SMOOTH-MORPHOLOGY ULTRASENSITIVE SOLUTION-PROCESSED PHOTOCONDUCTORS

BY

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ABSTRACT

Smooth-Morphology Ultrasensitive Solution-Processed Photoconductors

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Solution-processed optoelectronic materials offer a route to low cost photodetectors, large area solar cells, and integrated optical sources. While significant progress has been reported in organic and polymer spin-cast optoelectronics, colloidal quantum dots offer a distinct further advantage – the convenient tuning of absorption onset via the quantum size effect. Electronic transport has recently been enhanced in size effect tuned colloidal quantum dot films using ligand exchange, resulting in ultrasensitive photodetectors in both visible and infrared wavelengths. Solid-film ligand exchange, however, generally results in rough film morphologies that are incompatible with high uniformity image sensors. Here, we report a new route to visible-wavelength spin-cast lead sulfide (PbS) nanocrystal photoconductive photodetectors with a sub 1% roughness, compared to the ~10% roughness obtained using previously reported approaches. The new procedure yields devices that exhibit 10 AW⁻¹ responsivities and reveals an added significant advantage: when illumination conditions change, the photodetectors respond with a single time constant of 20 ms. This compares very favorably to the multi second and multi-time-constant response of previously reported PbS-nanocrystal photoconductive photodetectors.
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CHAPTER 1

Introduction

More than a billion image sensors are embedded in cameras and cellphones throughout the world[3]. These sensors rely on silicon photodiodes’ light to electrical current conversion that is limited to less than one electron’s worth of photocurrent per photon absorbed. In turn, photodiode based cameras depend on exceedingly low noise readout electronics to capture clear and uniform images under low light conditions because conventional photodiodes do not provide innate amplification.

In the present work we examine new synthetic techniques and novel ligand exchange procedures that result in colloidal lead sulfide quantum dots well suited for photodetection. Moreover, we apply these new materials to build photoconductive photodetectors that combine significant gain, video compatible speed, and excellent film morphology.

Photodetectors, are an important class of devices that underpin a significant portion of modern electronics. Fiber optics, missile guidance, digital cameras, solar energy devices, night and machine vision, and television, all rely on photodetectors’ optical to electrical transduction.

This work explores the potential of using ‘soft’-materials to build photodetectors. We do so using colloidal quantum dots, collections of semiconductor nanoparticles that are completely quantum confined and cast into films.

Unlike the photodetector materials of a previous generation, colloidal quantum dots are a flexible, conformal material with widely tun-
able optical and electronic properties. They are a class of materials that have the potential to exceed the processability, spectral selectivity, and performance of traditional bulk semiconductor photodetectors; provided we have the understanding and capability to realize this potential.

This chapter will describe some of the current practical applications of colloidal quantum dots and will introduce some of the properties salient to these applications. The attributes of film morphology that are necessary to top-surface imaging photodetectors are also described and the novel contributions of this work are outlined. Finally, the organization of this thesis is presented.

1.1 Applications of colloidal quantum dots

Colloidal quantum dots are suspensions of quantum confined semiconductors that are solution processable over large areas and over flexible surfaces. The innate processability of colloidal quantum dots reduces the infrastructure needed for scalable area or flexible applications that the single crystal bulk semiconductors of a previous generation required.

Colloidal quantum dots rely on an inexpensive, relatively straightforward synthesis that allow many of the material’s innate properties to be tailored. Unlike silicon, colloidal quantum dots can be highly luminescent and can selectively respond to different wavelengths of light through the engineering of their quantum confinement. This useful property allows devices requiring spectral specificity to be directly realized with a single material.

At present the challenge to produce highly crystalline, highly monodisperse, and well passivated colloidal quantum dots is successfully
addressed through organometallic synthesis (as shown in Figure 1). Materials produced through this synthetic route have a high photo luminescence quantum efficiency (PLQE), which is an indication of crystalline structure; they have a uniform and large interparticle spacing, which is an indication of sufficient passivation; and they have monodisperse particle morphology, which is an indication of low dispersion quantum confinement.

![Figure 1. TEM of lead sulfide organometallic synthesis with oleic-acid capping ligands with inset showing selected area electron diffraction demonstrating crystalline structure of the shown quantum dots; imaging performed by the author.](image)

The organometallic synthesis of colloidal quantum dots typically requires the use of long aliphatic chains to prevent irreversible aggregation and to engender high PLQE among the dots[4]. Such quantum dots can, for example, be used directly as luminophores for bio-labeling application[5, 6, 7, 8, 9]. The tunable absorption onset, photoluminescence onset, and ability to conjugate with bio-recognition molecules confer an attractive combination of traits, well suited for biomedical
imaging. In addition, the size of bio-compatible quantum dots can be kept small enough as to evade the immune system’s response. Finally, their emission wavelength can be tuned to the optimal transparency of tissues using a single material system.

The technique of making luminescent and stable quantum dot colloids by capping nanocrystals with bulky aliphatic ligands avoids aggregation. This technique works well in all-optical applications, but limits their applications in which sub-nanometer interparticle spaces are required to achieve efficient electronic transport.

These new opportunities for films of quantum dots derive from the optical absorption onset that depends on the dot’s physical size, the solution processability that draws from the dots’ colloidal stability, and the optoelectronic transport that is controlled through the dots’ interparticle spacing.

A host of new electronic applications for colloidal quantum dots is emerging. For example, the spectral tunability of colloidal quantum dots has the potential to eliminate the need for optical filters in camera technology – employing a single material to identify red, green, or blue – a trait not readily achieved by an organic molecule or a bulk semiconductor material alone. The optoelectronic transport properties of colloidal quantum dots, those often mediated by ligand chemistry, have enabled bandgap tunable photovoltaics, quantum dot lasers, and record sensitivity photodetectors. All those accomplishments have been demonstrated using a model quantum dot material system, shown in Figure 2, lead sulfide (PbS)[10, 11, 3].
Figure 2. Absorption spectra of varied lead sulfide organometallic quantum dots demonstrating spectral tunability of this material; with inset lattice imaging of a single quantum dot performed by the author.

This work explores the potential of solution processed colloidal quantum dots spin-cast to create a thin-film with useful optical and electronic properties that are innate. We hypothesize that the degree of electronic coupling between quantum dots can be engineered to exceed the performance of traditional photodetectors: exhibiting video frame rate response, with optoelectronic gain, and smooth film morphology.

The major difficulty with these new device applications is the same – how to prevent aggregation and sintering that result in a loss of quantum confined properties.

1.2 Top-surface photodetector film morphology

The challenges that are addressed by the top-surface photodetectors developed in this work include the simultaneous achievement of acceptable electronic transport, the retention of quantum confinement, and
the achievement of excellent film morphology\cite{12}. By scanning electron microscopy we show, in Figure 3, the surface morphology of as-synthesized oleic-acid ligand capped PbS quantum dot film. The rapid volume contraction of these ligands upon drying lead to unacceptable imaging device surface morphology.

![Figure 3. Top surface scanning electron microscopy of as-synthesized oleic-acid ligand capped lead sulfide quantum dot film.](image)

In addition, though the use of long aliphatic ligands in the synthesis and initial stages of processing prevent aggregation, films made from such materials are highly insulating. A procedure to exchange original ligands with shorter ones is needed to achieve sufficiently efficient carrier transport among the nanoparticles. Ligand removal, ligand replacement, and film cross-linking all produce the desired increase in mobility that may result in drastically increased imaging sensitivity. They are, however, also accompanied by a significant loss of film volume. This film contraction leads to film cracking – often on multiple length scales ranging from nanometers to micrometers – that renders the resultant film unacceptable for applications demanding exceptional uniformity\cite{13, 14, 15}.
Therefore, a homogeneous exchange preceding the deposition of a smooth film morphology is required to achieve fewer defects, fewer pinholes, and less aggregate material[10]. These attributes prevent transport-impeding heterogeneous film pockets, and give better electrode interfacial contacts that also result in better carrier extraction.

This work purposes to bring about a ‘no-compromise’ ligand strategy that is compatible simultaneously with solution processing, passivation, and coupling for efficient transport. Films deposited from this strategy comply with the requirement of spatial uniformity relevant to top-surface imaging application photodetectors.

1.3 Novel contributions of this research

Visible wavelength lead sulfide colloidal quantum dot synthesis and processing employing long aliphatic ligands were, prior to this work, well-tailored to applications in biology and optics; but were incompatible with applications requiring strong electronic coupling.

The goal of this research was to devise ligand strategies compatible with the realization of high-performance optoelectronic devices and to prove the power of these new approaches through the optimization and characterization of device operation.

We begin with an investigation of how ligands, including mononucleotides, can be used to build quantum dots[16]. We find that the single nucleotide Guanosine-5’-triphosphate (GTP) simultaneously acts as a competent ligand that results in luminescent colloidal quantum dots. We identify the specific functionalities of GTP that seed lead cations and confer colloidal stability to those quantum dots through GTP’s phosphate backbone. In addition, we identify the exocyclic amine of the G
nucleoside[17] serves to passivate the quantum dots.

Through lead’s strong binding to sulfur we engineered a phase-exchange ligand-exchange technique for organometallically synthesized lead sulfide quantum dots. This yields colloidal dispersions of lead sulfide quantum dots in an aqueous buffer with small bio-compatible hydrodynamic radii and with record 26% PLQE[18]. Based on our observations we hypothesize that decreasing PLQE with exchanged ligand length may result from a promising non-radiative pathway enhancement, rather than one due to a loss of colloidal stability or nanomorphology.

Based on the phase-exchange ligand-exchange PLQE hypothesis we devised a means of trading steric colloidal stability for charge colloidal stability by using an organic polar solvent cage to yield a stable colloid of ultra short ligand capped quantum dots. This ultimately enabled us to build a smooth-morphology photoconductive photodetector – one producing 26 times the number of electrons of collected photocurrent for each incident optical photon, and compatible with the video frame rate temporal response lifetime of 20 ms[19].

1.4 Thesis outline

Chapter 2 reviews lead sulfide colloidal quantum dots in three parts. First, a review of the physics that underpin quantum dots is given. The properties of colloidal suspensions are reviewed. Also, the general approaches taken to colloidal quantum dot syntheses are described. Second, a review of nanocrystal film carrier transport is given. A simple quantum mechanical model is presented that shows the relationship between ligand length and the onset of carrier transport between two
lead sulfide quantum dots. Third, photodetectors, photoconductors, and their figures of merit are described. Chapter 3, “First-generation ligand exchange photodetector strategy: Short amines in organic liquids” describes the loss of quantum confinement when traditional butylamine exchange techniques are performed on the visible wavelength organometallically synthesized[20] lead sulfide quantum dots. Chapter 4, “Second-generation ligand exchange strategy: Nucleic acid ligands in water” elucidates a novel synthetic technique used to confer colloidal stability as opposed to stability in a polymer of DNA. We specify the functionalities that GTP nucleotides possess with respect to colloidal lead sulfide quantum dot synthesis: nucleation, growth, and passivation. In addition, we articulate the role of GTP’s charge cage in conveying aqueous buffer colloidal stability. Chapter 5, “Third generation ligand exchange strategy: A new means of transferring quantum dots
from organic liquids to an aqueous buffer” describes a phase-exchange ligand-exchange that yields record PLQE bio-compatible lead sulfide quantum dots in an aqueous buffer. We find that hydroxyl terminated ligand length has little effect on colloidal stability, but a great impact on PLQE, which we hypothesize as a route to photoconductive nanocrystal films. Chapter 6, “Fourth generation ligand exchange strategy: Short thiols in organic liquids and smooth-morphology ultrasensitive solution-processed photoconductors” describes the culmination of the previous synthetic and ligand exchange works: an exchange that preserves colloidal stability and quantum confinement of lead sulfide quantum dots, employing ultrashort ligands in organic liquids for direct solution processable optoelectronics. We characterize the nano to micro morphologies of the novel all organic short ligand colloidal exchange technique. The optoelectronic characterization of the photodetector devices is presented and a comparison to existing ligand exchange strategies is contrasted. The thesis concludes with a brief future perspective of colloidal lead sulfide quantum dot photoconductor technology.
CHAPTER 2

Literature review

2.1 Introduction

This chapter reviews the prior literature relevant to colloidal quantum dot photodetectors. First, I present a review of colloidal quantum dots: the physical properties of quantum confined materials, the carrier transport properties of coupled quantum confined materials, the fundamental traits of colloidal dispersions, and the common approaches to colloidal quantum dot syntheses. Next, I introduce options for the implementation of photodetectors and outline the motivation for our pursuit of photoconductor devices. I then detail several figures of merit of good video compatible photoconductors: their optoelectronic gain, their temporal response, and their film morphology. Finally, I give a historical perspective on the development of solution-processed photodetectors.
2.2 Colloidal semiconductor quantum dots
2.2.1 Properties of semiconductor quantum dots

Any semiconductor can be a quantum dot when its generated electron-hole (e-h) pairs are spatially confined, by potential barriers in all three dimensions, to distances smaller than the semiconductor’s Bohr exciton radius given by,

\[ r_0 = \frac{\varepsilon \hbar^2}{m q^2}, \]  

(1)

where \( m \) is the effective mass of (e-h) particles, and \( \varepsilon \) is the permittivity of the material.

