SENSITIVE SOLUTION-PROCESSED QUANTUM DOT PHOTODETECTORS

By

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

Graduate Department of Electrical and Computer Engineering

University of Toronto

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Abstract

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Optical sensing for imaging applications has traditionally been enabled by single-crystalline photodetectors. This approach has dramatically curtailed monolithic integration of a variety of optically-sensitive materials onto silicon read-out circuits.

The advent of solution-processed optoelectronic materials such as colloidal quantum dots offers the potential of a revolution in optoelectronics. Their solution-processibility enables low-cost monolithic integration with an arbitrary substrate. This dissertation presents the first high-sensitivity solution-processed photodetectors. It does so by leveraging the high degree of control offered by nanoscale materials engineering.

Material processing routes are developed to achieve sufficient carrier mobility and sensitization that lead to high photoconductive gain up to \( 10^3 \) A/W, observed for the first time in soft materials. A method to remove charge-transport-inhibiting moieties from the nanocrystal surface is developed. Surface treatment procedures are then advanced to prolong the carrier lifetime and thus sensitize the material. The sequence of these processing stages is crucial for the noise performance of the device. Processing
conditions that lead to high photoconductive gain and low noise current are then reported to achieve highly sensitive photodetectors with reported D* on the order $10^{13}$ Jones.

The spectral tunability offered by colloidal quantum dots enables monolithic multispectral photodetectors. The material challenges, imposed by the behaviour of matter in the nanoscale, are addressed to report sensitive photodetectors in the visible and infrared parts of spectrum.

Carrier lifetime determines the temporal response of a photoconductor. The abundance of trap states on the nanocrystal surface and their associated carrier lifetimes mandate careful attention in order to preserve the trap states that yield temporal response acceptable for imaging applications. It is shown for the first time that the temporal response of a quantum dot photoconductor can be tailored by careful control over surface chemistry. Materials species were identified as responsible for particular photocurrent temporal components. These findings are then exploited to isolate and remove surface species responsible for undesirably long time constants. A solution-processed photoconductive detector is reported that exhibits high sensitivity ($D^* \sim 10^{12}$ Jones) and temporal response of 25 ms, suitable for imaging applications.
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<td>SWIR</td>
<td>Short-wavelength infrared</td>
</tr>
<tr>
<td>NIR</td>
<td>Near infrared</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary metal oxide semiconductor</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
<tr>
<td>ROIC</td>
<td>Read-out integrated circuit</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>NC</td>
<td>Nanocrystal</td>
</tr>
<tr>
<td>NEP</td>
<td>Noise equivalent power</td>
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Chapter 1

Introduction

Optical sensing and imaging underpin the transduction of our visual world into digital signals that can be stored, conveyed, and processed. Light detection has been traditionally facilitated by small-area, single-crystalline photodetectors, characterized by high cost, complexity, and rigidity.

In the present work, we demonstrate a novel approach to photodetection based on solution-processed colloidal quantum dots. This material platform enables large-area, low cost, flexible photodetectors.

In this chapter, several applications of photodetection are presented, with emphasis on imaging. The fundamental properties of a photodetector relevant to imaging are then described. The present-day photodetector technologies used for imaging applications are briefly reviewed, and advantages and disadvantages are discussed. The motivation for the present work is then set by the opportunities that arise from the proposed approach based on colloidal nanocrystals. Finally, this chapter concludes with the objectives and the organization of this thesis.
1.1 Imaging technology background

1.1.1 Imaging applications

Optical communications, remote sensing, spectroscopy, and imaging are just few of the applications enabled by the detection of optical signals. Here we focus on imaging, a huge commercial sector that touches each of our lives.

The advent of digital imaging and media has rendered photography and video capture widespread. A photosensitive material is required to absorb optical signals in the visible range (i.e. wavelengths of 400 – 700 nm) and transform them into electronic signals. Visible imaging applications also include surveillance, machine vision, industrial inspection, spectroscopy, and fluorescent biomedical imaging.

Figure 1.1: Nightglow irradiance spectrum under different moonlight conditions [1]. The semiconductor absorbance ranges that enable passive night vision are also illustrated.
Sensitive photodetection in the short wavelength infrared (SWIR) enables passive night vision. Emission from hydroxyl ions from the upper atmosphere levels illuminates the earth 24 hours a day [1, 2]. As shown in Figure 1.1 the emission spectrum of this nightglow, in the range from 1 μm to 1.7 μm, provides the optical background that is reflected or scattered by the objects allowing for their imaging. This facilitates imaging even in the absence of moonlight and irrespective of weather conditions.

Another emerging application of SWIR photodetection is in biomedical imaging. Lumophores are functionalized to attach specifically to tumor cells; the lumophores are optically excited and their emission is detected, revealing the tumor location and extent (Figure 1.2) [3]. There exist two optical windows around 900 and 1100 nm where tissue absorption is minimum, enabling deep (~10 cm) tissue imaging [4, 5]. Existing technologies of imaging were based largely on visible fluorescence imaging; this is conflated by tissue auto-fluorescence, limiting sensitivity and contrast. The need for ultrasensitive photodetectors in the SWIR to enable early stage tumour detection is thus evident.

Figure 1.2: *In vivo* imaging of tumours based on CdSe-ZnS quantum dot fluorescence (reprinted with permission from [3]).
Further applications of SWIR imaging are found in astrophysics [6], in remote sensing for climate and natural resources monitoring [7], in food and pharmaceutical industries for quality control and product inspection [8] and identification [9].

The combination of visible and infrared detection towards multispectral imaging provides a powerful tool that offers independent pieces of information extracted from the interaction of light of different wavelengths with matter. Such functionality is of limited use today due to the high fabrication cost and modest performance of such photodetectors. Present-day multispectral image sensors are required to embed on a single platform various semiconductor processes that are not monolithically integrable. This results in high complexity, high cost, and a sacrifice in performance [10].

1.1.2 Sensor requirements for imaging applications

The basic characteristics required for a photodetector suitable for imaging applications are discussed in this section.

The most important feature of a photodetector is sensitivity, which expresses the ability of a detector to distinguish signal from noise. In the chapter which follows, we present several figures of merit that describe detector sensitivity. These allow comparison amongst different detector technologies. Higher sensitivity enables imaging at lower levels of illumination. High sensitivity can be translated to high quantum efficiency and low noise. High quantum efficiency ensures that a large portion of the incident photons will create electron-hole pairs that contribute to photocurrent. A major contributor to the noise current is often shot noise arising from the dark current of the detector. Low dark current is typically required for low noise levels.

Video capture is facilitated by sampling images at a frame rate that matches the eye’s refresh rate. To avoid the appearance of ghosting, the temporal response of the photodetector must be sufficiently rapid that, within a period of a small number of frames (typically 5), no photocurrent remnant remains that is perceptible by human eye. The photocurrent time constant of the detector should, thus, be no longer than a few tens of
ms. Still imaging applications can tolerate longer temporal responses if a shutter is employed, and if the gain in sensitivity compensates for the loss of temporal fidelity.

