrystals

Figure 6.9 XPS S2p spectrum of ethanedithiol treated PbS nanocrystals heated in air. The spectrum has been fit using a sum of five S2p doublets with 2:1 area ratios and a splitting of 1.2 eV. The fit indicates the presence of PbSO$_3$, PbSO$_4$, PbS as well as both bound and unbound thiols. The magnitude of the PbSO$_3$ component relative to the PbS has is larger than before heating, indicating the growth of PbSO$_3$.

6.6. Summary and conclusions

We undertook these studies to provide some insight into the material changes underlying the changes identified in the electronic properties of seen in Chapter 5. TGA and HS-GCMS showed us that there is oxidation occurring in our nanocrystal films during heating in air and that ligand loss is also occurring during annealing both air and in inert atmospheres. This raises the question whether photovoltaic device performance can be
improved strictly through annealing or if growth of oxidation products is a prerequisite for performance improvements.

The results of the FTIR and XPS measurements have shown that PbS CQD films after ethanediethiol treatment exhibit a reduction in the PbO content but not the PbSO₃ or PbSO₄ content. They also show air annealing is required to re-introduce PbO content and while doing so simultaneously increases the content of PbSO₃ in the film. Nanocrystals that have been ethanediethiol treated and subsequently annealed in an inert atmosphere retain only their initial PbSO₄ and PbSO₃ content but have no observed PbO content. The chemical species identified from the XPS analysis at each stage of processing are summarized in Figure 6.10.

![Figure 6.10](image)

**Figure 6.10** O₁s (A,C,E) and S₂p (B,D,F) high resolution XPS spectra with peak positions indicated of species identified through spectral deconvolution.
We present the summary of the general trends observed during these material studies in Table 6.2. Here we show that untreated PbS nanocrystals initially contain PbSO$_4$, PbSO$_3$ and PbO. After treatment with ethanedithiol the PbO content is greatly reduced (and is in fact, undetectable in our measurements) while the PbSO$_4$ and PbSO$_3$ content increases. Not surprisingly, nanocrystals heated in inert atmospheres show no change in the extent of oxidation. However, the samples heated in air show a return of PbO, a small increase in PbSO$_4$ and a larger increase in PbSO$_3$.

<table>
<thead>
<tr>
<th></th>
<th>PbO</th>
<th>PbSO$_4$</th>
<th>PbSO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated Nanocrystals</td>
<td>present</td>
<td>present</td>
<td>present</td>
</tr>
<tr>
<td>Ethanedithiol Treated NCs</td>
<td>absent</td>
<td>↑</td>
<td>↑</td>
</tr>
<tr>
<td>Air Annealed Nanocrystals</td>
<td>↑</td>
<td>small ↑</td>
<td>↑</td>
</tr>
<tr>
<td>Inert Annealed Nanocrystals</td>
<td>no change</td>
<td>no change</td>
<td>no change</td>
</tr>
</tbody>
</table>

**Table 6.2** Summary of material changes observed in PbS nanocrystals during treatment and fabrication procedure
Chapter 7

Device Fabrication and Performance

At the beginning of this project we set out to produce photovoltaic devices having an infrared power conversion efficiency of 1%. Through the previous chapters we outlined an architectural strategy and developed processing insights needed to achieve this goal. In Figure 7.1 one can see the major components of this work that we now bring together in the fabrication of photovoltaic devices. These components include the information we have obtained about modifying the mobility and carrier concentration of PbS quantum dot films. Also of importance are the fabrication techniques we developed to create devices with sufficient thickness and optical density.