Quantum dots possess a set of quantized energy states that are larger than the bandgap energy of its parent bulk semiconductor. These states are described in 1D using the de Broglie wavelength, \( \lambda = \frac{\hbar}{p} \), where \( p \) is the momentum of a (e-h); confined by the size of the dot, \( d = \frac{n \lambda}{2} \), which expressed in energy is given by,

\[ E_n = E_g + \frac{n^2 \hbar^2}{8 m_e d^2} + \frac{n^2 \hbar^2}{8 m_h d^2}, \]  

(2)

where \( m_e \) and \( m_h \) are reduced (e-h) masses, \( n \) is an integer of the nth quantized energy level, and \( E_g \) is the bulk semiconductor bandgap energy.

One of the most striking effects of quantum confinement, shown by equation 2, is the emergence of quantized blue-shifted energy states that follow the parabolic band structure of its parent bulk semiconductor. Those quantized states collapse into a continuum of states as the dot size, \( d \), grows larger – illustrating that the transition of a quantum dot into a bulk semiconductor is a size dependent phenomena.

At very cold temperatures, the electrons and holes of bulk semiconductors may interact via their Coulomb potential to form bound
pairs with zero net charge denoted as excitons. Excitons are characterized by the exciton Bohr radius where the exciton mass is given by 

\[ m^{-1} = m_e^{-1} + m_h^{-1}, \]

and their binding energy, the Rydberg energy, is given by,

\[ \text{Rydberg energy} = \frac{q^2}{2\varepsilon^2 r_0}. \]  

\[ (3) \]

Excitons have spectral features that are quantized red-shifts, smaller than the bandgap energy as a result of the energy used in their Coulombic binding. With added energy their spectra converges to the bandgap energy liberating free e-h pairs that charge transport through a semiconductor’s crystal lattice.

Quantum dots, on the other hand, have physically confined e-h wave functions. They experience, even at room temperature, a Coulomb attraction often greater than the Rydberg energy of the bulk semiconductor exciton, which reduces their higher-than-the-bandgap blue-shifted energy states. Equation 2 modified to include the effect of Coulombic interaction energy, for the case of strong quantum confinement, is given by [4],

\[ E_n = E_g + \frac{n^2h^2}{8m_e d^2} + \frac{n^2h^2}{8m_h d^2} - \frac{1.8q^2}{\varepsilon d}. \]  

\[ (4) \]

Unlike excitons in bulk semiconductors, where Coulomb interaction prevents the travel of an electron or hole throughout the crystal, the important Coulombic binding of e-h pairs in quantum dots is itself the result of spatial confinement.

Table 1 contrasts the exciton Bohr radius, the carrier effective masses, the exciton binding energy, and the bandgap energy for a variety of semiconductors. It summarizes the influence of Coulomb at-

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traction on optical spectra, the maximum size threshold for quantum confinement, and the optical range that may be accessible via quantum confined size effect.

2.2.2 Carrier transport in quantum dot films

Carrier transport in quantum dot films occurs as a result of quantum mechanical tunneling.

Carrier transport in a perfectly ordered film of quantum dots – a lattice of potential wells – is analogous to the Bloch transport tunneling in bulk semiconductors because it follows the quantum mechanical solution of the Schrödinger equation known as the Kronig Penney model. Challenges, however, ascribed to carrier trapping, irregularities in interparticle spacing, quantum dot size distribution, and sintering have hindered the observation of mini-bands expected from this kind of long range wave function transport[21]. In practice, amorphous Mott carrier hopping[22] appears to better describe the long range carrier transport in films of quantum dots[23]. Hopping transport proceeds via delocalized states as a critical function of temperature called the mobility edge. It provides electrical conduction through incoherent tunneling

<table>
<thead>
<tr>
<th>Material</th>
<th>Exciton Bohr radius (nm)</th>
<th>$m_e/m_0$</th>
<th>$m_h/m_0$</th>
<th>Exciton binding energy (meV)</th>
<th>Bandgap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si$^a$</td>
<td>4.3</td>
<td>0.081</td>
<td>0.3</td>
<td>15</td>
<td>1.17</td>
</tr>
<tr>
<td>GaAs$^a$</td>
<td>12.5</td>
<td>0.06</td>
<td>0.47</td>
<td>5</td>
<td>1.52</td>
</tr>
<tr>
<td>CdSe$^a$</td>
<td>4.9</td>
<td>0.13</td>
<td>0.45</td>
<td>16</td>
<td>1.84</td>
</tr>
<tr>
<td>CdS$^a$</td>
<td>2.8</td>
<td>0.7</td>
<td>0.7</td>
<td>29</td>
<td>2.58</td>
</tr>
<tr>
<td>CuCl$^a$</td>
<td>0.7</td>
<td>0.4</td>
<td>2.4</td>
<td>190</td>
<td>3.4</td>
</tr>
<tr>
<td>PbS$^b$</td>
<td>8</td>
<td>0.09</td>
<td>0.09</td>
<td>7</td>
<td>0.43</td>
</tr>
</tbody>
</table>

Table 1. Comparison of exciton Bohr radius, electron effective mass, hole effective mass, exciton binding energy, and bandgap energy of select semiconductor materials. a) Source: [1], b) Calculated [2]
transitions, “hops”, between randomly distributed sites. In sum, the long range models used to describe carrier transport in quantum dot films have the unit of tunneling between two quantum mechanically coupled potential wells as a basis for their transport properties.

Briefly, I consider the wave function coupling between two lead sulfide quantum dots, shown in Figure 4, modeled by two 1D potential wells of equal length, $a = 2.5$ nm, separated by a potential barrier of length, $b$, and of energetic height, $V_0 = 6$ eV. The result suggests the interparticle spacing needed to achieve the onset of carrier transport in films of lead sulfide dots.

Figure 4. Two quantum mechanical wells of width $a$ separated by a potential barrier of width $b$ and height $V_0$. Solid line segments indicate symmetric wave function solutions. Dotted line segments indicate antisymmetric wave function solutions.

Solving the specific anti-symmetric wave function of Schrödinger’s equation yields a transcendental equation with eigen energy solutions to this system given by,

$$\alpha k \left( \coth \left( \frac{kb}{2} \right) + 1 \right) + \tan (\alpha a) \left( k^2 \coth \left( \frac{kh}{2} \right) - \alpha^2 \right) = 0,$$

and solutions to the symmetric wave function of the transcendental
equation given by,

$$\alpha k \left( \tanh \left( \frac{kb}{2} \right) + 1 \right) + \tan (\alpha a) \left( k^2 \tanh \left( \frac{kb}{2} \right) - \alpha^2 \right) = 0, \quad (6)$$

where $k^2 = 2m(V_0 - E)/\hbar^2$, $\alpha^2 = 2mE/\hbar^2$, $m = 0.09$ $m_0$ is the effective mass of carriers in lead sulfide quantum dots, and $E$ is the energy of the carriers in the coupled system.

In Figure 5(a) I plot the graphic representation of the transcendental equations 5 and 6 yielding the energy solutions to this model and note those solutions are compatible with the quantum confined energy of 2.5 nm sized lead sulfide quantum dots. Also in Figure 5(b), I plot the splitting of the solved transport states as a function of barrier width. The result for this model of lead sulfide quantum dots indicates an approximate onset of inter-dot coupling (coupling energy more than a few percent of the average eigen energy) for sub-nanometer barrier widths.

(a) Graphical representation of transcendental equations
(b) Energy coupling as a function of potential barrier width

Figure 5. a) PbS quantum dot coupling solution model of two wells of width $a = 2.5$ nm separated by a potential barrier of width $b = 0.5$ nm and height $V_0 = 6$ eV, $(m_0 = 0.09)$ b) Symmetric and antisymmetric energy splitting between the two quantum dots where the potential barrier width is varied from 0.1 nm to 1.5 nm.
2.2.3 Properties of colloidal dispersions

Like colloidal quantum dots, liquid crystals, milk, paint, and fog are examples of colloids: dispersions of particles sized between 1 nm and 1 \( \mu \)m in diameter that form a homogeneous phase with another substance. A colloidal dispersion of particles occurs when their mixing in a substance is not spontaneous and often requires stabilizing agents, when the system is thermodynamically unstable, and when the mixture is strongly dependent on the route of its preparation. Steric or charge interactions are necessary to mitigate the kinetic unmixing of a colloid and protect its particles from aggregation, as shown in Figure 6. In contrast, a solution occurs when a solvent dissolves its solutes spontaneously, when the product is thermodynamically stable, and when the product is independent of the way the solution is prepared.

![Figure 6. Left) Schema of colloidal steric repulsion mechanism, Right) Schema of colloidal charge repulsion mechanism](image)

Colloidal stability is the result of interparticle attractive London-Van der Waals forces being overwhelmed by repulsive steric or electrostatic forces in a way that preserves a homogeneous mixture. First, London-Van der Waals forces, varying over many orders of magnitude, attract like particles exponentially as a function of their interparticle distance, their physical size, their geometry, their density, and their po-
larizability. Second, electrostatic forces also repel or attract particles within the extent of their Debye-Hückel length given by,

$$L_{DH} = \sqrt{\frac{\varepsilon kT}{q^2 I}},$$

(7)

where I, is the ionic strength of the interacting mobile ions. Ionic strength is analogous to the net doping concentration in the interpretation of the Debye-Hückel length screening that is familiar in semiconductor physics. Thus, similar to the net doping in semiconductor physics, the Debye-Hückel length is greatly reduced as the concentration of mobile ions increases. Electrostatic repulsion forces, however, typically increase with colloidal particle size due to an expected increase in colloidal surface charge which implies that larger colloids are potentially more electrostatically stable than smaller ones. Finally, steric factors also affect colloidal stability in two ways: osmotic repulsion or compression forces. Steric repulsion prevents aggregation only by: a) sufficient coverage on colloidal particles, b) by firm anchoring to the colloid, c) by a good electrostatic dispersion of the untethered moiety, and by d) self repulsion.

When inter colloidal spacings are made short, excessive attractive forces will often irreversibly cause a dispersion to aggregate. At significantly larger inter colloidal spacings a secondary, often reversible, region of potential aggregation exists where attractive forces may exceed the magnitude of repulsive electrostatic ones. Therefore, between these inter colloidal spacing extremes is a region of greatest colloidal stability. This region is due to repulsive colloidal forces exceeding attractive ones, providing their magnitude is significantly greater than the force of ambient thermal agitation. Put another way, a perfectly neutral
colloid will invariably seek to aggregate through thermal kinetics and London-Van der Waals attractive forces. Colloids in this work will be characterized through the interplay of these forces.

2.2.4 Colloidal quantum dot synthetic approaches

Semiconductor quantum dots are grown using a number of techniques that include molecular-beam-epitaxy\cite{24}, metalorganic-chemical-vapor-deposition\cite{24}, syntheses in glasses\cite{1}, syntheses in ionic crystals\cite{1}, microwave plasma syntheses\cite{1}, syntheses in polymer matrix\cite{25}, and a variety of colloidal syntheses. Two advantages of colloidal syntheses are that they permit quantum dots to be ‘freestanding’ dispersions that enable solution processability and they permit ligand exchanges that allow coupling or isolation of their quantum confined energy states.

A monodisperse colloidal synthesis, as illustrated in Figure 7, is typically the result of a controlled condensation of super saturated solutes occurring in four stages that are generalized by LaMer theory\cite{26}: rapid precursor injection, burst nucleation, growth, and occasionally self size focusing (a second slower growth process). In LaMer theory, nucleation is due to the rapid reaction of injected precursors that produce a super saturated burst of monomers that seed initial particles. As precursor reactants are consumed the production of new monomers yields itself, instead, to a growth phase of existing seedlets. It is critical to monodisperse colloids that unreacted precursor concentrations fall below the existing nucleated concentration before a growth process ensues. Otherwise, the competition of growth and nucleation results in aggregates, or a non-monodisperse colloid. Finally, when all reactive precursors are
consumed and monomers incorporated into larger particles, the greater surface energy of small particles may lead to a final diffusion of mass from smaller colloids to larger ones – a process called Ostwald ripening.