When it comes to practical implementation the issue of convenient integration of sensing materials with read-out electronics arises. Ideally, a photosensitive material should be readily monolithically integrated with a simple, low-cost CMOS read-out integrated circuit, offering low fabrication cost, low complexity, and high pixel count.

1.1.3 Present-day technologies for imaging applications

Imaging in the visible is largely facilitated by silicon photodiodes. The first imaging arrays were based on charge-coupled devices (CCD). This approach involves a photoactive sensor array with several stages of photo-charge transfer to the read-out circuit for electronic processing. For this purpose the interconnection of two chips is required to transfer the photo-charge from the sensor to the electronic circuitry. CCD cameras offer a fill-factor - the ratio of the optically active area of the chip to its total area - that may vary from 100% to 50% depending on the cell design [11]. CCDs suffer high fabrication and integration cost due to multiple chip interconnections and the incompatibility of CMOS with the process required for the CCD platform.

In 1997, an integrated CMOS image sensor was reported on a single chip for optical sensing and signal processing [12]. Its fill factor was limited to 30% due to the coexistence of photoactive elements and read-out circuitry on the same chip. Amorphous silicon photodetectors have been proposed as a top-surface photodetector with promise for 100% fill factor [13]. However, these suffer from very long time constants [14] and material instabilities under high illumination [15]. Silicon photodiodes demonstrate superb transient time in the sub-microseconds, well exceeding the requirements for imaging applications. Their photodiode mode of operation however limits their internal quantum efficiency to 100% as one carrier can be generated per absorbed photon. Their sensitivity is then limited by the read-out circuit noise.

In order to overcome this limit, Si avalanche photodiodes (APD) were proposed for use in CMOS image sensors [16]. The high required applied bias limits their integration in
conventional CMOS circuits. Further design considerations are required to suppress the high leakage currents present in such structures [17].

For sensing and imaging in the SWIR the use of InGaAs photodiodes leads the market. In\textsubscript{0.53}Ga\textsubscript{0.47}As lattice matched with InP and with bandgap of 0.73 eV addresses the SWIR spectrum and is suited for night vision applications. Their sensitivity is very high, with noise equivalent intensity (minimum light intensity that can be detected) in the order of a few pW/cm\textsuperscript{2}, and their transient response provides frame rates up to several kframes/sec. The molecular beam epitaxy (MBE) technique required for the growth of InGaAs imposes a high materials cost per unit area of sensor. Hybrid integration of the light sensing InGaAs array requires complex bump-bonding techniques that increase the cost further and also limit the pixel resolution to a few hundreds of kpixels. Typical price for a night vision camera based on InGaAs exceeds $40,000. Moreover, conventional InGaAs-on-InP-substrate sensitivity drops dramatically below 900 nm due to substrate absorption, making it impractical for visible imaging applications.

Efforts to develop a CMOS compatible infrared detector were taken by growing germanium on silicon. Even though these devices require costly epitaxial growth techniques they show promise for monolithic integration of infrared detectors on CMOS. SiGe photodiodes have been reported with infrared sensitivity [18]. These detectors were developed with emphasis on high-speed performance for optical communications and exhibit bandwidths in excess of 1 GHz [19]; their responsivity, however, was reported \textasciitilde 0.1 A/W, resulting in insufficient sensitivity for imaging applications. Their integration onto CMOS focal plane arrays for imaging was also reported [20]. SiGe technology, promising as it is, requires further efforts towards successful fabrication of sensitive imaging systems.

1.2 Colloidal Quantum Dots for Light Detection

Colloidal quantum dots have recently attracted significant attention as a candidate material for many optoelectronic applications. Light emitting diodes [21, 22], lasers [23], optical modulators [24] solar cells [25, 26], and photodetectors [27] have all been
reported. One major benefit of colloidal quantum dots arises from their solution processibility; this facilitates ready integration with an almost limitless variety of substrates, including post-processing atop other integrated circuits. Additionally, quantum dots’ optical absorption and emission spectra are widely tunable through the quantum size effect [28]. The impact of these traits on photodetector technology is discussed in the present section.

1.2.1 Solution processibility

Device fabrication based on conventional single-crystalline semiconductors such as silicon and InGaAs requires high temperature processing and high vacuum conditions accompanied by high cost equipment. Monolithically integrated optoelectronics also mandates growth on crystalline substrates using lattice-matched semiconductors. Unlike electronic devices, low cost optoelectronic devices are hard to achieve in view of the materials incompatibilities and highly customized deposition systems.

The realization of thin-film top-surface photodetectors would offer the field of flexible electronics new functions to deliver atop its low cost, light weight, flexible platform. Recent progress in organic transistors and their integration [29] has led to the demonstration of various large area, flexible, low cost, portable sensors [30, 31] and displays [32]. Conventional single-crystalline semiconductors are precluded from their application in flexible organic electronics due to the incompatibility of their growth conditions with the process windows required by organic semiconductors. Their up-scaling from silicon-wafer-area to larger-area applications is also limited by the serialized nature of wafer processing in contrast with the roll-to-roll processing of sheets of flexible substrates.
Figure 1.3: Demonstration of a sensor array structure based on colloidal quantum dots.

Solution-synthesized colloidal quantum dots can readily be deposited using spin-coating, spray-casting on inkjet printing techniques on any substrate conducting or insulating, crystalline or amorphous, rigid or flexible. Lattice mismatch considerations do not arise, and large-area processing is facilitated by roll-to-roll processing onto flexible substrates. Colloidal nanocrystals are synthesized using wet chemistry techniques: reagents are injected into a glass flask and, through control of reagent concentrations, ligand selection, and temperature, nanocrystals of a desired size and shape can be delivered. Synthesis and growth of nanocrystals of the desired size is followed by isolation and redispersion in organic solvents for subsequent solution processing. As an example, Figure 1.3 demonstrates the applicability of colloidal quantum dots in the fabrication of a monolithically integrated sensor array. Nanocrystals from solution are spin-coated on a read-out integrated circuit (ROIC). Individual pixels are delineated by the area of the metal pads presented on the top surface of the ROIC. After nanocrystal film deposition, a transparent metal contact (indium tin oxide) is deposited to form individual photodetectors. This architecture, called top-surface photodetector, not only is fully compatible with CMOS technology but also offers a 100% fill factor, since all the area of the chip can be used for light sensing.
1.2.2 Spectral tunability

The ability to control the spectrum of absorption or emission in optoelectronic devices is useful in many applications: lasers with tunable spectrum can be employed for wavelength division multiplex (WDM) optical communications systems [33]; light emitting diodes that combine red, green, and blue light can be used for white light illumination for displays and high efficiency lighting systems [34].