In this chapter we present performance results from devices fabricated using porous oxide electrodes, cross-linking molecules and post-fabrication annealing. We also correlate the chemical changes observed in PbS quantum dots during inert and air annealing with the performance of photovoltaic devices that have undergone the same treatments. Using these findings we optimize our devices and surpass our performance target.
7.1. Device fabrication

Completed devices were fabricated in a multi-step process partially outlined in our earlier discussions of nanocrystal ligand exchange, porous oxide fabrication, and nanocrystal infiltration and crosslinking. To these processes we add the deposition of top metal contacts which is accomplished by thermal evaporation.
7.1.1. Contact deposition

The devices fabricated in this work used a low-work function Mg contact for extraction of electrons from the PbS quantum dot film. This Mg contact was capped with Ag to reduce oxidation of the Mg. A metal shadow mask was used to define the area of the finished contacts. The metals contacts were deposited via thermal evaporation using a BOC Edwards Auto 306 deposition system. The contact deposition procedure is as follows:

1. Samples were loaded into the deposition chamber and then pumped down to a pressure of $1 \times 10^{-5}$ Torr.

2. Mg was then deposited at a rate of about 1 nm/s to thickness of 100 nm. The rate and final thickness was monitored using a crystal thickness monitor built into the Auto 306.

3. Once the Mg deposition was complete Ag was deposited on top of the Mg at a rate of about 0.5 nm/s to a thickness of about 100 nm.

4. The samples were then removed from the chamber for testing.

7.1.2. Device fabrication steps

To summarize the fabrication parameters and procedures used to make devices presented in this chapter a typical device fabrication run is outlined below. Device fabrication can be broken down into five major processing steps.

1. **PbS nanocrystal synthesis and ligand exchange.** Nanocrystals are synthesized via a standard organometallic route. The ligand exchange is carried out in a nitrogen-atmosphere glove box. The exchange is accomplished by precipitating as-synthesized nanocrystals from solution and then redispersing them in an excess (approximately 100 mg/ml) of butyl-amine. This mixture is left to sit at room temperature for three days. To
complete the exchange the nanocrystals are again precipitated from solution and redispersed in octane to a concentration of 150 mg/ml.

2. Fabrication of a porous oxide film on a glass substrate. A porous oxide electrode on ITO coated glass serves as the starting substrate. These were created by spinning a slurry of ITO in distilled water at a concentration of 1g/ml at 800 rpm for 60 sec onto a 1” square of a planar ITO coated glass slide. The sample was annealed at 310 °C for 1 hour and yielded films approximately 3 μm thick.

3. Infiltration and crosslinking of the PbS quantum dots on the substrate. To deposit nanocrystals a substrate was then dip-coated into a butylamine capped nanocrystals solution at concentration of 5 mg/ml. It was then placed into an acetonitrile solution containing ethanedithiol at a concentration of 4% by volume. This procedure was repeated three times and resulted in a PbS-infiltrated porous oxide films.

4. Annealing of the device. Devices were then either annealed in vacuum, or in air, as described below in the main body of the text.

5. Evaporation of top metal contacts. Finally, the top metal contact was deposited by the vacuum evaporation of a 300 μm diameter circular pad which consisted of 100 nm of Mg followed by 100 nm of Ag.

An illustration showing the cross section of a finished device can be seen in Figure 7.2.

Figure 7.2 Illustration of a cross section of a complete device
7.2. Initial device results

We first sought to demonstrate the value of quantum-size-effect tuning of quantum dot absorption onset by constructing classes of devices having two different excitonic spectral locations. We selected one nanocrystal batch with a first excitonic transition at 1340 nm; and for the longer-wavelength device, at 1590 nm.

As-fabricated, devices illuminated under monochromatic 975 nm illumination exhibited short-circuit external quantum efficiencies of 2.3% in the 1340 nm device and 0.3% in the 1590 nm nanocrystal device, in both cases with illumination intensities of 12 mW/cm$^2$. A summary of these results can be seen in Table 7.1.

As we had seen significant changes in the electronic and material properties of the PbS quantum dots during annealing in air we believed that thermal treatment of the devices offered the potential to improve performance. As such we annealed our devices in air for 3 hours, deposited top contacts and then measured their photovoltaic performance. After annealing the EQE in the 1340 nm devices increased to 9% and the EQE of the 1590 nm devices increased to 16%. Table 7.1 summarizes the effects of annealing on the performance of the devices.