The application of LaMer theory manifests itself in a wide variety of colloidal synthetic routes including colloidal syntheses by organometallic pyrolysis[24], colloidal syntheses in reverse micelles[27], and aqueous colloidal syntheses[25]. These synthetic techniques differ in the resulting particle sizes, inherent crystalline structure, and size dispersion of the produced colloids by a number of factors including nucleation and growth temperatures, nucleation and growth durations, precursor concentrations, stabilizing ligands, and coordinating solvents.

![Diagram of LaMer colloidal synthesis theory](image)

Figure 7. Schema of LaMer colloidal synthesis theory.

2.3 Photodetectors

Photodetectors convert radiation into an electrical format. These devices exist in two broad categories: those with gain and those without.
Photoconductors, avalanche photodiodes, phototransistors, and photomultiplier tubes are photodetector devices that may have gain. Potentially, these devices collect multiple electrons per photon incident on them. They do so, however, at the expense of their response speed. Of these devices the most robust are photoconductors. Photoconductor devices enable the detection of extremely low light levels through a basic semiconductor property: its photoconductivity.

Photodetectors without gain are either P-I-N photodiodes, Schottky barrier photodiodes, or phototubes. These devices provide a maximum of one electron’s worth of current per incident photon, but with significantly higher response speed than photodetectors with gain. For the small pixels and very low-light conditions of modern devices, this necessitates the use of extremely low-noise electronic amplifying circuits.

Ideally, a modern video capable photodetector would provide built-in gain and video frame rate response speeds, lessening demands on readout circuitry.

2.4 Photoconductive photodetectors

The definition of photoconductivity is a change in electrical conductivity by the absorption of light, or other form of radiation. Photoconductors are two-port devices that channel current through crystalline or amorphous, inorganic or organic, powders of, single crystals of, sintered networks of, evaporated, sputtered, or chemically deposited semiconductors. Their properties depend on the semiconductor employed, its sensitization, and on the nature of its electrical contacts. Few materials – only ones with special imperfections – demonstrate usefully large changes in conductivity with illumination[28]. These materials include
silicon, germanium, cadmium chalcogenides, and lead chalcogenides.

The conductivity of a material is related to the product of its carrier mobility and the density of its free carriers. Carrier mobility is the constant of proportionality relating carrier velocity to electric field: it is a transport property. The change in conductivity in a photoconductor arises from changes in carrier mobility, carrier density, or both, and can be described by [28],

\[
\Delta \sigma = \Delta n q \mu_n + n q \Delta \mu_n + \Delta p q \mu_p + p q \Delta \mu_p, \tag{8}
\]

where \( n \) is the density and \( \mu_n \) is the mobility of conducting electrons, and \( p \) is the density and \( \mu_p \) is the mobility of conducting holes.

### 2.4.1 Carrier lifetimes and temporal response

Free-carrier lifetime is the characteristic length of time a charge carrier is able to contribute to conductivity and plays a critical role in the effect of photoconductivity. Free-carrier lifetime is terminated by a free carrier’s recombination, or by a free carrier’s lack of replenishment at the opposite contact. It is interrupted by trapping centers. It is undisturbed by extraction at one contact and simultaneous injection at the other. Thus, changes in photoconductor carrier densities are related to the intensity of illumination, \( f \), and to the free-carrier lifetimes, \( \tau_n \) and \( \tau_p \) given by:

\[
\Delta n = \Delta f \tau_n + f \Delta \tau_n, \tag{9}
\]
\[
\Delta p = \Delta f \tau_p + f \Delta \tau_p. \tag{10}
\]

The conductivity of a photoconductor as a function of its free-carrier lifetime, \( \tau \), is related to the density of its recombination centers, \( N_r \), each
with a capture cross section, $S$, given by:

$$\tau = \frac{1}{vSN_r}, \quad (11)$$

where, $v = (kT/m)^{1/2}$, is the carrier thermal velocity.

Trapping and releasing of carriers from trap centers may significantly impact the free-carrier lifetime[29] – potentially slowing the observed photoconductive response significantly beyond its intrinsic free-carrier lifetime. In the same fashion as equation 11, the trapping rate, $R_{tc}$, of the free-carrier density, $n$, for a density of traps, $N_{tc}$, is given as[30],

$$R_{tc} = nvSN_{tc}. \quad (12)$$

The rate of thermal detrapping of the density of trapped carriers, $n_{tc}$, their escape frequency, $\vartheta$, and detrapping activation energy, $\Delta E$, is given by[30],

$$R_{td} = n_{tc}\vartheta e^{-\Delta E/kT}. \quad (13)$$

One of the consequences of trapping is the increase in the rise time observed in photoconductor current. By removing free-carriers from conduction, trapping causes a longer delay for total carrier re-equilibrium to occur. Similarly, the delayed release of trapped carriers lengthens the decay time observed in photoconductor current, as they continue to contribute to current flow after illumination is terminated.

Under low illumination and when the density of trapped carriers greatly exceeds the density of free carriers, the photoconductive decay time is equal to the detrapping time $1/R_{td}$, and not the usual free-carrier lifetime $\tau$. 

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2.4.2 Carrier mobilities

Illumination can influence mobility, and hence photoconductivity, in a number of ways.

Firstly, photoexcitation may reduce the height of potential barriers that previously hindered the mobility of carriers through a photoconductive photodetector[31, 32]. This mode of transport, however, can be described in terms of changes to lifetime and illumination intensity.

Secondly, photoexcitation may modify the charge of scattering centers that are limiting the mobility of its carriers’ transport[33, 34]. An example of this process can be seen in the case where photoexcitation fills charged ionized scattering centers, thereby increasing carrier mobility with illumination. This change can be described by[28],

\[ \Delta(1/\mu) = 10^4(mT)^{1/2}SN, \]  

where N is the density of ionized scattering centers that are neutralized by photoexcitation. The determining factor in this mode of enhanced conductivity is that there is a larger difference in mobilities than in the free-carrier lifetimes over the temperature range of interest.

Finally, photoexcitation of low mobility carriers in one quantum state may be excited to another quantum state with higher carrier mobility[35]. The determining factor in this mode of enhanced conductivity is a larger difference of mobilities than in free-carrier lifetimes between the lower and higher conductivity states.

2.4.3 Responsivity and gain

The sensitivity of a photoconductor is defined by its capacity to convert light into electrical form. As shown in Figure 8, that electrical
form is described, in part, by the conductivity transit time, $t$, of a free carrier with carrier mobility, $\mu$, to move in a field defined by the application of a voltage, $V$, over a distance, $L$, given by,

$$t = \frac{L^2}{\mu V}. \tag{15}$$

One measure of the sensitivity of a photoconductor is its responsivity, which is the ratio of the delivered photocurrent to the incident optical power. Responsivity, $R = I_p/P \, [\text{A/W}]$, is related to the delivered photocurrent which is given by,

$$I_p = \sigma VL \tag{16}$$

$$= q(\mu_n \Delta n + \mu_p \Delta p)VL \tag{17}$$

$$= q(\mu_n f\tau_n + \mu_p f\tau_p)VL \tag{18}$$

$$= q(\frac{\tau_n}{\tau_p} + \frac{\tau_p}{\tau_p}) \frac{P\lambda}{hc}; \tag{19}$$

and to the incident optical power which is given by, $P = \frac{WLDfhc}{\lambda}$. 

Figure 8. Schematic diagram of a typical photoconductor: a semiconductor with ohmic contacts at each end.
Equations 8 and 17 associate changes in conductivity with changes in free carrier density. This is not the only model possible: as noted before, illumination could potentially change mobility as well. The free-carrier-density-change picture does have the advantage of unifying the field of photoconductive photodetectors with photodiodes. The primary photocurrent, \( I_{ph} \equiv \frac{n_{ph} \lambda}{hc} \), corresponds to the current available in a photodiode having unity external quantum efficiency. The gain of a photoconductive photodetector can then be pictured as deriving from a secondary photocurrent proportional to the primary.

2.5 Historical context of solution-processed photodetectors

The first published solution-processed photodetector, based on conjugate polymer, was reported by Heeger et al. in 1994[36]. These visible wavelength devices, based on a polymer, demonstrated responsivity of 0.3 A/W at an external bias of 10 V. In 1998, a P3OT-PCBM composite polymer photodetector was reported to have much improved dark current (10 nA/cm\(^2\)) and a similar responsivity of 0.2 A/W[37]. An interesting architecture known as the phototransistor was reported in 2004[38]; these devices were, however, limited to a low responsivity of 0.0007 A/W. Similarly low responsivities were reported using a dye-sensitized solar cell analogue that year[39].

The first colloidal quantum dot photodetectors were reported in 1996[40]. These comprised a MEH-PPV polymer blended with cadmium chalcogenide quantum dots. These devices provided external quantum efficiencies of 12%. The results indicate the importance of exchanging long TOPO capping ligands for shorter ligands compatible with electronic transport. Photoconductive colloidal quantum dot devices were
first reported in 2000[41], though without an account of responsivity. In 2004, the change in conductivity of similar devices upon solid-state ligand exchange was reported[42]. These findings confirmed the importance of interparticle spacing in achieving optoelectronic coupling among the quantum dots. However, the maximum responsivity of these devices remained below 0.002 A/W.

The first infrared colloidal quantum dot photodetectors were reported in 2005[10]. These devices, based on PbS, achieved responsivities of 0.003 A/W at 975 nm wavelength. In 2006, the field was considerably advanced through the realization of high-gain – responsivities of > 1000 A/W – devices[43].

Visible wavelength photodetectors are central to mainstream imaging and video application. In 2007, the first study of visible-wavelength photoconductive photodetectors based on PbS colloidal quantum dots was reported[3]. These devices provided 100 A/W responsivities. The butylamine ligand exchange strategy employed to realize this photconductor, however, resulted in devices having slow temporal responses that, in video applications, would produce unacceptable lag. In addition, as discussed in this work, the solid-state film treatments led to unacceptable morphologies. The present work seeks to address, through a fundamentally different approach, these two key challenges: temporal response and physical uniformity.

2.6 Conclusions

This chapter described subsets of the following topics: the theoretical properties of quantum dots, carrier transport properties among quantum dots, the theoretical forces that underpin colloidal stabiliza-
tion, and the techniques used to fabricate quantum dots in practice. In addition, several photodetector implementations were introduced, the potential benefits of photoconductive photodetectors’ simple infrastructure and sensitivity were outlined, and the historical context of solution processed photodetectors was presented.
CHAPTER 3

First-generation ligand exchange: Short amines in organic liquids

3.1 Introduction

This chapter presents a first strategy: one that aims to produce highly conductive colloidal quantum dot films by ligand exchanges in solution and in solid state.

As previously discussed, the interest in PbS colloidal quantum dot devices stems from their solution processing, as well as the potential for gain in photoconductive devices. In imaging applications, their tunability offers convenient access to different spectral regimes without the need for light losses associated with the use of filters. Photodetector and electroluminescent devices could leverage this feature efficiently in planar applications that employ a stacked multi-spectral pixel, a voxel, based on layers of the same material composition.

At the time of this work, new evidence demonstrated that PbS colloidal quantum dot films could achieve high gains and appreciable dark resistivities[14]. These devices relied on a ligand exchange – the removal of long oleate ligands and their replacement with shorter ones. We believed that a ligand exchange would also be required in our work.
3.2 Photodetector requirements and their implications for quantum dot films

In this section, we define several performance requirements that leverage the potential benefits from ligand exchanged colloidal quantum dot films as useful photoconductors; in addition, we discuss how these requirements had yet to be achieved in the prior literature.

We focus on two key areas of unfulfilled need: film morphology, and colloidal quantum dot spectral sharpness. It is important to produce films of consistent thickness and composition\[44]\ because these parameters influence both the dark current and the photoresponse of a photodetector\[45]. The field of optoelectronic imaging devices defines two key terms – dark signal nonuniformity and photoresponse nonuniformity – that specify the consistency of dark signal and photoresponse across an array. Thickness and photoresponse nonuniformity deviations must generally lie within 1% of the average to avoid the appearance of excessive spatial noise in images\[12].