In photodetectors, spectral tunability eliminates the need for optical filters to address the spectrum of interest, leading to lower cost implementation and avoiding loss of signal that arises when filtering and sensing are implemented in series rather than within a single spectrally-selective sensing medium. Furthermore, the absorption onset of the detector can be selected to match the longer wavelength of the intended spectrum. This avoids absorption of longer wavelength photons that are not of interest in certain imaging applications but that do contribute excess noise.

In bulk semiconductors, wavelength tunability is achieved via changes in the stoichiometry of ternary or quaternary compounds (In$_x$Ga$_{1-x}$As$_y$P$_{1-y}$). This introduces extra complexity during growth. Colloidal quantum dots offer quantum size effect tuning wherein the absorption onset (as determined by the first excitonic peak) as well as the emission spectrum may be controlled through the size of the nanocrystals. It is possible therefore to achieve tunable emission and absorption from a single material quantum dot system to address various spectral windows.

Figure 1.4 illustrates the tunability in absorption offered by PbS colloidal nanocrystals. By varying the dot size from ~10 nm to ~2 nm in diameter, the whole SWIR and visible spectrum can be selectively addressed from 1800 nm to 700 nm. PbS quantum dot photodetectors can address spectral windows of interest in a range of important applications: visible for video and photography; near-infrared for biomedical imaging; SWIR for night vision applications, and all of the above for spectroscopy and broadband applications. We exploit the wide-ranging tunability of PbS in the present work to demonstrate multispectral photodetection.
Figure 1.4: Quantum size effect tunability of the absorption spectrum in PbS colloidal quantum dots. The quantum dot size varies from 10 nm (red) to 3 nm (black) in diameter.

1.3 Thesis Objectives

PbS colloidal quantum dot photodetectors hold great promise in imaging applications for they can extend silicon functionality to longer wavelengths and also provide a new technological platform of flexible-organic-electronics compatible photodetectors. This thesis is focused on investigating the potential of solution-processed photodetectors to address the standards required for imaging applications. More specifically the following issues are addressed in this work:

- **Maximization of quantum efficiency**: The quantum efficiency of conventional photodiodes is restricted to at most one electron per photon. Herein, we explore the possibility of instead building a sensor whose responsivity is not confined by the limits of unity quantum efficiency. Specifically, we ask the question: Can nanoscale materials be manipulated such as to provide for the realization of significant photoconductive gain?
• **Minimization of noise:** Photoconductors suffer from fundamental shot noise due to their dark current, while, in addition, polycrystalline photoconductors’ internal interfaces introduce excess generation-recombination noise. Might it be possible to uncover materials processing routes that leverage colloidal synthesis followed by further processing to enable the fabrication of photoconductors that possess high gain and low noise at the same time? Could record levels of sensitivity be achieved as a result?

• **Spectral tunability:** Quantum dots are known to exhibit spectral tunability of their optical properties (absorption and emission) through control over their size. Can this tunability be maintained in the optoelectronic properties of a fully-fabricated, substantially conductive, device? Is it possible to fabricate photoconductive photodetectors of different nanocrystal size to achieve multispectral detection? Would their underlying performance be preserved when size is altered to tune the spectral onset of detection? Or will material processing modifications be required to achieve high sensitivity within new spectral regimes of interest?

• **Investigation of the effects of the nanocrystal surface on the photoconductive performance:** The performance of photoconductors is sensitive to surface trap states. In particular their temporal response is affected dramatically by the particulars of the surface trap states. Is it feasible to acquire control of the matter in the nanoscale in order to fine-tune the macroscopic photodetector properties of gain and temporal response?

1.4 Thesis Outline

The remainder of this thesis is organized as follows:

Chapter 2 introduces photoconductivity and reviews its preexisting literature. In this chapter we present the first solution-processed photodetector to address the SWIR portion
of spectrum. The device, based on the photodiode principle of operation, represents an important first, and yet is seen to show poor sensitivity. This chapter thus sets the opportunity for the work, but also highlights its central challenge: performance.

Chapter 3 reports the first report of an infrared solution-processed photoconductive photodetector with high sensitivity. The photoconductive device reported herein exhibits high photoconductive gain achieved through the simultaneous achievement of high mobility and long carrier lifetime. We launch a detailed investigation of the material processing routes that led to this achievement. In particular, we studied the role of the oxidized surface species in the sensitization of this material and their effects on noise performance. We found processing routes that minimized noise current resulting in high sensitivity.

Chapter 4 illustrates the potential of spectral tunability offered by colloidal quantum dots. We report the first solution-processed photodetector to address the visible spectrum with high sensitivity. This sensitivity is reported as a result of combined high gain and low noise. The effects of sensitizing centers on the device performance characteristics and in particular the dynamic range and the temporal response, are then discussed. The identification of the energy levels of the sensitizing centers in this chapter also sets the grounds for trap state engineering towards faster photoconductive response as addressed in Chapter 5.

In Chapter 5 we investigate the connections between the composition of colloidal quantum dot photoconductive films and a key performance property: time-domain performance. Specifically, we report on the correlation between the specific oxide species present on the nanocrystal surface and the observed photocurrent decay time constants. We then exploit these findings to engineer of the first demonstration that trap state engineering at the nanoscale allows us to generate PbS colloidal quantum dot photoconductive detectors with suitably rapid temporal responses. We do so by suppressing those oxide species that contribute to the undesired longer decay times. Through such control, we report the simultaneous achievement of high sensitivity and temporal response suitable for imaging applications. The thesis concludes with a summary of the contributions of the present work and a discussion of the future prospects and requirements in the field.
Chapter 2

Photoconductivity and Solution-Processed Photodetectors

The present work focuses on the development of photoconductive photodetectors based on colloidal quantum dots. In the present chapter, the known science underlying this type of photodetectors is discussed. Photodetector figures of merit employed throughout this thesis are then presented. Prior work on solution-processed photodetectors is reviewed to set the challenges and motivate the efforts undertaken in the present work. The chapter concludes with the demonstration of solution-processed photodiodes based on PbS colloidal quantum dots that provide sensitivity at infrared wavelengths. The limitations of this first approach establish the need, and set the performance baseline, for the realization of photoconductive photodetectors that provide the needed high sensitivity.
2.1 Theory of Photoconductive Photodetectors

A photoconductor typically consists of a semiconducting material, single-crystalline, polycrystalline or amorphous, and two metal contacts to form a two-port electrical device. Upon illumination, the conductivity of the material changes, arising from change in mobility or carrier density or both [35]. Conductivity increase upon illumination is most typically attributed to generation of electron-hole pairs resulting in a carrier density increase. The classification of different types of photoconductive systems generally distinguishes based on the nature of the contacts and the presence or absence of impurity trap states:

- Trap-free material with ohmic contacts: Photoexcitation produces electrons and holes that drift across the material towards the contacts, being replenished when they leave the material at the contact, until recombination occurs. Photoconductive gain \( G \) - defined as the ratio of circulated carriers per absorbed photon - is equal to the sum of the hole and electron gain. \( G = \tau_n/\tau_{\text{trn}} + \tau_p/\tau_{\text{trp}} \), where \( \tau_n \) and \( \tau_p \) are the electron and hole lifetimes and \( \tau_{\text{trn}} \) and \( \tau_{\text{trp}} \) the electron and hole transit times respectively.