<table>
<thead>
<tr>
<th></th>
<th>Voc (mV)</th>
<th>Jsc (mA/cm$^2$)</th>
<th>$\eta_P$ (%)</th>
<th>EQE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1340 nm device no annealing</td>
<td>170 +/- 5%</td>
<td>0.2 +/- 10%</td>
<td>0.02</td>
<td>2.1</td>
</tr>
<tr>
<td>1340 nm device 150 C annealing</td>
<td>400 +/- 5%</td>
<td>1.0 +/- 10%</td>
<td>1.3</td>
<td>10</td>
</tr>
<tr>
<td>1590 nm device no annealing</td>
<td>70 +/- 5%</td>
<td>0.02 +/- 10%</td>
<td>0.003</td>
<td>0.2</td>
</tr>
<tr>
<td>1590 nm device 130 C annealing</td>
<td>85 +/- 5%</td>
<td>1.5 +/- 10%</td>
<td>0.3</td>
<td>16</td>
</tr>
</tbody>
</table>

Table 7.1 Effects of annealing treatment on the performance of photovoltaic devices. All measurements performed under 12 mW/cm$^2$ 975 nm illumination. Note that errors in Voc and Jsc are approximated based upon contact to contact variations within a single device and up multiple measurements of a single contact. Calculation of efficiencies were made using typical Voc and Jsc values.
We provide current-voltage traces for the 1340 nm device in Figure 7.3. We include data taken under 100 mW/cm$^2$ AM 1.5 illumination using an Oriel solar simulator. These devices showed AM 1.5 power conversion efficiencies of 0.5%. Monochromatic power conversion efficiencies at 975 nm were 1.25% for 12 mW/cm$^2$ illumination and 0.95% for 70 mW/cm$^2$ illumination.

![Figure 7.3](image)

**Figure 7.3** Current-voltage curves of sintered device made with nanocrystals having a first excitonic transition at 1340 nm. The AM 1.5 illumination intensity was 100 mW/cm$^2$. Monochromatic illumination intensities of 12 and 70 mW/cm$^2$ were with 975 nm light.

### 7.3. Spectral EQE

We measured the external quantum efficiency of our devices by illuminating them with monochromatic light and measuring the current generated under short circuit photovoltaic operation.
7.3.1. Measurement method

To measure the spectral external quantum efficiency the leads of a device were fed directly into the differential input of a lock-in amplifier (SR803 DSP) with an input impedance of 20 MΩ. This resulted in peak voltages on the order of a 0.1 to 2 mV, sufficiently far enough below the observed open circuit voltages of 85 to 400 mV to approximate short circuit conditions. Illumination was provided by a white light source dispersed by a monochromator (Triax 320) and mechanically chopped at a frequency of 10 Hz. Various filters were used to avoid harmonic overtones from illuminating the sample. The potential drop across the lock-in amplifier’s internal load resistor was measured for each illumination wavelength from which the current was calculated. The light intensity at each wavelength was separately measured. After the photocurrent spectral shape was determined in this way, the absolute external quantum efficiency taken 975 nm was used to obtain the absolute spectral response in the range of 600 nm to 1800 nm.

7.3.2. Spectral EQE results

We plot in Figure 7.4 and Figure 7.5 the spectrally-resolved external quantum efficiency which reveals a photoresponse extending to more than 1700 nm in the device fabricated with 1590 nm first exciton transition nanocrystals and photoresponse extending to more than 1500 nm in the device fabricated with 1340 nm first exciton transition nanocrystals. The spectral EQE for both devices follows closely their respective absorption spectra. A peak EQE of 32% occurred at 500 nm in the sintered 1590 nm device while the sintered 1340 nm device exhibited a peak EQE of 15% at 590 nm. The decrease seen in EQE below about 650 nm is due primarily to increasing absorption in the ITO.
Figure 7.4 External quantum efficiency of a sintered 1340 nm device.
In an effort to further improve device performance and to gain insight into the impact the chemical changes observed during annealing had on performance, a set of devices were fabricated and the processing conditions were varied for each.