Optoelectronic transport within a quantum dot film that preserves – through controlled and consistent ligand exchange – its sharp spectral features, allows for simultaneous spectral control, trap state control, and desired mobility. In contrast, uncontrolled aggregation of quantum dots into a locally bulk-like material may improve carrier mobility within regions of the film; however, it eliminates spectral control from the quantum size effect in the constituent material. Extensive sintering of quantum dots may also improve carrier mobility; however, it may introduce a number of different-energy-depth trap states that would produce multi-time-constant photoconductive responses. Spectral broadening in general eliminates the opportunity for coherent transport effects across
multiple dots – a lost opportunity for mobility and, in photoconductors, gain. In sum, achieving quantum dot films combined benefits of spectral control, consistent temporal response, and adequate transport requires that distinctive, size-effect-tuned spectral features be preserved at all stages, including solution-phase ligand exchange.

To benefit from spectral control, controlled trap state engineering, and improved coupling simultaneously, requires the degree of spectral broadening among homogeneously ligand exchanged quantum dots to satisfy the following conditions. First, to fulfill their promised value of spectral tunability to produce an image sensor that uses quantum dots to distinguish the green (∼ 530 nm) from the red (∼ 630 nm), the spectral breadth of the onset of absorption in the smaller of the two quantum dot populations must be less than ∼100 nm. Second, to maintain video frame rate compatible single time constant response requires a spectral broadening to be less than 0.1 eV[46], corresponding to less than 30 nm for a center wavelength between green and red.

In the present chapter, we investigate the use of a promising, short ligand – butylamine – in the quest to achieve the needed combination of transport, morphology, and spectral selectivity. We present a description of the procedures for producing organometallic visible wavelength oleic-acid capped lead sulfide colloidal quantum dots used throughout this work. With these quantum dots we explore the effect of previously developed colloidal[13], and solid-state[47] butylamine ligand exchanges, and we find that these butylamine techniques fail to preserve the film morphology and spectral specifications we defined for quantum dot photoconductive photodetectors.
3.3 Synthesis and methodology

Our synthesis\(^1\), of oleic-acid capped visible wavelength lead sulfide quantum dots uses the following standard equipment\([4, 20]\): three necked flask – reaction vessel for the synthesis, magnetic stir bar – Teflon coated to homogenize reactants, condenser - to capture evaporated gases, compressed argon – to keep the reaction vessel under inert conditions, rubber septums – to seal the flask necks through which precursors are injected, heating mantle, temperature probe, and temperature controller – to provide uniform heat, monitor, and control the temperature of the synthetic reaction. A typical synthetic procedure is as follows:

1. PbO (0.9 g, 4.0 mmol), oleic-acid (2.67 g, 9.50 mmol), and octadecene (4.73 g, 18.8 mmol) were mixed at 80 °C under vacuum for 12 hours – to remove water created when these reagents are mixed (solution A).

2. Hexamethyldisilathiane (210 mL) was mixed with octadecene (10 mL) in a nitrogen glove box, and then degassed by heating at 80 °C under vacuum for 48 hours (solution B).

3. Solution A (19.5 mL) was injected into a three-necked flask under argon and the temperature of the solution was raised to 120 °C under heavy stirring.

4. Solution B was then injected into this flask, after which the solution was allowed to cool.

\(^1\)Dr. L. Levina executed the overwhelming majority of organometallic syntheses used in this work – with the author’s grateful acknowledgment.
5. When the temperature reached 35 °C the reaction was quenched with acetone (40 mL).

6. The mixture was then washed repeatedly by suspensions in toluene and precipitations in acetone.

3.4 Characterization

We used atomic force microscopy (AFM) to study the films’ surface morphology and thickness. We investigated i) films made from original oleic-acid capped, unexchanged nanocrystals, ii) films made by spin-casting original nanocrystals, subsequently treated with butylamine, and iii) films made by spin-casting nanocrystals previously exchanged to butylamine ligands in the solution phase.

We present in Figure 9 the profilometry of these exchange procedures on film morphology. The average roughness (Ra) of a film, which relates the average deviation of a profile from its mean, and percentage thickness non-uniformity (%TNU) are computed by

\[
R_a = \frac{1}{L} \int_0^L |y| \, dx, \quad (20)
\]

\[
%TNU = \frac{R_a}{\bar{d}} \times 100, \quad (21)
\]

where L is the length of a profile y(x), and \(\bar{d}\) is the average height of a profile. A scribe was used to remove a portion of the films from their substrates, allowing for direct measures of their average thickness. Upon drying, films made from original nanocrystals exhibit large gaps that are the result of extensive cracking, with a roughness of 25% of their thickness. When such films were subsequently treated with butylamine, they continued to show cracks but their roughness was somewhat reduced to 9% of their thickness. Films made from nanoparticles
exchanged to butylamine in the colloidal-phase exhibited 15% roughness of their thickness.

![Graph showing the percent normalized thickness against distance (nm) for different films.]

Figure 9. AFM profilometry of PbS nanocrystal 700 rpm spin-cast films on clean glass surfaces.

We sought to investigate further why colloidal exchange to butylamine ligands fail to produce films with good morphologies. We compare in Figures 10(b) and 10(c) transmission electron microscopy (TEM) images of as-synthesized, and butylamine ligand exchange PbS nanoparticles that absorb visible light. The butylamine colloidal ligand exchange nanoparticles have aggregated considerably, some of them forming worm-like structures, with clusters of nanoparticles as large as 20-40 nm, and fail to pass through 200 nm pore-sized filters.

We anticipated that the effects of aggregation in butylamine solution-exchanged particles would be noticeable in their absorption
spectrum. A pronounced loss of quantum confinement and a significant red tail in absorption can be seen in Figure 10(a). The spectral broadening of the butylamine exchanges are respectively 116 nm and 166 nm larger, in FWHM, than in the FWHM of their original pre-exchanged oleicacid capped quantum dots: 126 nm and 118 nm respectively.

Absorption spectra were collected using a Cary model 500 spectrophotometer. Electron microscopy images were acquired using a Hitachi HD-2000 operating at 200 kV.

3.5 Conclusions

In summary: applying the previously developed solid-state butylamine ligand exchange to visible wavelength lead sulfide organometallic quantum dots results in rough film morphologies incompatible with high-uniformity image sensors. The frequent cracking of these films is attributed to the significant loss of volume during the solid-state exchange process. When a solution-phase butylamine ligand exchange is applied instead, it results in a loss of quantum confinement, negating one of the compelling features of quantum dot photodetectors.

AFM, TEM, and absorption spectra of butylamine-exchanged quantum dots suggest several mechanisms underlying the loss of morphology and quantum confinement in films. Solvent trapping, including in regions to which the removed ligands have segregated, may aggravate poor morphology during drying. Local aggregation of quantum dots may lead to the formation of large, local nanoparticle clusters. While the devices do show gain, their spectral broadening exceeds 100 nm, and their thickness nonuniformity considerably exceeds the 1% requirement.
Figure 10. a) Absorption spectra of drop-cast PbS nanocrystal films. Samples A and B are from different syntheses. The figure enables the comparison between original (oleic-acid capped) unexchanged, and butylamine colloidal exchange PbS quantum dots. b-c) Dark field electron microscopy images at 200 kV x 250 k magnification on formvar-coated 200 mesh copper grids comparing the deposition of typical b) original (unexchanged) nanocrystals, and c) butylamine colloidal exchange nanocrystals.
3.6 Direction

To provide utility in visible wavelength imaging, quantum dot photoconductive photodetectors must possess, at a minimum, the following attributes:

- spectral broadening (< 30 nm)
- gain
- smooth morphology (thickness non uniformity < 1%)

We believe that the solution exchange of quantum dots failed to preserve spectral sharpness because nanoparticles aggregated in the non-polar organic solvent. Butylamine, we propose, offered too little steric hindrance, and provided too little surface charge toward ensuring that quantum dots stayed distinct in solution.

We now turn our attention to a strategy that offers the charge-based stability of working in a polar liquid with charge-bearing ligands. In the chapter that follows, we present a nucleotide-based lead sulfide synthetic strategy in water. The results of this strategy suggest that steric stability can be replaced with a charge cage to yield a stable colloid.
CHAPTER 4

Second-generation ligand exchange strategy: Novel nucleic acid ligands in water

4.1 Introduction

This chapter explores the synthesis of colloidal PbS quantum dots that are dispersed by their ligands’ electrostatic behaviors in a polar solvent. We consider this study a necessary clarifying step toward a rationale for electrostatic based dispersions that enable the use of short ligands toward optoelectronic transport in directly cast films of quantum dots.

Our studies employ nucleotides, the building blocks of DNA and RNA. We review, briefly, related work on the binding of nucleotides to metals and metal-chalcogenide nanoparticles.

Biological molecules have been used in the realization of monodispersed magnetic and semiconductor nanoparticles[48, 49, 50, 16]. The study of nucleotide templated synthesis, specifically, entails understanding the functional interactions between the environment, the nucleotides, and their precursors. Nucleotides have been extensively stud-
ied toward their binding modes to a variety of metals[51, 52, 53]. At physiological pH, the interaction between metal cations and nucleotide phosphate backbones have also been extensively studied[52, 54, 55, 56, 57]. Despite these advances, prior to the work presented in this chapter, a detailed physical picture of how nucleotides can control the synthesis of colloidal quantum dots was not reported.

In this chapter, we systematically investigate how nucleotide functionalities influence nanoparticle growth. We derive a set of rules for using nucleotides as ligands and as programmable templates for nanoparticle synthesis. We then test the hypothesis that aqueous syntheses may yield a electrostatically dispersed and stable colloid of nucleotide amine tethered ligands on quantum dots. This pH neutral synthetic approach has a key advantage toward optoelectronic materials in that it enables a colloidal dispersion supported by, the nucleotides’, clear electrostatic repulsion rather than by, the long aliphatic ligands’, steric repulsion – which is essential to contemporary organometallic synthesis.

We proceed to the following model of nanoparticle growth: a ligand binds the precursor’s metal cation during the initial crystal growth and then serves as part of a stabilizing cap for a nanoparticle when most of the reagents are consumed. Ligands also aid in terminating crystal growth, passivating defect states that would otherwise exist on the nanocrystal surface, and ensure that the nanoparticles remain stably dispersed in aqueous solution. The chemical functionalities present on a given ligand control the proficiency of the ligand in each of these roles.

We identify from the general functionalities of these nucleotides that

the specific role of exocyclic amines preferentially coordinate to a lattice of lead sulfide. In addition, we identify that these colloidal dispersions were a function of the nucleotide backbone charge. These conclusions support our hypothesis that a sufficient electrostatic repulsion among colloidal particles may function in place of DNA, polymer, or oleic-acid ligands’ steric repulsion.

4.2 Synthesis and methodology

In the present work our PbS quantum dot synthesis begins by seeding a chosen ligand, a nucleotide, with Pb2+. A S2- source is subsequently added to the solution. Under suitable conditions (i.e. an excess of ligand), the ligand binds to Pb2+ and prevents the formation of a bulk semiconductor. Here, the nucleotide:Pb2+:S2- molar ratio was set to 3:1:1, corresponding to the stoichiometry used in our previously reported CT DNA PbS syntheses[16] and conditions where Pb2+ would be complexed with the nucleotide ligand[2]. Throughout this work, while individual functionalities on the bases were varied by choosing different nucleotides, the remaining synthetic parameters were fixed.

All syntheses were performed at 1:1 lead-to-sulfur precursor molar ratio in 2 mL Eppendorf tubes at room temperature with vortex agitation. In a typical synthesis, 100 µL of 10 mM lead precursor, Pb(NO₃)₂, was added to 250 µL of 13.4 mM nucleotide/nucleoside and mixed, followed by 5 min incubation. Then 100 µL of 10 mM sodium sulfide was quickly injected into the reaction tube. The solution immediately turned from transparent to red-brown, indicating the formation of PbS nanocrystals. The supernatant was removed from any precipitate after centrifuging at 4000 rpm for 5 min. These syntheses were reproducible
and did not require post synthesis manipulation or processing.

4.3 Characterization

We began by testing four nucleotide triphosphates, ATP, CTP, GTP, and UTP. We sought to determine whether these nucleotides, which display the base, sugar, and phosphate functionalities found in polynucleotides, could serve as useful ligands.