- Trap-free material with ohmic contact for electrons and non-ohmic for holes: the electron and hole lifetimes are pinned by the hole transit time and therefore gain \( G = 1 + \tau_{\text{trp}}/\tau_{\text{trn}} \).

- Trap-free material with non-ohmic contacts: the lifetimes of both electrons and holes are simply equal to their transit times and therefore the maximum gain equals to unity.

- Electron trap material with ohmic contacts for holes: Upon illumination, electrons are excited and then captured into trap states, whereas photo-holes are free to traverse the device until recombination occurs. The holes, upon reaching one contact, can be replenished by the other contact, giving rise to photoconductive gain \( G \) equal to \( \tau_p/\tau_{\text{trp}} \). The hole lifetime is equal to the electron lifetime. For recombination to take place then, electron emission from the trap states is required.
The last case of sensitized photoconductive photodetectors has attracted the most attention. Many commercial photoconductors, such as PbS and CdS photodetectors, fall into this category. The devices reported in this thesis are also examples of this type of photoconductors.

The underlying physical mechanism of this type of photoconductivity has been extensively studied [36, 37]. The trap states that contribute to photosensitization, also called sensitizing centres, make a special case of trap states in that they exhibit a disproportionate value of capture cross section for one type of carrier (e.g. electrons) versus the other (e.g. holes). Upon photoexcitation, electrons are captured by these centres whereas holes remain free to traverse the device. The low capture probability for holes prolongs their carrier lifetime. The number of passes of a hole across the device is then equal to the ratio of the carrier lifetime to its transit time, giving rise to photoconductive gain.

A thorough investigation of the implications of this mechanism on the optoelectronic characteristics of such detectors is discussed by Rose [38]. In particular, the effects of the density, energy levels and distribution of the sensitizing centres with respect to speed, dynamic range and gain were studied. The temporal response of a sensitized photoconductor is limited by the carrier lifetimes associated with the sensitizing centers. These are determined by the emission rates of the centres which in turn depend on their energy depths from the band edge as well as their cross sections. Shallow centres yield faster but lower-gain photodetectors, whereas deeper centres lead to higher gain, followed by slower temporal response. Similar, but less pronounced effects have also the cross sections of the traps: Large cross section yields shorter lifetime and thus faster response.

The effect of temperature on device performance has also been studied [39]. Desensitization of the detectors has been observed at elevated temperatures; the photoconductive gain decreases with increasing temperature due to the increasing thermal emission rate from the traps. This is followed by acceleration of the temporal photoresponse.
The dependence of photoconductive gain on the illumination intensity has also been reported to vary depending on the density, the energy depths, and the energy distribution of sensitizing centres [40]. At optical intensities at which the excited carrier density is lower than the trap state density, the photoconductor is considered fully sensitized, resulting in a linear dependence of photocurrent on illumination intensity. With increasing optical power, however, saturation of the sensitizing centers begins, causing a decrease in the photoconductive gain. This decrease is evident by the sub-linear dependence of photocurrent on illumination level.

### 2.2 Photodetector Figures of Merit

A set of figures of merit has been formulated to evaluate various photodetector technologies for sensing applications [41]. These are outlined in the present section.

#### 2.2.1 Responsivity

The concept of responsivity has been introduced to quantify the electrical signal output of the detector per optical signal input. Responsivity $R$ is the ratio of photocurrent to the optical power impinging on the detector and measured thus in A/W. The general expression for responsivity is given by:

$$R = \frac{\eta q \lambda}{hc} \frac{1}{\sqrt{1 + \omega^2 \tau^2}} G$$  \hspace{1cm} (2.1)

where $q$ is the electron charge, $h$ Planck’s constant $c$ the speed of light, $\omega$ the electrical modulation frequency, $\eta$ the quantum efficiency, $\tau$ the time constant and $G$ the photoconductive gain.

The quantum efficiency is defined as the efficiency with which an incident photon results in the excitation of an electron. It is a normalized value and is equal to number of electrons excited divided by the number of photons incident on the detector’s active area.
Typically, quantum efficiency takes into account reflectance, absorbance and scattering and in this case it may be also called external quantum efficiency (EQE). The term internal quantum efficiency has also been defined to take into account solely absorbance and counts the number of generated electrons per absorbed photon. Quantum efficiency follows the absorbance spectrum of the device, rendering responsivity a function of wavelength and temperature. In photoconductive photodetectors, the time constant that determines the 3-dB bandwidth of responsivity is related to the carrier lifetimes introduced by the associated sensitizing trap states. Responsivity thus depends on the electrical modulation frequency at which optical sampling takes place. In the case of multiple time constants associated with multiple trap states each one having a characteristic lifetime equation 2.1 can be rewritten as:

$$R = \frac{\eta \lambda}{hc} \sum_i \frac{a_i \tau_i}{\sqrt{1 + \omega^2 \tau_i^2}} G_i$$  (2.2)

where $G_i$ is the gain arisen from the $i^{th}$ trap given by $\tau_i/\tau_{tr}$, with $\tau_i$ the characteristic lifetime of the $i^{th}$ trap; $a_i$ are the weights expressing the probability of capture of each trap.

Photoconductive gain $G$ yields the number of carriers per absorbed photon that can be gained due to the mechanisms described in the previous section. For electron-trap sensitized photoconductors having ohmic contacts for holes, gain is given by the ratio of the carrier lifetime to the transit time. Gain can be rewritten as $\mu_p \tau_p E/L$, where $\mu_p$ is the hole mobility, $\tau_p$ is the hole lifetime $E$ is the applied field across the device of length $L$. Mobility is sensitive to temperature and for polycrystalline and nanocrystalline solids has been found to increase with temperature. Carrier lifetime is also dependent on the thermal emission rate from the sensitizing traps and thus varies with temperature. Electric field has the potential to influence carrier lifetime via field-assisted trap ionization.

Responsivity describes the electrical signal resultant from a given intensity of illumination. On its own, it provides only a limited view into the sensitivity of a photodetector. Noise in the photodetector must also be taken into account in order to
estimate the signal to noise ratio of the device, which yields the minimum detectable optical power of the detector and thus its sensitivity limit.

2.2.2 Noise in photoconductors

There exist four major sources of noise in photoconductors: Johnson noise, shot noise, generation-recombination (G-R) noise, and $1/f$ noise [41].