One set of devices was annealed in air at 110 °C, 130 °C, and 150 °C for three hours. Another set of devices was annealed under inert conditions in a vacuum oven at 110 °C, 130 °C, and 150 °C for three hours. An additional device was also set aside without annealing. These devices all then had their top metal Mg contact deposited by thermal evaporation.
As-fabricated, without annealing, the devices exhibited a very weak photovoltaic effect with open circuit voltages of less than 100 mV under 970 nm monochromatic infrared illumination and external quantum efficiencies (EQEs) of 0.2%.

The vacuum annealed devices showed a trend of increasing EQE with increasing temperature (Figure 7.6A). Here EQE improved from 1% after 110 °C inert annealing up to 6% after 150 °C. However, the open-circuit voltage remained low (Figure 7.6B) at ~90 mV for all inert annealing temperatures tested. Figure 7.6C shows the maximum power conversion efficiency under monochromatic illumination is 0.08%. We provide the J-V characteristic under monochromatic illumination in Figure 7.7A of the device heated in vacuum at 150 °C.

The device annealed under air showed more pronounced photovoltaic performance gains with external quantum efficiency, open circuit voltage and power conversion efficiency all increasing with increased temperature. The EQE of these devices (Figure 7.6A) increased to 8% after annealing at 110 °C and to 18% after 150 °C annealing. The open circuit voltage under monochromatic IR illumination showed a marked increase from an initial 100 mV without annealing to 425 mV after 150 °C air annealing. Figure 7.6B shows the trend of larger open circuit voltages with higher processing temperatures. Finally, the power conversion efficiency (Figure 7.6C) increased to 2% at the 150 °C annealing temperature. The 2% power conversion efficiency achieved here represents a 54% improvement over that reported in earlier in this chapter [89]. We provide the J-V characteristic under monochromatic illumination in Figure 7.7B of the device annealed at 150 °C.
Figure 7.6 Photovoltaic device performance characteristics for devices treated in air and vacuum at different temperatures. All measurements were taken under monochromatic 975 nm illumination at 12 mW/cm². (A) shows that an increase in open circuit voltage only occurs when the PbS CQD solid is annealed in air. (B) indicates the increase in external quantum efficiency attributed to improved charge transport characteristics after heating. Air annealing devices had a marked impact on power conversion efficiency as indicated in (C), with a maximum infrared power conversion efficiency shown of 2%. 
Figure 7.7 (A) and (B) show the photovoltaic performance of two different devices, one heated in vacuum at 150 °C (A) and one heated in air at 150 °C (B) under monochromatic 975 nm illumination at 12 mW/cm².

7.5. Air stability

Devices fabricated in the manner described here were subsequently left under ambient conditions in an open circuit configuration for approximately seven months. After this time it was observed that the top deposited contacts had oxidized, significantly degrading device performance. Once new contacts were deposited, however, the devices continued to function with photovoltaic efficiencies only slightly degraded from that obtained seven months earlier.
The relative stability of these air annealed PbS devices is in contrast to devices made using semiconducting polymers and Cd(Se,Te) nanocrystals. This is likely a result of the role oxygen has in both the doping and the passivation of our devices. We present in Figure 7.8 the performance of a device stored under ambient conditions.

![J-V characteristics of a device stored under ambient atmosphere conditions.](image)

**Figure 7.8** J-V characteristics of a device stored under ambient atmosphere conditions.

### 7.6. Conclusions

The results of the FTIR and XPS measurements show that PbS CQD films after ethanedithiol treatment exhibit a reduction in the PbO content but not the PbSO$_3$ or PbSO$_4$ content. Furthermore, air annealing is required to re-introduce PbO content and while doing so simultaneously increases the content of PbSO$_3$ in the film. Nanocrystals that have been ethanedithiol treated and subsequently annealed in an inert atmosphere retain only their initial
PbSO$_4$ and PbSO$_3$ content but have no observed PbO content. When these results are viewed alongside the performance of similarly processed photovoltaic devices it appears that the formation of PbO and PbSO$_3$ leads to increased open circuit voltages and power conversion efficiencies.