Syntheses using GTP produced PbS nanocrystals with IR luminescence (Figure 11(a)) corresponding to photoluminescence quantum efficiencies in the range 1-2%. In the presence of ATP, CTP, and UTP, colloidal nanocrystals were not the major product, and instead the syntheses produced mainly precipitate or nonemissive solutions. The results indicate that under the synthetic conditions chosen here only GTP served as a competent ligand for nucleation, growth, and capping of colloidal PbS nanocrystals. Transmission electron microscopy (TEM) analysis of the products of the GTP reaction, presented in Figure 11(b), reveals ~4 nm spherical nanoparticles. The emission from GTP-PbS is slightly red shifted relative to materials synthesized in the presence of CT DNA under analogous conditions[16].

Syntheses performed with 7-methyl GTP produced nanocrystals with luminescence similar to that seen with GTP (Figure 12(a)). From the spectra, it appears that the N7 influences nanoparticle size; however, it does not serve as a binary determinant of whether a successful, stable luminescent product is generated. In contrast to the results seen with 7-methyl GTP, syntheses employing ITP did not produce nanocrystals or luminescent material. The exocyclic N2 of GTP appears crucial to nucleotide-mediated PbS nanocrystal synthesis. We used FTIR spec-
Figure 11. Effect of varying the nucleotide on the results of PbS nanocrystal synthesis. (a) Photoluminescence spectra under 633 nm, 3.3 mW excitation from a HeNe laser. The use of GTP ligand results in strongly luminescent, stably dispersed nanocrystals. In the presence of ATP, CTP, and UTP syntheses produced mainly precipitate. CT DNA produces a strong luminescence spectrum that is narrower than and blue-shifted relative to GTP-NCs. (b) TEM of PbS quantum dots synthesized in the presence of GTP.
troscopy to directly determine the extent of interaction between the N2 and Pb2+ and PbS. We found that the addition of Pb2+ cations minimally perturbed N2-correlated features, but that the synthesis of nanoparticles through the subsequent addition of S2- yielded a change in N2-correlated features. These findings indicate that the N2 does bind to the surface of PbS.

![Image](image_url)

Figure 12. a) Effect of specific chemical functionalities present on GTP on PbS quantum dot synthesis. Luminescence spectra obtained when GTP, G, ITP, and 7-CH3-GTP were used for PbS synthesis. b) Illustration of G, ITP, and 7-CH3-GTP structures.

To probe the role of phosphates in PbS synthesis further, FTIR was used to monitor this functional group through the course of the synthesis. These experiments provided evidence that the phosphate group binds Pb2+ initially but reverts to the unbound state after the addition of S2- (see Figures 13, 14, and Table 2). Therefore, it appears that phosphates participate in nanocrystal growth by binding Pb2+ from the solution, thereby altering (following sulfur source injection) the
degree of super saturation and thus the conditions for nucleation and the rate at which nanoparticles grow. Given their charge, the phosphates also likely play a key role in suspending the nanoparticles in water.

Figure 13. FTIR spectra of GTP, GTP with added Pb$^{2+}$ + S$^{2-}$ (conditions under which PbS nanocrystals are formed). Transitions marked with stars are assigned in Table 2. The 1654 cm$^{-1}$ stretch, associated with the G N2, is enhanced in the presence of PbS, but not Pb$^{2+}$. The phosphate stretches at 1087 - 1242 cm$^{-1}$ appear perturbed in the presence of Pb$^{2+}$, but shift back to their original positions after PbS is formed. These results are consistent with the primary role of the phosphate acting as a feeding source for Pb$^{2+}$ cations, and the N2 as a ligand for PbS nanocrystals.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wavenumber of stretch (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTP</td>
<td>1242 1123 1087</td>
<td>$\nu_\alpha(\alpha,\beta$-PO$<em>2$) $\nu</em>\alpha(\alpha,\beta$-PO$_2$) $\nu_s(g$-PO$_2$)</td>
</tr>
<tr>
<td>GTP + Pb$^a$</td>
<td>1235 1113 1075</td>
<td></td>
</tr>
<tr>
<td>GTP + Pb + S$^a$</td>
<td>1247 1129 1085</td>
<td></td>
</tr>
<tr>
<td>Assignment</td>
<td>$\nu_\alpha(\alpha,\beta$-PO$<em>2$) $\nu</em>\alpha(\alpha,\beta$-PO$_2$) $\nu_s(g$-PO$_2$)</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Figure 13 phosphate FTIR shifts of interest. Shifts$^a$ are representative of typical data. The direction and magnitude of the shifts in the positions of individual stretches varied by less than 20%.
Figure 14. FTIR spectra of GTP, GTP with the addition of Pb and Pb + S, transition marked with a star is assigned as corresponding to the G N2. The assignments were made through a comparison of GTP, ITP, and G.

4.4 Conclusions

On the basis of these results, we propose a general mechanistic framework describing how nucleotides promote and control nanocrystal growth (Figure 15(a)). At the concentrations, stoichiometries, and temperature employed herein, it appears that G-based nucleotides, through a combination of amine and phosphate functionalities, are effective at controlling PbS growth and capping the structures with a stable ligand system. Having at least two distinct classes of Pb binding functionalities appears to be crucial to the growth of stable, luminescent nanoparticles. One class of functionalities (e.g. the phosphate backbone) appears to feed nanoparticle growth and provide electrostatic derived dispersions, while the other functionality (e.g. the N2 on G) stabilizes the products. Differences in ATP versus GTP, for example, point to the importance of the binding affinities, and possibly even the geometries and relative
placements of these functionalities. It is also noteworthy that the N7
does play a role, as nanocrystals produced with 7-methyl GTP exhibit
blue shifted luminescence. This shift may reflect a change in the size of
the nanocrystals. Alternatively, changing the binding of the N7 through
alkylation could change the binding mode of GTP and result in a shift in
the spectra, indicating cooperation exists among the different function-
alities in G. Cooperative and spatial effects like this may help explain
why GTP is unique relative to the other nucleotides.

![Diagram](image)

Figure 15. Proposed roles of phosphate and base functionalities on GTP in
nanoparticle nucleation, growth, termination, stabilization, and passivation.

No photoconductors were made from these materials due to the
prohibitive cost of reagents needed to increase the optical density of the
transparent films of GTP synthesized PbS quantum dots spin cast at 700
rpm from its < 2 mg/mL dispersions. The electrostatic means of dis-
persion achieved in this work, however, is promising toward engineering
direct optoelectronic coupling using short ligands.

4.5 Direction

We observed through this synthetic technique that electrostatic repul-
sions offer colloidal stability beyond that of steric hindrance. In ad-
dition, we observe the particle morphology of this material is a marked improvement over the butylamine ligand exchanged lead sulfide particles presented in Chapter 3. The materials produced in this chapter, however, have luminescence quantum yield of 2%, which is much lower than that of oleic-acid capped organometallically-synthesized nanocrystals. This suggests that an undesirable non-radiative pathway exists that would compete against efficient photodetection. We believe that the positive outcome of this chapter – a stable colloid exploiting the simple electrostatic repulsion of its ligands – could be combined with the use of an end functional group, a thiol, to provide stronger tethering to the nanoparticle surface and improve its quantum yield.
CHAPTER 5

Third-generation ligand exchange strategy: A new means of transferring quantum dots from organic liquids to an aqueous buffer

5.1 Introduction

In the present chapter, we seek to build on the findings of Chapter 4: beyond simple electrostatic dispersions we now exercise ligand length control, while using polar ligands to provide stability by electrostatic means in a polar solvent. This strategy enables optoelectronic coupling, when short ligands are employed, and luminescence, when long ligands are employed. In addition, we seek to address the problem of passivation, which resulted in the non-radiative pathways demonstrated in the previous chapter, by moving to a promising end functional group on the ligands: a thiol.
We\textsuperscript{1} apply the hypothesis that organometallic lead sulfide quantum dots will retain colloidal stability through electrostatic repulsion by exchanging oleic-acid ligand’s non polar free end-groups for a hydroxyl ligand’s polar free end-group. This electrostatic repulsion ligand-exchange we engineer demands a phase-exchange of original oleic-acid capped lead sulfide quantum dots from an organic liquid to an aqueous one. Simultaneously, we apply our hypothesis that the tethering capacity of thiols, due to the strong binding affinity of sulfur to lead, will better protect the particle morphology of exchanged quantum dots than previous amine ligand exchanges.

The results preserve the particle morphology of lead sulfide quantum dots both during their exchange out of organic liquid, and during their transfer into buffered water – a liquid that tends to aggregate colloidal dispersions through a lowered Debye-Hückel length. These results also permit the linear chain length between tethered and untethered moieties to vary between 3 and 19 carbon atoms, and yet preserve colloidal stability. Finally, the results further support our hypothesis that the electrostatic charge repulsion of the miscible free end-group moiety can greatly confer colloidal stability to lead sulfide quantum dots.

An important result of the phase transfer to water in this exchange process suggests its application toward a critical need in bioscience: high quantum efficiency, biologically compatible, and optimally tissue transparent luminophores.

To date, no single material displaying all of these attributes simultaneously has been reported. Instead, >10\% quantum yield (QY) has been

reported at tissue-penetrating SWIR emission wavelengths, but these materials were unstable in physiologically relevant buffer[58, 59, 60]. IR-emitting quantum dots with hydrodynamic diameters <10 nm were reported following a III-V/II-VI core-shell colloidal synthesis; however, these particles exhibited sub-10% QY in water[61]. Efficient size-effect tunable >10% QY nanoparticle suspensions in water have been achieved using TOPO copolymer-PEGylation of II-VI core-shell nanoparticles; however, this approach produced nanoparticles with 15-30 nm hydrodynamic diameters[62].

Here we report high QY infrared luminophores that are stable under buffered conditions for greater than 5 days. The result was achieved through mercaptan-PEGylation ligand exchange that rendered organometallically synthesized lead sulfide (PbS) quantum dots stable in buffered water.

These infrared luminophores simultaneously meet requirements on brightness, stability, wavelength, and hydrodynamic diameter. The particles exhibited hydrodynamic diameters less than 10 nm and, through quantum size effect tuning have emission peaks tunable from 700 nm to 1600 nm.

5.2 Ligand exchange and methodology

The material was transferred from organic into aqueous liquid by replacing oleate capping ligands with (1-mercaptoundec-11-yl)tetra(ethylene glycol) (MTPEG). A solution of MTPEG in HEPES, Tris, or phosphate buffer was mixed with oleic-acid capped PbS nanocrystals (~80 mg/mL) in toluene. An aqueous phase containing nanoparticles was separable from the toluene phase that previously dis-
persed the PbS. These results contrast with previous reports describing aqueous suspension of organometallic lead sulfide nanocrystals using carboxylic acid or amino mercaptan strategy. Experimentally, we found that thioglycerol, 6-mercapto-1-hexanol, and 2,3-dimercapto-1-propanol all produce high QY stable colloids in polar solvents following this strategy; however, only when we used MTPEG did we obtain high QY PbS nanocrystals stable in biologically relevant buffer.

We selected the MTPEG ligand for three reasons. First, monodentate complexation of the thiol group is expected to achieve good passivation of PbS nanocrystals in view of sulfur-lead binding affinity (strong thiol-metal affinity has been widely exploited in, for example, Au nanoparticle functionalization)[63]. Second, its hydrophobic single-bonded carbon chain was expected to conserve QY. Third, its polar terminal group was expected to yield stable suspensions in aqueous liquids at physiological pH. Finally, these compact ligands enable hydrodynamically small nanoparticles that are comparable in size with a single antibody.

5.3 Characterization

Dynamic light scattering was used to investigate nanoparticle hydrodynamic diameters before and after exchange, as shown in Figure 16. Prior to ligand exchange, oleate capped nanoparticles in toluene constitute a monodispersed colloid with hydrodynamic diameter of ~6 nm. Following exchange, 90% by mass of these particles have 10 +/- 0.5 nm hydrodynamic diameter. The remaining 10% of these nanoparticles have formed small 40 - 60 nm and larger aggregates. Ligand exchange is also supported by density phase segregation of MTPEG exchanged
nanocrystals in 20 mM HEPES buffer from fresh excess addition of organic liquid as shown in Figure 17.

Figure 16. Dynamic light scattering measurements of hydrodynamic radius, by percent mass modeled as solid Rayleigh spheres, of unexchanged PbS nanocrystals with oleic-acid ligands (solid bars) in toluene, and PbS nanocrystals exchanged to having MTPEG ligands (shaded bars) in water.

Figure 17. MTPEG exchange process photograph: left vial) unexchanged organometallic oleic-acid capped lead sulfide quantum dots in organic phase above 20 mM HEPES buffered aqueous phase, right vial) free organic phase above phase-exchanged MTPEG ligand-exchanged same organometallic lead sulfide quantum dots transferred to 20 mM HEPES buffered aqueous phase.