**Johnson noise**

Johnson (or Nyquist) noise is the fluctuation in current caused by the thermal motion of carriers in any resistive element. The expression for Johnson noise current is given as:

$$i_n = \sqrt{\frac{4 k T B}{R}}$$  \hspace{1cm} (2.3)

where $k$ is Boltzmann’s constant, $T$ is the temperature, $R$ the resistance of the detector and $B$ is the electrical bandwidth.

**Shot noise**

Shot noise is associated with the dc current flowing across potential barriers. Even though shot noise does not exist in single crystalline photoconductors, it is present in polycrystalline photoconductors when carrier transport takes place along potential barriers. The current noise expression for shot noise is:

$$i_s = \sqrt{2 q I_d B}$$  \hspace{1cm} (2.4)

where $q$ is the electron charge, $I_d$ is the dark current flowing in the device and $B$ is the electrical bandwidth.
G-R noise

Generation-recombination noise results from statistical fluctuation in the rate of generation and recombination of carriers which are generated either by optical excitation or thermal generation. This fluctuation arises from variation in the carrier lifetimes arose from random population and depopulation of trap states. This phenomenon also introduces a random barrier modulation across the charge transport path resulting in excess noise observed in multi-crystalline photoconductors. The current noise expression for G-R noise is:

\[
i_{gr} = 2qG\sqrt{(n_{op} + n_{th})B}
\]

where \( q \) is the electron charge, \( G \) is the photoconductive gain, \( n_{op} \) is the number of optically generated carriers, \( n_{th} \) is the number of thermally generated carriers and \( B \) is the electrical bandwidth. Unlike Johnson and shot noise the power spectrum of which is white, G-R noise spectrum is expected to follow the spectrum of the carrier lifetimes associated with the traps that cause the generation recombination noise.

1/f noise

The spectrum of this noise demonstrates an 1/f dependence and therefore is eminent in lower frequencies. This becomes significant in imaging applications where electrical frequencies associated with imaging lay in the order of some Hz to a few tens of Hz. Excessive 1/f noise is therefore detrimental for imaging as it leads to current drifts that are hard to correct. The origin of this noise is still an open field of study; the magnitude of this noise however is affected by non-ohmic contacts and metal-semiconductor interface trap states. The careful choice of metal contact to ensure good ohmic behavior is, therefore, essential to minimize 1/f noise.
2.2.3 Noise-equivalent power (NEP) and D*

The minimum optical power level a detector can discern depends on the responsivity and the noise level. The signal current produced by the input power must be above the noise level in order to be detected. The signal to noise ratio SNR is given by:

\[
\text{SNR} = \frac{RP}{i_n}
\]  

where \( R \) is responsivity, \( P \) the incident optical power and \( i_n \) is the noise current. The optical power at which the SNR is equal to unity, is the minimum optical power that the detector can discern is called noise equivalent power NEP and is given by:

\[
\text{NEP} = \frac{i_n}{R}
\]  

The disadvantage of using NEP to describe detector performance is that it is specific to detectors having a particular surface area.

The figure of merit D* called normalized or specific detectivity [42] is widely used as a descriptor of detector’s sensitivity that is insensitive to device area. This parameter allows for comparison among detectors of different geometries, thus enabling the evaluation of sensitivity of photoconductive materials rather than specific devices. The expression for D* is given by:

\[
D^* = \sqrt{\frac{A_d B}{\text{NEP}}} = \frac{\sqrt{A_d B R}}{i_n}
\]  

where \( A_d \) is the detector’s area, \( B \) is the electrical bandwidth, \( R \) is the responsivity, \( i_n \) is the noise current and \( \text{NEP} \) the noise equivalent power. The units of D* are cmHz\(^{1/2}\)W\(^{-1}\) or Jones. It can be interpreted as the SNR produced by a detector of 1 cm\(^2\) surface when 1 W of optical power impinges, measured with electrical bandwidth of 1 Hz. Similarly to responsivity, D* is also a function of many parameters: applied bias, temperature,
modulation frequency, wavelength; D* should also then be reported followed by the measurement conditions.

2.3 Prior Art in Solution-Processed Photodetectors

The attractive characteristics of solution processibility have been exploited towards large-area, low-cost, flexible thin-film optoelectronic devices. Photodetectors have thus been reported from conjugated polymers and colloidal nanocrystals. We now present a review of the literature to demonstrate the progress in the field and also to establish the challenges to be addressed in the present work.

2.3.1 Polymer photodetectors

In 1994, Heeger et al. reported the realization of solution-processed photodetectors based on conjugated polymers [43]. The photodiodes consisted of P3OT or MEH-PPV - C60 (fullerenes) composite, spin-coated on an indium tin oxide (ITO) covered glass substrate followed by metal evaporation of the cathode. The devices were sensitive to visible and ultraviolet and demonstrated responsivity of 0.3 A/W across this spectral range. C60 was employed to facilitate extension of sensitivity to 700 nm, but no longer than this. The required applied bias of the device was 10 V. A large-area full-color image sensor based on polymer composites was reported four years later [44]. The active layer consisted of a mixture of P3OT and PCBM to form an interpenetrating bicontinuous network resulting in low dark current (in the order of 10 nA/cm²) and high charge separation efficiency with responsivity up to 0.2 A/W. The spectral response of the image sensor was limited to visible wavelengths. A solution-processed F8T2 polymer-based phototransistor was also reported in 2004 [45] but the reported responsivity was limited to 0.7 mA/W.

A different approach, reported in 2004, was based on dye-sensitized photovoltaic photodetectors to address the near infrared [46]. The device consisted of a nanoporous
TiO$_2$ layer infiltrated with various anionic dyes that acted as the light-absorbing material. The heterojunction was formed at the interface of the dye with TiO$_2$; upon illumination the electrons were extracted through the TiO$_2$ and holes via a CuSCN overlayer used as a hole transport layer. The nanoporous TiO$_2$ was chosen to increase the interface area of the heterojunction leading, thereby, to higher external quantum efficiency. The sensitivity of the device was extended from the visible to near infrared up to 950 nm. The reported responsivity was limited to $\sim$2 mA/W; the sensitivity of the device was reported as $D^* \sim 10^{10}$ Jones.

To overcome the carrier mobility bottleneck in conjugated polymers that limits their temporal response to several tens of $\mu$s, another class of flexible thin-film photodetectors has also been proposed [47]; These are organic-based photodetectors consisting of small organic molecule layers that have been evaporated onto ITO substrates; even though they lack solution processibility, they are promising for higher modulation frequency applications. The reported device consisted of alternating layers of CuPC and PTCBI to form a thin film of 32 nm in thickness. The resultant performance includes responsivity of 0.3 A/W, dark current in the order of $10^2$ nA/cm$^2$ and frequency response of $\sim$400 MHz.