Recent results utilizing semiconductor nanocrystals in electrical devices have shown that many of the properties of bulk semiconductors also apply to solution-processed semiconductor nanocrystals. (For example Schottky junctions are formed when conductive PbS CQD films are brought into contact with Al and when ZnO tetrapods are coated with Pt [56, 113].) In a manner analogous to that seen in bulk metal-semiconductor Schottky photovoltaic cells, it is likely that the growth of oxidation products in PbS nanocrystal CQD films leads to the improvements in photovoltaic devices by modifying the mid-gap states formed at nanocrystal boundaries.

In particular the observation that the presence of PbSO$_4$ (and PbSO$_3$ in smaller quantities) alone does not significantly impact the open circuit voltage (as is the case in the inert atmosphere annealed devices), indicating that the passivation of mid-gap states is primarily influenced by the formation of PbO and PbSO$_3$. Using the combination of a thiol-terminated bidentate linker and oxide formation during the fabrication of a photovoltaic device leads to an increase in open circuit voltage from less than 100 mV to 425 mV; and ultimately results in a record 2% infrared power-conversion efficiency in solution-processed photovoltaics.
Chapter 8

Conclusions

8.1. Thesis objective and device performance gains

In this thesis we set out to fabricate photovoltaic devices using infrared sensitive quantum dots and porous oxide substrates. We had set a goal that exceeded previous infrared power conversion efficiency and external quantum efficiency dramatically obtained from PbS quantum dot devices prior to this work. Specifically we aimed to achieve a power conversion efficiency of 1% under infrared illumination at ~1000 nm. To achieve this goal we needed to learn how to build working devices with high optical density and we needed to develop an understanding and a means of controlling carrier mobility, concentration and passivation within nanocrystal solids. To this end we developed the techniques needed to fabricate porous oxide films and used crosslinking molecules to achieve smooth continuous coverage of these films with colloidal quantum dots. We also learned that by using crosslinkers we could improve the mobility by altering the interparticle spacing of our nanocrystals. This change in mobility was accompanied by a decrease in carrier concentration which we attributed to a
reduction surface oxidation which we confirmed by FTIR and XPS. We were then able to reintroduce these dopants by lightly reoxidizing without sacrificing our gains in mobility.

We then explored the impacts of annealing and crosslinking on the performance of photovoltaic devices. We fabricated devices having infrared photovoltaic power conversion efficiencies of 2% using solution-synthesized PbS nanocrystals. Air-annealing was used to increase the PbO and PbSO$_3$ content which was central to increasing the open circuit voltage. This effect is attributed to the modification of mid-gap interface states in the colloidal quantum dot film. We present in Figure 8.1 a chart showing progress in the performance of solution-processed photovoltaic devices. We indicate on this chart the improvements in infrared power conversion efficiency achieved as a result of our work on porous oxide/PbS quantum dot devices.
Figure 8.1 Progress in the power conversion efficiency of solution-processed photovoltaics. The devices only sensitive to visible light have their efficiencies reported for broadband illumination. The devices sensitive to infrared light have their efficiencies reported for illumination at ~ 1000 nm.

8.2. Novelty of work

The novelty of this work can be summarized by the following accomplishments:

1. The fabrication of solid state porous oxide/PbS quantum dot photovoltaic devices with an IR power conversion efficiency of 2%, four orders of magnitude higher than that previously reported for PbS quantum dot devices [16].
2. The use of cross-linking molecules for the assembly of smooth nanocrystal films on rough, high surface area electrodes.


4. Evaluation of the changes in electronic properties of PbS colloidal quantum films during annealing and treatment with cross-linking molecules.