We use transmission electron microscopy to monitor the nanomorphology of the quantum dots before and after MTPEG ligand exchange, as shown in Figures 18(a), and 18(b). We observe neither the size nor
the particle morphology of the dots are significantly impacted by the process; despite the complete transfer from the organic to the aqueous phase of the quantum dots, and despite the large number of ligands exchanged in the transfer.

Figure 18. a) TEM of unexchanged organometallic oleic-acid capped lead sulfide quantum dots. b) TEM of MTPEG phase-exchanged ligand-exchanged same lead sulfide quantum dots in water.

Figure 19 reports the absorbance and photoluminescence spectra for the nanoparticles prior to and following exchange. The excitonic structure remains but is somewhat reduced in sharpness following exchange. There is a red shift of $\sim 70$ meV in the photoluminescence and a red shift of $\sim 60$ meV in the absorbance as a result of the exchange procedure. One mechanism that may explain the observed red shifts is an effective growth in the nanocrystal size upon exchange[2].

We measured the QY of the materials’ luminescence in the infrared using the 2-port integrating sphere approach of Mello[64]. Two sample positions, corresponding to direct and indirect excitation regimes were used with collected power spectra acquired using a calibrated monochro-
Figure 19. Absorption and luminescence spectra of (~10 mg/mL) PbS quantum dots prior to and following exchange to water. Solid lines represent absorption spectra. Dashed lines represent photoluminescence spectra. Dark lines represent original OA capped PbS nanocrystals in toluene. Gray lines represent MTPEG-exchanged capped PbS nanocrystals in 20 mM HEPES buffer. Solid bar represents excitation wavelength used for PL spectra collection.

...
duction in lifetime between unexchanged and exchanged samples scales proportionally with the ~ 1.7 reduction in their QY within the interpretation that the radiative lifetimes stayed approximately fixed at 3.5 $\mu$s. We attribute the reduction in QY following the exchange to an increased nonradiative rate. We note that the ratio of quantum yield to luminescence lifetime agrees, to within experimental uncertainty, with the cases of pre-exchange versus post-exchange.

![Figure 20. Time resolved PL of MTPEG exchange on PbS quantum dots](image)

The stability of exchanged colloids under dark storage and illuminated conditions was investigated for quantum dots dispersed in 20 mM HEPES buffer. Figure 21 reports the evolution over 5 days of the material’s photoluminescence intensity. Illuminated samples experienced 6 mW HeNe laser continuous excitation and degraded in photoluminescence intensity with a half-life of 10.6 h over 1 day’s active use. Samples stored in the dark were periodically characterized for brief periods under these same excitation conditions; these samples demonstrated no appreciable loss in PL over 5 days.
The application of this electrostatically dispersed colloid toward photoconductors is presented in Figure 22. Films of the phase-exchanged ligand-exchanged quantum dots, to substantially shorter ligands, were deposited on glass substrates with gold interdigitated electrodes spaced 5 µm apart, and then tested under light and dark conditions. We observe these materials produce directly cast optoelectronically sensitive photoconductors. The necessity of polar solvent exchange, however, yields photodetectors that possess abnormal dark current behavior that is, we posit, a direct consequence of their colloidal exchange to aqueous environment. In appendices A and B we present evidence to substantiate the effects of humidity exposure that result in uncontrolled corrosion by chemi-adsorbed sulfoxy species and degrade the optoelectronic performance of unsensitized PbS photoconductors.

![Figure 21. Photoluminescence intensity of luminophores in buffer. The dashed line is for a sample stored in the dark and periodically measured. The solid line is for a sample that was illuminated continuously using a 6 mW, 300 µm excitation spot from a HeNe laser.](image)
Figure 22. IV photoconductive characterization of thioglycerol (TGL) and 6-mercapto-1-hexanol (MCH) devices under $\sim$ AM 1.5 full spectrum illumination and in the dark.

5.4 Conclusions

The presented modification of organometallic route synthesized nanocrystals results in hydrodynamically small, bright nanoparticles emitting in the short-wavelength infrared. The aqueous suspensions are stable over days at physiological pH.

The results suggest aliphatic ligand length can be varied, using the described phase-exchange ligand-exchange technique on organometallic lead sulfide quantum dots, with minimal loss to particle morphology. Therefore, a complete short ligand visible wavelength lead sulfide quantum dot solution phase ligand exchanged is achieved. One, in theory, compatible with smooth morphology lead sulfide quantum dot photoconductors.

Despite these advancements, creating colloidally stable exchanges in water and subsequently spin-casting these colloids did not result in smooth morphology solution processable and efficient photoconductive
films. This was likely due to the low evaporation rate of polar solvents and due to uncontrolled sulfoxyl species resulting from colloidal over-exposure to water and oxygen (see Appendices A and B).

5.5 Direction

We posited that to circumvent an over-exposure of oxygen and humidity required an exchange free from water. An exchange that however benefits from short ligand charge repulsion based colloidal stability, rather than steric hindrance, in favor of efficient quantum dot carrier tunneling. We hypothesized a polar organic solvent cage would be sufficient to disperse short thiolated visible wavelength lead sulfide quantum dots, yielding sensitive video frame rate photoconductors with smooth morphology.
CHAPTER 6

Fourth-generation ligand exchange strategy: Short thiols in organic liquids and smooth-morphology ultrasensitive solution-processed photoconductors

6.1 Introduction

Here, we\(^1\) demonstrate for the first time that useful levels of photoconductive gain and excellent morphology are not mutually exclusive. Colloid-phase ligand exchange is the key to this achievement. We show that colloid-phase ligand exchange from long to very short ligands can produce a sufficiently stable colloid, and that quantum-size-effect tunability and smooth morphology can be preserved, alongside improved electronic transport.

Specifically, we sought to produce a stable colloid in an organic liquid. For the exchange, we selected short, ethanethiol-terminated lig-

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ands, an approach that would have the advantages of enhanced carrier transport in view of the minimal length of its aliphatic chain and homogeneously pre-exchanged quantum dot volume during film casting.

We postulated a chemistry that seems contrary to prior work involving oleic-acid capped organometallic lead sulfide quantum dots, but one that follows from our previous works\cite{17, 18}: an organic colloid short thiolated ligand exchange based on precipitation with a nonpolar organic liquid and colloidal stability in a ‘polar’ organic liquid.

6.2 Ligand exchange and methodology

We began with oleate capped PbS nanoparticles dispersed in toluene and having a first quantum confined feature at 950 nm. We added an equal volume of ethanethiol and allowed the mixture to incubate for times ranging from 15 min to multiple hours. We ended the exchange process by precipitating the colloid using hexane. Purely oleate capped PbS nanoparticles are stable in non-polar solvents such as hexane and toluene. The fact that the addition of hexane precipitated the nanoparticles thus suggests a significant degree of exchange to the thiol. We centrifuged and resuspended the nanocrystals in chloroform and fabricated devices by spin-coating the exchanged materials onto planar glass test chips patterned with gold interdigitated electrodes.

6.3 Characterization

To be useful to imaging applications, a top-surface photodetector must exhibit high spatial uniformity across an imaging array. Spatial uniformity better than 1% across a pixel array is sought to minimize the introduction of spatial noise, which produces an image photoresponse
nonuniformity of the same order.

Ligand exchanges used in previous work resulted in films with volume contraction, cracking, flaking, and heterogeneous compositions. These films also had pockets of displaced ligands which resulted in poor detector uniformity. In this chapter we contrast those films to the film morphology of small, visible wavelength PbS quantum dots that are the result of the novel ethanethiol colloidal exchanges developed in this work.

We used atomic force microscopy (AFM) to study the films made by spin-casting nanocrystals previously ligand exchanged to ethanethiol in solution. In addition, we contrast those films to the ones presented in Chapter 3: films made from unexchanged oleic-acid capped nanocrystals, films made by spin-casting original nanocrystals and then subsequently treated with butylamine, and films made by spin-casting nanocrystals previously ligand exchanged to butylamine in solution.

Figures 23(a), 23(b), 23(c), 23(d), and 23(e) contrast the impact of these exchange procedures on film morphology (as previously described in Chapter 3). Films made by spin-coating ethanethiol colloidal ligand exchange quantum dots are smooth and crack-free with 0.7% roughness of their thickness. These morphologies show superior uniformity than the cracked films made by oleic-acid ligand spin-coated quantum dots, or the significantly rougher films made by butylamine treated quantum dots that were described in Chapter 3. A quantitative summary of all the characterized films’ percentage roughness to film thickness is presented at the end of this section in Table 3.

The film shown in Figure 23(d) is slightly over 200 nm thick, and is
therefore suited to optical sensor fabrication in view of the substantially complete absorption of visible light.

We investigated the particle morphology of ethanethiol colloidal exchanged quantum dots that result in uniform morphology spin-coated films. Figure 24(d) shows the transmission electron microscopy (TEM) image of ethanethiol colloidal ligand exchange PbS nanoparticles that absorb visible light. Their particle morphologies are compared with those in Figures 24(b) and 24(c) that were studied in Chapter 3: the TEM image of as-synthesized and the TEM image of butylamine colloidal ligand exchanged PbS quantum dots. In Chapter 3 we had found butylamine colloidal ligand exchange form worm-like nanoclusters that fail to pass through 200 nm pore-sized filters. In contrast, the ethanethiol colloidal ligand exchange nanoparticles remain as discrete and monodisperse dots, pass through 200 nm pore-size filters, and yield optically flat films. A comparison of oleate capped with ethanethiol colloidal ligand exchange nanoparticles reveals a smaller interparticle spacing in the ethanethiol case. Because spin-cast ethanethiol colloidal exchange films were optically smooth, we were able to use interference features in their absorption spectra to estimate their refractive index. We obtained a value of 2.38, compared to the previously reported value of 1.64 for oleic-acid capped nanoparticle films[65]. This finding is consistent with the considerably closer packing of the ethanethiol colloidal exchange nanoparticles seen in the TEM images.
(a) AFM original oleic-acid capping, average roughness 103 nm
(b) AFM butylamine film treatment, average roughness 64 nm
(c) AFM butylamine colloidal ligand exchange, average roughness 335 nm
(d) AFM ethanethiol colloidal ligand exchange, average roughness 1.4 nm
(e) percent average height normalized metrology of above exchanges

Figure 23. (a-d) AFM morphology and average roughness of studied PbS nanocrystal 700 rpm spin-cast films on clean glass surfaces. (e) profilometry of normalized height, computed as \((d - \bar{d})/d \times 100\) where \(d\) is the thickness of the film, of (a) thickness 429 nm, (b) thickness 712 nm (c) thickness 1978 nm, and (d) thickness 213 nm films
We show in Figure 24(a) that the ethanethiol exchange produces only very modest broadening in the absorption spectrum. The exchange adds between 10 nm to 20 nm to the FWHM of the original nanoparticles.

To be relevant to imaging applications a top-surface photodetector must exhibit high sensitivity to the illumination of interest and video frame rate speed of response. Sensitivity derives from the photoconductive gain: the number of electrical carriers collected per incident photon given at a specific light level. Speed of response allowing video-capture frame rates demands sub-100 ms time constants.

The current-voltage curves (Fig. 25(a)) of ethanethiol colloidal exchange devices reveal that the devices are photoconductive photodetectors, have high dark resistivity, and have high sensitivity over a large variation in bias. The devices exhibit a photoconductive gain of 26 at 10 V bias. The difference in temporal response among the different photodetectors is particularly noteworthy. Devices made using butylamine treatments produced multiple temporal component responses, including a significantly slow tail of response on the timescale of seconds[13, 14], which evoke long lived ghosting in their video response. In contrast, ethanethiol colloidal exchange devices exhibit a single 20 ms time constant, as shown in detail in Figure 25(b). As seen in Figure 25(c), the decay time and responsivity of ethanethiol colloidal exchange devices do not vary greatly as a function of illumination intensity. The vertical axis titles in Figures 25(b) and 25(c) are intentionally different to emphasize two distinct messages. First, Figure 25(b) relates a particular device with a great combinations of gain, lag, and dark current.
(a) Absorption spectra of drop-cast PbS nanocrystal films

(b) Original (unexchanged) oleic-acid capped nanocrystals

(c) Butylamine colloidal ligand exchange nanocrystals

(d) Ethanethiol colloidal ligand exchange nanocrystals

Figure 24. a) Absorption spectra of drop-cast PbS nanocrystal films. Samples A and B are from different syntheses. The figure enables the comparison among original (oleic-acid capped), butylamine colloidal exchange, and ethanethiol colloidal exchange films. b-d) Dark field electron microscopy images at 200 kV x 250 k magnification on formvar-coated 200 mesh copper grids comparing the deposition of typical b) original (unexchanged) nanocrystals, c) butylamine colloidal exchange nanocrystals, and d) ethanethiol colloidal exchange nanocrystals.
Figure 25. Optoelectronic properties of typical ethanethiol colloidal ligand exchange nanoparticle devices. a) IV under dark illumination and under illumination intensities of 7 nW cm$^{-2}$, 188 nW cm$^{-2}$, and 3.3 mW cm$^{-2}$. b) Photocurrent temporal response at 815 nW cm$^{-2}$ illumination intensity. c) Photosignal as a function of time for illumination intensities of 20 nW cm$^{-2}$, 188 nW cm$^{-2}$, and 3.3 mW cm$^{-2}$.
Second, Figure 25(c) illustrates that under illumination intensity variations the devices tend to respond with the same responsivity and lag. This observation further suggests the presence of a single-valued trap state lifetime. Butylamine-treated devices, in contrast, exhibit a significant dependence of temporal response and responsivity on illumination intensity[14].