### 2.3.2 Colloidal quantum dot photodetectors

The solution processibility and spectral tunability of colloidal quantum dots render them attractive for their application in photodetectors. Their compatibility with conjugated polymers allows for their integration to form nanocomposites with high interface area. These bulk heterojunctions provide high photon absorption and efficient exciton dissociation followed by charge separation. Upon illumination, excitons dissociate and electrons and holes are transported to the contacts through separate paths within different physical media (polymer and nanocrystals), reducing recombination, thereby increasing extraction efficiency.

A polymer-nanocrystal composite photodetector was reported in 1996 [48]. It consisted of a blend of CdSe or CdS nanocrystals mixed with MEH-PPV. This material system
exhibits a type-II heterostructure wherein electrons are energetically favoured to stay in the nanocrystals, whereas holes are transferred to the polymer matrix. The mixture was spin-coated on an ITO substrate, followed by metal evaporation to form the cathode. The efficiency of exciton dissociation was observed via the quenching of photoluminescence emitted by the nanocrystals. These devices were investigated as photovoltaic photodetectors and the reported quantum was ~12% at zero bias conditions while it reached ~60% at 3 V. The spectral sensitivity of the reported device was limited by the absorption of MEH-PPV and Cd(S, Se) nanocrystals to the visible up to 650 nm.

A different approach based on neat colloidal nanocrystal films was reported in 2000 [49]. Photoconductivity in CdSe quantum dot solids was studied as function of applied electric field and nanocrystal surface passivation. In this device, photogenerated excitons are ionized by the electric field and dissociate into electrons and holes that hop amongst nanocrystals either via quantum dot bound states or surface trap states. In this approach, photocurrent competes with radiative and non-radiative recombination due to the fact that both types of carriers are transported via the same medium. The spectral sensitivity of this device was within the visible range but absolute responsivity values were not reported.

Orders of magnitude increase in photoconductivity was reported [50], from this material system, after post-deposition treatments of ligand exchange on the nanocrystal surface. It was found that shorter ligands were necessary to improve carrier transport among nanocrystals by decreasing inter-nanoparticle spacing. The functionality of the ligand head group was also critical in order to passivate surface recombination states, prolonging thereby the carrier lifetime. Increasing exciton ionization efficiencies were also reported as a result of the ligand modification.

### 2.3.3 Conclusions from literature review

To summarize: Polymer photodetectors have previously been shown to demonstrate promising responsivities; however, their spectral sensitivity is limited to the visible range. Colloidal nanocrystal based photodetectors were reported in the literature but without any
demonstration of the capabilities offered by their spectral tunability. Infrared sensitivity from solution-processed photodetectors has yet to be demonstrated. The performance of the colloidal quantum dot photodetectors has also yet to be recorded and reported relevant to photodetection applications. Finally, there exist no prior reports of solution-processed photodetectors having D* in excess of $10^{10}$ Jones; however, modern imaging applications require at least $10^{12}$ Jones D*.

### 2.4 Solution-Processed Photodetector with Infrared Sensitivity from PbS Nanocrystal – Polymer Composites

We now turn to our own contributions to early efforts aimed at achieving infrared sensitivity from solution-processed photodetectors.

We took the approach of introducing PbS nanocrystals into a conjugated polymer matrix to sensitize the polymer into the infrared. This architecture is based on a photodiode principle of operation wherein photogenerated electrons and holes are extracted by the anode and cathode respectively [51]. The fabrication techniques and the proposed device structure are described, followed by the resultant performance.

#### 2.4.1 Material processing and device fabrication

As synthesized PbS nanocrystals, capped with oleic acid, underwent a ligand exchange to replace the long oleate ligands (comprising an eighteen carbon atom chain) with a shorter molecule in order to shorten the barrier to carrier traversal at the polymer nanocrystal interface. Oleate-capped nanocrystals were precipitated with methanol dried and redispersed in octylamine – a molecule with an eight-carbon-atom chain and an amine head group. The mixture was heated at 70°C for 8 hours and then precipitated with dimethylformamide (a non-solvent for octylamine-capped nanoparticles) in order to remove the detached oleate ligands. The process of exchange was then repeated for
another 8 hours and nanocrystals after the final dimethylformamide precipitation were redispersed in chloroform. The nanocrystals were then mixed with MEH-PPV polymer solution in the same solvent to form a mixture of given weight fraction.

The devices were fabricated as follows: A 40 nm pre-poly(\(\rho\)-phenylenevinylene) (pre-PPV) hole transport layer was spin-coated on 2.5 x 2.5 cm\(^2\) indium tin oxide (ITO) coated glass slide and annealed at 200\(^{\circ}\)C for 3 hours in vacuum for polymerization. A MEH-PPV/nanocrystal blend (80-90% nanocrystal by weight) dissolved in chloroform was spin-coated on the PPV layer to form a film of thickness 100 - 150 nm. Finally, the upper contact was deposited by vacuum evaporation forming a 3 mm\(^2\) metal stack of 150 nm Mg/100 nm Au. The device structure is illustrated in Figure 2.1.

![Device structure of the proposed solution processed photodiode based on MEH-PPV and PbS nanocrystals.](image)

**Figure 2.1**

**2.4.2 Physical mechanism**

MEH-PPV was chosen due to the high hole mobility and the favourable band offset with the PbS nanocrystals that forms a type-II heterostructure. This means that electrons favorably stay confined in the quantum dots whereas holes are energetically favorable to tunnel to MEH-PPV. Upon photoexcitation therefore, electron hole pairs created in the nanocrystals separate and electrons hop amongst nanocrystals to the anode whereas holes are transported via the polymer towards the cathode.
In addition to acting as a hole transport layer, the PPV layer provided a number of improvements over samples with the MEH-PPV/nanocrystal layer deposited directly on the ITO; it provided better electrical stability by forming a smooth and pinhole-free pre-layer on which the blend films could be cast, eliminating catastrophic shorts from the upper contact directly through to the ITO; it decreased the dark current by introducing an injection barrier at the ITO contact, allowing larger photocurrent to dark current ratios; and it allowed a higher bias to be applied to the samples before electrical breakdown, allowing the establishment of a higher internal field, more efficient photogenerated carrier extraction, and consequently higher photocurrents. It was observed that the PPV layer slightly reduced the photocurrent internal quantum efficiency compared to samples without the PPV layer because it also poses a barrier to the extraction of both photogenerated holes in the reverse bias and photogenerated electrons in the forward bias; it will be shown below that the barrier to extracting holes from the active region is less than that for electrons, resulting in higher photocurrent in the reverse bias. However, the PPV layer poses less of an extraction barrier than it does an injection barrier, which allows for the improved photocurrent-to-dark-current ratio. The slight reduction in efficiency was a compromise to obtain low dark current and to maximize the on:off ratio, of critical importance in detection and imaging applications.