5. An understanding of the chemical and material changes which underpin the changes in electronic properties observed during crosslinking and annealing.

The findings in these areas have been reported in peer reviewed journals and have also led to a number of patent applications, invention disclosures and conference proceedings. A complete list of these contributions can be seen in Chapter 9.

8.3. Future directions and challenges

There exists a continuing interest in the application of solution-processed quantum dots in a wide area of applications, including photovoltaics, photodetection, and optical modulation. Although solution-processed quantum dots have been studied for over two decades demonstrations of these materials in devices exhibiting performance levels on par (or better) than their crystalline semiconductor counterparts have only emerged in the past few years. In the field of photovoltaics, the performance of devices using solution-processed quantum dots still has not yet reached levels required for commercial viability. The results obtained over the course of our research, however, have both taken a significant step towards competitive levels of power conversion efficiency and point to future directions in applying these materials in other device applications. Specifically, there are opportunities to apply the
general concepts of cross-linker mediated assembly and oxide doping of nanocrystals to applications other than photovoltaics.

To further improve the performance of infrared sensitive photovoltaic devices fabricated using nanocrystals and high surface area metal oxides there are three primary routes that can be pursued. The first is to explore other choices of oxides such as SnO₂ or WO₂ which were identified as candidate materials in Chapter 3. These materials may lead to improved performance and improved cost advantages. A second route is to explore the use of different morphologies of oxides. There has been much work in recent years fabricating oxide brushes, pillars and wires that could result in more direct transport paths for both carriers. Finally, further work improving the transport properties and the surface passivation in colloidal quantum dot films could dramatically improve the photovoltaic device efficiency. The carrier mobility found in our materials is still rather low. As mobility has a direct impact on charge extraction, increases in mobility will translate to improvements in device performance.

If photovoltaics fabricated from solution-processed quantum dots are going to find widespread commercial application there will need to be sizable gains in power conversion efficiencies. Despite this challenge, the ease of synthesis and the fabrication options to be had using these materials, ensures that there will continue to be strides made towards achieving the goal of commercial viability.
Chapter 9

Publication List and Other Contributions

9.1. Refereed journal publications


### 9.2. Patents and invention disclosures


9.3. Conference presentations and seminars


Appendix A

Water in PbS and PbO Samples for FTIR

To confirm that our identification of PbO was not the result of water we performed the following experiment comparing PbS with water to PbO and to PbS without water exposure.

We treated baseline nanocrystals with 4% ethanedithiol in acetonitrile and rinsed with acetonitrile. Figure A.1(A) shows the loss of the PbO feature in the nanocrystals treated ethanedithiol. Figure A.1(B) shows baseline nanocrystals with no PbO and after a 30 minute soaking in water. A water reference spectrum is also included. All samples except water lack water’s 1600 cm$^{-1}$ feature. Figure A.1(C) shows baseline nanocrystals containing PbO compared to a water reference and a PbO reference. In addition, another water absorption feature at 2130 cm$^{-1}$ was monitored in our samples since near this wavenumber, PbS, PbO, and the ligands used herein are spectrally featureless: this feature was not observed in any of our subsequent measurements.
Figure A1. Full range of FT-IR spectra of PbS nanocrystals (NC) with various treatments. 
A. Baseline nanocrystals (black) rinsed with 4% ethanedithiol in acetonitrile (Red) and rinsed with acetonitrile (Blue), showing the loss of PbO with ethanedithiol. B. Baseline nanocrystals with no PbO (black) and after a 30 minute soaking in water (blue) show no water absorption. Water reference spectrum (red) is also included. All samples except water lack water’s 1600 cm\(^{-1}\) feature. C. Baseline nanocrystals containing PbO (black) compared to water reference (red) and PbO reference (blue). In addition, another water absorption feature at 2130 cm\(^{-1}\) was monitored in our samples since near this wavenumber, PbS, PbO, and the ligands used herein are spectrally featureless: this feature was not observed in any of our subsequent measurements.
Bibliography