<table>
<thead>
<tr>
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<th>unexchanged</th>
<th>butylamine treated film</th>
<th>butylamine colloidal exchange</th>
<th>ethanethiol colloidal exchange</th>
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<td>dark current [nA]</td>
<td>0.001</td>
<td>2</td>
<td>116</td>
<td>1.6</td>
</tr>
<tr>
<td>photo response time constant [ms]</td>
<td>-</td>
<td>2000</td>
<td>&gt; 500</td>
<td>20</td>
</tr>
<tr>
<td>photoconductive gain</td>
<td>-</td>
<td>55</td>
<td>210</td>
<td>26</td>
</tr>
<tr>
<td>average roughness [nm]</td>
<td>100</td>
<td>60</td>
<td>340</td>
<td>1.4</td>
</tr>
<tr>
<td>% thickness nonuniformity</td>
<td>24</td>
<td>9</td>
<td>17</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 3. Comparison of photoconductive photodetector performance for PbS colloidal quantum dot devices made using the films of Figures 24(b), 24(c), and 24(d). Percent thickness nonuniformity is defined as RA/thickness × 100. All devices characterized using 5 µm Au interdigitated gaps biased at 10 V under 470 nm excitation at 815 nW/cm². note: experimental comparison to butylamine treatments are commensurate with their previously reported performance.

We now turn to the optoelectronic characterization of the devices. Data were obtained at a bias of 10 V applied between two coplanar Au electrodes separated by a 5 µm wide gap and running parallel over a 3 mm device width. We summarize in Table 3 the dark current, photoconductive gain, time response to optical transients, and the percentage variation in film thickness in each case.
6.4 Conclusions

It was recently shown that the temporal response of PbS colloidal quantum dot photodetectors may be traced to specific chemical species on nanoparticle surfaces [46] (see Appendix A). Long-tailed transient components are associated with Pb-carboxylates (associated with unre- moved oleic acid ligands) and other sulfoxy species. There, ethanethiol was found to replace oleic acid and remove sulfoxies. These and the present work’s findings illustrate that while these photoconductive photodetectors do exploit trap states to achieve gain, it is possible to engineer the combination of transport and trap lifetime to achieve an attractive combination of gain and temporal response. Indeed, the response of the butylamine-treated film provides no advantage in gain over its ethanethiol-exchanged counterpart, in exchange for its undesired long-lived temporal response.

In summary, we report ethanethiol colloidal ligand exchange PbS quantum dot devices that combine a $< 20$ nm spectral broadening, a photoconductive gain of 26, a single time-constant temporal response of 20 ms, and a smooth film morphology with roughness equal to 0.7% of the average thickness.
CHAPTER 7

Thesis conclusions and findings

7.1 Conclusions

In this thesis, we sought to develop and apply a novel strategy to realize solution-processed photodetectors that combine gain, speed, and smooth films.

To achieve that goal we developed a colloidal dispersion engineered from a novel set of routes that deal with the various forces of quantum dot colloidal stability. The final results were all organic ultra-short ligand colloidal quantum dots that deposit directly as high-performance photoconductive films with excellent combinations of surface morphology, gain, and lag.

7.2 Thesis findings

In this section we summarize the challenges resolved in this work to achieve smooth morphology, sensitive, and video frame rate compatible visible wavelength quantum dot photoconductors.

Though a variety of synthetic routes create lead sulfide colloidal quantum dots, so far none yield better nanocrystals than organometallic synthesis. This technique, however, demands large aliphatic organic molecules present in the synthesis to control nanocrystal growth, to passivate their surfaces, and to prevent their aggregation by the mechanism of steric hindrance. These same large aliphatics inhibit, however, the desired carrier transport needed for optoelectronic applications.

Previous generation solid state and colloidal amine ligand exchange treatments replace the large aliphatics of ‘as synthesized’ organometal-
lic quantum dot ligands to shorter ones that enable carrier transport. However, these techniques engender, due the resulting volume contraction and nanoparticle sintering, films that do not generally yield homogeneously exchanged smooth morphology video frame rate compatible photoconductors.

We believed a homogeneous short ligand exchange is rationally achieved in colloidal form. We set out to develop colloidally-stable quantum dots capped with very short ligands that would make them compatible with efficient electronic transport when processed into films.

First, we explored trading steric hindrance for colloidal charge repulsion. We took a lead sulfide synthesis that was stabilized by a polymer (DNA) and engineered a ‘freestanding’ colloidal dispersion from it based on a single nucleotide. In doing so we demonstrated that steric hindrance can be replaced by the charge repulsion of its ligands’ free moieties.

Second, we developed a means of trading the long organic ligands of organometallically synthesized PbS quantum dots to a variety of aliphatic chain lengths, without aggregation, by phase-exchange ligand-exchange. We did so using the stronger binding affinity lead has toward sulfur than toward a carboxylic acid, and by the phase miscibility of the free ligand’s moiety between organic and inorganic liquid phases. This resulted in a colloid dispersion highly resilient to aggregation in liquid and to sintering in film.

Third, we developed a means of avoiding the requirement of non-polar liquid to polar-liquid phase transfer that maintained colloidal stability. We did so by hypothesizing that strongly tethered short thiol
ligands in addition to the quantum dot’s own surface charge could disperse or precipitate the colloidal dispersion by the effect of its ‘solvent’ cage – a hypothesis contrary to the established practice of as-synthesized organometallic dispersion and precipitation.

The cumulation of these findings resulted in homogeneously exchanged smooth morphology, with roughness equal to 0.7% of the average thickness photoconductors, with a gain of 26, and with a temporal response lifetime of 20 ms.

7.3 Future perspectives

Materials that comprise both inorganic and organic moieties have the potential to benefit from the strengths of each to form complex functions that are difficult to achieve using traditional means. Films of opto-electronic quantum confined materials benefit from their size dependent optical properties, from their low cost and relatively easy synthesis, and from the practical devices they make by their direct colloidal deposition, as shown in this work. In addition, such devices have demonstrated they can exceed the performance traits of their single crystalline semiconductor bulk counterparts in sensitivity and speed of response. There are many opportunities, to take the processing strategies developed in this work to broader communities for future photodetectors, photovoltaics, light emitting sources, biological labeling, and biological screening applications. In this section we describe a few of these promising research opportunities.

Future photodetector research may be derived from the potential of quantum dots and the results achieved in this work. First, photoconductor architectures that use transparent conductive oxides, like indium
tin oxide, instead of opaque contact metals, like gold, may allow the formation of vertically stacked devices that greatly enhance the sensitivity of these detectors without penalty to their speed of response. This architecture may, in addition, comprise layers of different sized dots. Those layerings could eliminate the need for color specific filters that are common to traditional photodetectors within a single pixel. Second, any means to circumvent the requirement for oxygen in order to achieve the best sensitivity for the photoconductors developed in this work, as described in Appendix A, offers a promising avenue for future research. One means to accomplish that goal would be to engineer from these materials a new class of photodetector: a phototransistor. A phototransistor’s gain mechanism and response speed is predicated on design and not the comprised material’s sensitization by traps or the direct chemical modulations of its mobility by oxidation. By eliminating interface traps in hetero-junctions that form blocking layers to one carrier type phototransistors provide an artificial trapping mechanism that offer a route to circumvent the major difficulty in bringing the present work’s photoconductors to a commercial market. Conversely, engineering chemical analogues to oxygen that enable equivalent or superior sensitization into encapsulated films of photoconductors presents another potential research direction. Finally, the photoconductors we engineer in this work have a capacity to study multiple exciton generation (MEG) through the direct transduction of incident light into a photocurrent. MEG in quantum dots has been observed in solution form and in solid form previously. The work we’ve presented here suggests a potential route to the realization of direct optoelectronic, device
based, MEG observations for the first time.

The uniformity of the films deposited through this work’s ethanethiol colloidal exchange have a potential for future photovoltaic research in addition to colloidal quantum dot solution processability and its quantum dot size controlled absorption onset. These advantages may offer a path to mitigate the effect of pinholes and shorts to the large area photovoltaic devices by virtue of their enhanced film uniformity. In colloidal form ethanethiol ligand capped quantum dots may offer a significantly higher deposited packing fraction than those techniques that require post infiltration ligand exchange. These may yield substantively higher dot infiltration into porous architectures photovoltaic devices. Porous to liquid interface architecture photovoltaics, like the Grätzel cell, have shown superior solar power conversion efficiencies that are ascribed to the surface area sensitization between infiltrated molecules and a porous matrix. Thus, future photovoltaic devices derived from this work may benefit from a greater infiltration of quantum dots that are directly cast into a porous matrix. In turn, devices made from these materials may yield a better solid-state analogue to the Grätzel cell, one that benefits from its directly enhanced solar active surface area.

Traditional multi-junction light emitting diodes (LEDs) have spatially separate and beam pattern divergent designs that offer another potential avenue of research derived in part from this work. There exists a path now to produce a new kind of display technology by making diode contacts with transparent conductors to uniform films of conductive quantum dots like the ones engineered here. The idea is similar to the design of organic stacked photoconductive photodetectors being
developed at Fujifilm by Takada’s group. LEDs devised through this kind quantum dot film engineering may possess several key advantages to traditional ones: they might provide color to the next generation of E-ink, they might be powered by sunlight or result in low power consumption displays, they may achieve beam pattern uniformity unparalleled to traditional LEDs, and they may eliminate the physical boundary requirement defined by traditional single color per pixel display techniques.

The luminophores we presented in Chapter 5 demonstrated record infrared luminescence quantum efficiency for quantum dots that are colloidal in biologically relevant media and offer a potential advancement in pharmaceutical labeling and bio-labeling applications[66, 67, 68]. A mixture of (1-mercaptoundec-11-yl)tetra(ethylene glycol) (MTPEG) and thiolated bio-conjugates may provide a means of tethering these materials to specific biological target sites. The cytotoxicity of these luminophores, shown in Figure 7.3, suggests there is a significant potential in their use in view of their capacity to emit light at the wavelengths of greatest tissue transparency[69].

The following is a brief description of the cytotoxicity experiment performed by the Kelley Group. The cytotoxicity of HeLa cells exposed to PbS MTPEG QDs were quantitated using a standard CCK-8 assay. In this assay, live cells react with WST-8 by the activity of dehydrogenases to produce WST-8 formazan. The absorbance of WST-8 formazan, which is proportional to the number of live cells, is calibrated at 450 nm. For each experimental concentration three trials were performed; the error bars indicate the standard deviation. HeLa cells (ATCC)
were cultured as subconfluent monolayers on cell culture plates (25 or 75 cm²) with vent caps (Corning) in 1 minimum essential medium (Gibco) supplemented with fetal bovine serum (10% v/v, ATCC) in a humidified incubator at 37 °C containing CO₂ (5%). HeLa cells that had been grown to subconfluence were dissociated from the surface with a solution of ethylenediaminetetraacetic acid (EDTA, 0.53 mM)/trypsin (0.25%) (2 mL, Cellgro) for 10 min at 37 °C, and aliquots (100 µL) were seeded (12,000 cells) into 96-well clear flat-bottomed microplates (Costar). After overnight incubation, the medium was replaced with freshly prepared solutions containing MTPEG-PbS quantum dot solutions with different concentrations in 1 serum-free minimum essential alpha medium. Cells were incubated in the dark at 37 °C for 10 and 20 min. Cells treated with media alone and Triton X-100 were used as low and high cell death controls, respectively. After incubation with CCK-8 (Dojindo) at 37 °C for 2 h, the absorbance of each sample was measured at 450 nm on a Spectramax plate reader (Molecular Devices).