Figure 2.2: Dark- and Photo- current-voltage characteristics of the device at different illumination levels. The inset shows the dark current-voltage characteristic of the device.
The dark current and photocurrent are shown as a function of bias applied at the ITO electrode in Figure 2.2. The data were taken using an Agilent 4155C Semiconductor Parameter Analyzer and microprobe station. The optical excitation was provided by a 975 nm CW semiconductor laser. The dark current is 0.216 μA at a bias of 5 V and 0.144 μA at –5 V (Inset of Fig. 2.2). The photocurrent-voltage curves show diode behaviour, with higher photocurrents in the reverse bias. At a bias of -5 V, the photocurrent is 8.43 μA for 2.7 mW incident power and 90.61 μA for 207 mW incident power, which represents a ratio of photocurrent to dark current of 59 and 630, respectively. The above photocurrent under 2.7 mW of illumination power represents a responsivity of 3.1 \times 10^{-3} \text{ A/W}. When ITO is positively biased at 5 V, the photocurrent is reduced to 5.39 and 28.12 μA for incident powers of 2.7 and 207 mW, respectively.

Figure 2.3: Proposed band diagram of the device. Holes are transported through the polymer towards ITO whereas electrons hop among nanocrystals towards Mg.

The asymmetry of the photocurrent I-V curves can be ascribed to the work function difference between ITO (~4.8 eV) and Mg (3.8 eV) and the energy levels of the PPV layer. Figure 2.3 shows a possible band diagram for the structure after the Mg contact has been deposited, and the device reaches the equilibrium state. For this diagram, the lowest energy absorption peak is assumed to be the first excitonic absorption of the PbS nanocrystals. This is used to estimate an increase in bandgap energy relative to bulk PbS, which has a bandgap of 0.41 eV. Because of the nearly equal effective masses for holes and electrons in PbS, it is also assumed that the confinement energy is shared equally in
the conduction and valence bands so the bands move up and down, respectively, by equal energies. The barrier for electrons comes from the octylamine ligand, which passivates the nanocrystal surface, and/or MEH-PPV (ionization energy \( \sim 4.9 \) eV and electron affinity \( \sim 2.9 \) eV [52]), which surrounds the nanocrystal. To align the Fermi level in all layers, the Mg side tilts down and the ITO side tilts up [53]. After an electron in the valence band of the nanocrystal is transferred to the conduction band by absorbing a photon, the hole in the valence band may transfer to the hole conducting MEH-PPV, and the electron can either remain in the quantum dot or move to another nanocrystal by hopping or by tunnelling. Depending on the polarity of the built-in field and/or applied field, the electron and hole can move towards the ITO or towards the Mg. When the electron moves to the ITO side, it will see a higher barrier by the tilted band and PPV (ionization energy = 5.1 eV and electronic affinity = 2.7 eV [54]) than when moving to the Mg electrode. When the hole moves to the ITO, it also faces a barrier between MEH-PPV and PPV, and no barrier if it moves to the Mg side. Reverse bias results in photogenerated holes being extracted through the ITO/PPV side of the sample, while forward bias results in electrons being extracted through that side. Thus, the higher photocurrent in the reverse bias suggests that the electron barrier posed by the PPV may be more severe than the hole barrier in carrier extraction.

2.4.3 Device performance

Figure 2.4 presents the dependence of photocurrent and internal quantum efficiency on the incident power at \(-5\) V bias. The internal quantum efficiency is defined as the ratio of the number of collected charges to the number of absorbed photons at the pump wavelength. The calculation of internal quantum efficiency using absorption values obtained in reflection mode [55], the handling of optical interference effects, and the error bars on these efficiency values are described in detail in the Methods section below. The absorption at the 975 nm wavelength used to obtain the main efficiency points in Figure 2.4 was 12.7\%. It can be seen in Figure 2.5 that the photocurrent does not increase linearly with incident power. Above \(\sim 50\) mW, the photocurrent increases more
slowly with increased power. In the low power region, the recombination of trapped electrons in the nanocrystal network with holes in the neighboring polymer dominates. When more photons are absorbed at higher powers, bimolecular recombination between free holes and electrons occurs, in addition to the recombination of trapped electrons [56]. The additional bimolecular recombination reduces the number of photo-excited carriers and, hence, lowers the internal quantum efficiency as shown in Figure 2.4. At an incident power of 2.7 mW the internal quantum efficiency is about 3%, while at 207 mW the internal quantum efficiency is reduced to about 0.4%.

Figure 2.4: Photocurrent dependence on incident optical power and resultant internal quantum efficiency.

Figure 2.5 shows the absorbance spectrum of the nanocrystals (measured using a Varian CARY 500 Scan Spectrophotometer) used in three different devices, each tuned to a different part of the infrared spectrum, and the measured photocurrent spectral response of each device. No bias was applied to the devices during measurement of the photocurrent spectrum, and the excitation was provided by narrow wavelength bands selected from a white light source by a monochromator. Various filters were used to avoid overtones of the monochromator’s grating from illuminating the sample. At
wavelengths longer than 600 nm, the absorption of MEH-PPV is negligible; thus, all absorption at these wavelengths is assigned solely to the PbS nanocrystals. The absorption peaks at 955, 1200, and 1355 nm correspond to the first excitonic absorption features in the three different choices of PbS nanocrystals. The photocurrent spectra show peaks that match closely the absorption peaks associated with the PbS nanocrystals. Along with demonstrating control over the spectral response, this result adds further evidence that the photocurrent is due to exciton formation in the nanocrystals followed by charge separation. Inset shows the spectral response of the device with the 955 nm response peak and also includes shorter wavelengths where the polymer is also excited.

Figure 2.5: Photocurrent and absorption spectra of 3 devices made of different sized quantum dots. The first excitonic peak of the quantum dots in each device is 950 nm, 1200 nm and 1355 nm. The inset shows the absorption of pure MEH-PPV polymer film relative to the absorption of the polymer nanocrystal blend device and the corresponding photocurrent spectrum.
2.5 Summary

In this chapter we presented a solution-processed photodetector based on PbS colloidal quantum dots and polymer composites. The device operated as a photodiode and exhibited responsivity on the order of $10^{-3}$ A/W. Spectral tunability offered by the PbS quantum dots within the short and near infrared was also demonstrated. The limiting factor of the presented device was the poor transport of electrons among nanocrystals and holes via the polymer. Recombination effects within nanocrystals are also responsible for low charge separation efficiency. Even in the ideal case however the responsivity of such device is limited by the 100% of maximum quantum efficiency in photodiodes.