![Cytotoxicity of Hinds' MTPEG PbS QDs (4hr + 24hr)](image)

Figure 26. Cytotoxicity screening of bio-compatible PbS MTPEG quantum dots developed in this work, performed by collaborators in the Kelley group at the University of Toronto.
The multiple functionalities of ligands we demonstrate in Chapter 4 have research potential for applications in remote chemical sensing and in the construction of complex nano-scale assemblies. Sulfur leaks, lead contamination, and oxygen sensing all have the potential to be engineered from the techniques presented in Chapter 4 that may evoke a luminescent signature in response to the presence of these chemical or physical events. As a major benefit, the excitation and readout of those events can be accomplished over wide areas and over great distances. Complex nano-scale assemblies may also be used to yield matrices of quantum dot materials that respond to stimuli that are different from those ascribed directly to the reaction of pure colloidal quantum dots. For example, quantum dots wrapped by DNA strands may respond to temperature by the action of this nano-scale assembly. Light scattering or electronic coupling ascribed to the quantum dots’ interparticle spacing may be modulated with temperature by conformal changes in the DNA strands to which they are tethered. The example presented above describes a type of nano-scale bolometer, a sensitive device that characterizes temperature, capitalizing on the multiple functionalities of quantum dot ligands to form complex devices.

The photoconductors we engineer in Chapter 6 using largely organic means may instead benefit from the aqueous transfer technique described in Chapter 5 toward a bio-electrochemical screening chip. Such devices would not depend on their optical readout, like ELISA assays do, and could easily be multiplexed to the detection size scales of multi micron areas per specific bio-sensor. In this way many bacteria, RNA, and DNA inputs may be screened simultaneously from the trans-
duction of targeted binding events to segments of films that are made biologically selective through means derived in part from the present work.

Finally, a complex avenue of significant research to the one presented in this work includes engineering alternative material systems that are free from the toxicological stigma of heavy metal chalcogenides in the applications of all colloidal quantum dots. Addressing those concerns about the technology’s impact on the environment and its toxicological impact on living systems offers promising avenues of study to synthetic chemists, biologists, and engineers. To be competitive with existing green-platforms, like silicon based devices, the survivability of new technologies in a greener-market place have inherent public advantages if they are demonstrated to be safe and sustainable as well as technologically advanced.

7.4 Refereed journal publications


7.5 Invention disclosures


APPENDIX A

Appendix A - The evolution of conductivity enhancement in smooth-morphology ultrasensitive solution-processed photoconductors

Gain, through conductivity enhancement, may reduce or eliminate the need for supporting amplification electronics in photoconductors. Also, photoconductors with gain may provide ever smaller pixel miniaturization in their devices. In this section, we explore the origin of gain in visible wavelength lead sulfide smooth-morphology ultrasensitive solution-processed photoconductors. We investigate how mobility and lifetime evolve as a function of atmosphere. We demonstrate that exposure to molecular oxygen (O\textsubscript{2}), reversibly alters photoconductor conductivity by more than changes to only carrier lifetime at constant illumination intensity allow: we demonstrate the modulation of conductivity through mobility by varying the measurement atmosphere. We show eventual irreversible changes with prolonged oxygen exposure result in changes to conductivity that evoke fast response and superior conductivity when measured in O\textsubscript{2} rich environments. This sensitization corresponds to those results modelled in Chapter 2, and characterized in Chapter 6: a state where conductivity can be completely described by changes in lifetime and illumination intensity alone. We use X-ray photoelectron spectroscopy to correlate the irreversible change we observe with sulfoxy species growth into the PbS quantum-dot films with exposure to oxygen. These investigations reveal that exposure to air is both a temporary physi-adsorbed and a permanent sulfoxy species modulator of our photoconductors’ gain.

The incident light that creates an excess of free electron hole pairs
within a photoconductor cannot result, by itself, in photoconductor gain, or to exceed the primary photocurrent. Gain must derive from the transport of those carriers through changes in lifetime, changes in mobility, or simultaneous changes in lifetime and mobility.

We, surprisingly, observe that ethanethiol colloidal ligand exchange photoconductors constructed by completely anaerobic means have quick temporal response, but no gain. We hypothesize that exposure to air sensitizes these photoconductors; and we study their dynamic photoconductive properties: their conductivity, and free carrier lifetime as a function of the duration over which they are exposed to oxygen and compare the effects between measurement in oxygen and measurement in nitrogen (N₂) environments. We dynamically cycle between the two atmospheric environments and note that devices exposed to oxygen for less than ~28 minutes demonstrate completely reversible changes in conductivity and completely reversible changes in lifetime also. However, exposing devices to oxygen for periods longer than ~78 minutes result in both irreversible and reversible changes between O₂ and N₂ environment measurements. We show, in Figures A.1(a) and A.1(b), the cumulative influence of oxygen exposure on changes in conductivity and free-carrier lifetime measured between these atmospheres.

Examining the dynamics of photoconductor conductivity between 25-75 minutes, measured under N₂ atmosphere, we note irreversible changes in the conductivity and lifetime correlate to the onset of gain. These subtle changes are masked by significantly faster free-carrier lifetime, and greater changes in conductivity that are observed with measurement in O₂ atmosphere. We observe, after the irreversible changes,
Figure A.1. a) Changes in free-carrier lifetime observed under O$_2$ and N$_2$ atmospheres as a function of the photoconductor’s total exposure to O$_2$. b) Changes in conductivity observed under O$_2$ and N$_2$ atmospheres as a function of the photoconductor’s total exposure to O$_2$. 
that for a constant 470 nm illumination of 46 pW, lifetimes are shorter and conductivities are larger in O₂ than in N₂ environment. The change in conductivity in a single-carrier semiconductor, one often attributed to p-type lead sulfide, given by,

\[ \Delta \sigma = q \left( \Delta \tau_p \Delta f \right) \mu_p + pq \Delta \mu_p. \]  

(A.1)
suggests a change in material mobility may be the result of these photoconductors’ measurement atmosphere.

We suggest the onset of gain is in part due to the irreversible changes in material with O₂ exposure, and in large part due to reversible changes in material that depend on the measurement environment. Finally, we note that changes in conductivity and lifetime, that are reversible, eventually saturate with prolonged O₂ exposure when measured in one static environment. Those conditions do not lead to the conclusion of simultaneous changes in lifetime and mobility; this more typical condition was described by the characterization presented in Chapter 6.

Next we investigate the static, permanent, effect O₂ exposure has on the photoconductors’ surface using XPS: those permanent changes that partially modify these photoconductors’ conductivity. XPS allows the surface chemistry of a material to be probed by measuring the binding energy of electrons ejected off the material upon x-ray irradiation[70].

To study the permanent changes in the photoconductors with exposure to oxygen we take XPS spectra of the atomic constituents of oxygen, sulfur, and lead on their surfaces. We contrast the effect of permanent oxidation by taking spectra of: ethanethiol lead sulfide colloidal ligand exchange supernatant, films anaerobically processed ethanethiol colloidal ligand exchange films (aETS) encapsulated in sulfur, aETS
films that are directly measured without encapsulation, and aETS films exposed to 600 minutes of O₂ and measured without encapsulation. We contextualize the oxygen, sulfur, and lead spectra by simultaneously measuring some relevant controls: blank gold substrates, PbSO₄ films, and PbO films.

All films were deposited on gold over-coated silicon substrates using the same procedures taken in device fabrication as presented in Chapter 6. XPS spectra were generated¹ by an Al Kα source calibrated to (C)1s (C-C,C-H) at 285.0 eV.

All aETS samples demonstrate the presence of oxygen, as shown in Figure A.2, contained within those films; possibly due to the use of PbO as a precursor, or due to traces of permanent oxygen species that do not result in permanent changes in photoconductor behavior as shown by Figures A.1(b) and A.1(a). However, there is a clear evolution from the spectra of aETS films that were not exposed to oxygen to those aETS films exposed to 600 minutes of oxygen. A pronounced weakening in the oxygen’s electron binding energy observed in the oxygen exposed films suggests a new permanent change occurs within the 600 minute time frame. This change, we suggest, may be consistent with a change in the electrical scattering properties of the photoconductors’ carrier transport.

The Sulfur (S)2p spectra, shown in Figure A.3, are fit with a doublet due to spin-orbit splitting[70]. Though masked in the oxygen spectrum we clearly observe a lack of PbSO₄ formation in any of the studied aETS films within 600 minutes of exposure to oxygen. PbSO₄ by many is

¹XPS measurements were performed at the University of Toronto Surface Institute of Ontario laboratory by Dr. Peter Brodersen.
Figure A.2. XPS Oxygen (O)1s spectrum of: a) oxygen adsorbed on bare gold substrate used for analysis, b) PbSO$_4$ control sample, c) PbO control sample, d) supernatant from precipitation step of anaerobic ethanethiol colloidal exchange ligand-exchange (aETS), e) encapsulated, in sulfur, aETS film, f) aETS film without sulfur encapsulation or exposure to oxygen, and g) aETS film without encapsulation exposed to 600 minutes of oxygen.

thought to be the most likely oxide to form on the surface PbS[71]. Also, though Sulfur species exist in the colloidal ligand exchange supernatant their exposure to oxygen there, shown in Figure A.2, does not persist as a measurable surface species, unlike those of the studied films.

Finally, the Lead (Pb)4f spectra demonstrate a stronger binding energy of its electrons as they are shielded by a greater number of oxygen atoms; we contextualized the results between the PbO and PbSO$_4$ controls shown in Figure A.4. We observe a significant increase in the binding energy of their electrons in films exposed to 600 minutes of O$_2$. This observation suggests more than one oxygen is permanently shielding lead’s electrons when the photoconductors are exposed to oxygen.
Figure A.3. XPS Sulfur (S)2p spectrum of: a) PbSO₄ control sample, b) supernatant from precipitation step of anaerobic ethanethiol colloidal exchange ligand-exchange (aETS), c) encapsulated, in sulfur, aETS film, d) aETS film without sulfur encapsulation or exposure to oxygen, and e) aETS film without encapsulation exposed to 600 minutes of oxygen.

In summary, we found permanent changes in photoconductor lifetime and conductivity occur with exposure to oxygen. Those changes, under the single-carrier semiconductor model, can only be rationalized by a modulation of carrier mobility. We measure the permanent chemi-adsorbed effect of prolonged oxygen exposure by XPS and related its influence on the binding energies of lead’s, sulfur’s, and oxygen’s electrons. Perhaps most strikingly, however, we found the change in free carrier lifetime and conductivity that results in gain, though dependent in some way on these chemi-adsorbed film changes, are more greatly influenced by the reversible, physi-adsorbed, presence of an oxygen rich environment.
Figure A.4. XPS Lead (Pb)4f spectrum of: a) PbSO₄ control sample, b) PbO control sample, c) supernatant from precipitation step of anaerobic ethanethiol colloidal exchange ligand-exchange (aETS), d) encapsulated, in sulfur, aETS film, e) aETS film without sulfur encapsulation or exposure to oxygen, and f) aETS film without encapsulation exposed to 600 minutes of oxygen.
APPENDIX B

Appendix B - The effect of exposure to humidity in smooth morphology ultrasensitive photoconductors

In this section we demonstrate the degrading effect of exposure to humidity on temporal response, dark current, and gain in visible wavelength solution-processed photoconductors. We expose the anaerobically exchanged materials described in Appendix A to cycles of wet and dry nitrogen environments. The impact on lifetime, gain, and dark current with humidity is summarized in Figure B.1(a). A typical dry nitrogen environment current-time trace is presented in Figure B.1(b). A typical wet nitrogen environment current-time trace is presented in Figure B.1(c).

We observe that exposure to humidity degrades the performance of these photoconductive devices with respect to dark current, gain, and temporal response simultaneously.
Figure B.1.  a) Summary of gain, dark current, and lifetime of anaerobically processed solution processed quantum dot photoconductors exposed to timed durations of wet nitrogen and dry nitrogen environments b) Current-time modulated optical response of aETS devices at 10 V bias exposed to dry nitrogen environment between 500 nW cm$^{-2}$ illumination and dark response c) Current-time modulated optical response of aETS devices at 10 V bias exposed to wet nitrogen environment between 500 nW cm$^{-2}$ illumination and dark response.
LIST OF REFERENCES