In the following chapters the main focus of the present work turns to the investigation of photoconductive photodetectors made of pure PbS nanocrystal films. Photoconductors are known to exhibit photoconductive gain and offer promise for high sensitivity photodetector applications.
Chapter 3

Sensitive Solution-Processed Infrared Photoconductive Photodetectors

The previous chapter presented an infrared solution-processed photodetector operating as a photodiode. This was a proof-of-principle demonstration of the first solution-processed infrared photodetector. The reported performance, however, was prohibitively low for practical applications. Photodiodes benefit from pristine crystalline materials, with their performance deteriorating when trap states are present.

Photoconductors, on the other hand, are based on photosensitization via introduction of the appropriate trap states that prolong the carrier lifetime. Herein, we sought to exploit the abundance of surface states on nanocrystalline materials to demonstrate a sensitive solution-processed sensor. The present chapter reports the first sensitive solution-processed photodetector. Specifically, the device provides photoconductivity-based light sensing in the infrared using solution-processed PbS colloidal quantum dot films.

Photoconductive gain posits not only long carrier lifetime but also sufficiently high carrier mobility. In the present chapter, we sought material processing routes that led to simultaneous achievement of high mobility and long carrier lifetime. We report as a result PbS photoconductive photodetectors that provide very high photoconductive gain – responsivities up to 1000 A/W. The origin of this gain is then discussed on the basis of the observed high mobility and the surface oxides grown on the nanocrystal surface. The crucial role of the material processing on the noise performance of the device is then studied. The optimum process that leads to a combination of high gain, low noise and thereby high sensitivity, is finally reported.
3.1 Material Processing and Device Fabrication

3.1.1 PbS nanocrystal synthesis

The synthesis of PbS nanocrystals was carried out in a single, three-neck, round bottom flask using the air/moisture free Schlenk-line technique. The lead precursor was prepared by pumping in vacuum the mixture of lead oxide (PbO) and oleic acid at 80°C for three hours to remove water. The resulting transparent solution of lead-oleate precursor was stirred vigorously while being heated under argon at 150°C for 30 minutes. The stock solution of the sulfur precursor was prepared by mixing bis(trimethylsilylsulfide) (TMS) with octadecene (ODE) in nitrogen-filled glove box and the portion, corresponding to 4:1 Pb:S molar ratio was rapidly injected into the reaction flask. Nucleation occurred instantly, upon injection. The rapid injection is critical to achieve a narrow size distribution. After the injection the temperature dropped down and the heating mantle was kept under the reaction flask to allow for slow cooling.

A typical synthesis of PbS nanocrystals with first excitonic transition between 1200 and 1300 nm involved injecting 10 mL of sulfur stock solution (1.0 mmol of TMS) into the reaction flask containing 4.0 mmol PbO (0.9 g) and 63 mmol of oleic acid at 150°C. The reaction was quenched with the 1:1 volume ratio mixture of anhydrous methanol and ethylacetate when the temperature reached 30-35°C. The mixture of final nanocrystals, side products and initial unreacted compounds was centrifuged. The precipitate was re-dispersed in toluene, re-precipitated again with methanol and centrifuged. Final PbS nanocrystals were dried with nitrogen and re-dispersed in toluene.

3.1.2 Ligand exchange

Oleate-capped as-synthesized nanocrystals yielded films with insulating properties. The ~2.5 nm long ligand - consisting of an eighteen-carbon-atom chain - inhibited carrier transport among the nanocrystals. To improve carrier mobility, a post-synthetic ligand
The ligand exchange process was employed to replace oleic acid with a shorter ligand attachable to the nanocrystal Pb sites. Amines were known to attach to the surface cations of nanocrystals [57]. N-butylamine was, therefore, employed, that consists of a four-carbon-atom chain, of length ~0.6 nm. The ligand exchange process involved precipitation of nanocrystals in methanol (MeOH), drying and redispersion in n-butylamine at a concentration of 100 mg/ml (nanocrystals by weight/butylamine by volume). Nanocrystals were left in the butylamine solution for a period of three days. The ligand exchange was terminated by precipitation with anhydrous isopropanol, drying and final redispersion of butylamine capped nanocrystals in chloroform for device fabrication. The whole process took place under inert atmosphere to prevent oxidation. The ligand exchange as shown in the inset of Figure 3.1 led to a dramatic decrease in inter-nanoparticle spacing compared to oleate-capped nanocrystals.

Figure 3.1: Absorption spectra of as-synthesized nanocrystals, butylamine capped and subsequently methanol soaked for necking. Z-contrast TEM images of PbS nanocrystals before and after ligand exchange are shown in the inset.
Chemically, the ligand exchange was confirmed using Fourier transform infrared spectroscopy (FTIR). FTIR is a powerful tool, in organic chemistry, that identifies covalent chemical bonds from their specific vibrational frequencies [58]. These frequencies depend on the length of the bond, and the mass of the atoms at either end of it; thus, the frequency of the vibrations can be associated with a particular bond type (see Appendix A for FTIR principle of operation). A Bruker Tensor 27 FTIR spectrometer was used for the FTIR measurements.

Figure 3.2 illustrates FTIR spectra of the neat solvent $n$-butylamine, the neat solvent chloroform and $n$-butylamine-exchanged nanocrystals dispersed in chloroform. The measurements were taken by placing the solutions in a KBr (potassium bromide) cavity, which is transparent to the wavelengths of interest. N-H stretching and bending vibrations are tabulated to lie between 3200-3600 cm$^{-1}$ and 1450-1650 cm$^{-1}$, respectively. Carbonyl stretching vibration of pure oleic acid is tabulated to be found at 1712 cm$^{-1}$ [59]. The
results indicate that oleate ligands originally attached to PbS nanocrystals have been replaced by \textit{n}-butylamine, indicated by the absence of a carbonyl stretching vibration, a significant shift of the N-H stretching vibrations after exchange from 3294 and 3367 cm\(^{-1}\) (\(\Delta = 73 \text{ cm}^{-1}\)) for \textit{n}-butylamine to 3610 and 3683 cm\(^{-1}\) (\(\Delta = 73 \text{ cm}^{-1}\)), and the presence of N-H bending vibrations for the \textit{n}-butylamine exchanged sample [59].

3.1.3 Device fabrication

Photoconductive devices were fabricated by spin-coating butylamine exchanged nanocrystals to form a solid state film on a pre-patterned interdigitated gold electrode structure, as shown in Figure 3.3. The active area of the detector is determined by the 3 mm length of the electrodes and their 5 \(\mu\)m gap spacing. The detector can be illuminated from the bottom through the glass substrate or from the top onto the nanocrystal film. The thickness of the film can be controlled by the rotation speed of the spin-coating and the viscosity of the nanocrystal solution. The film thickness for the devices investigated herein was approximately 800 nm. Gold was chosen for electrode due to its ohmic contact for holes to the nanocrystal solid. This is critical in achieving photoconductive gain in such devices and is discussed in detail in section 3.6.
3.1.4 Nanocrystal necking

Carrier transport in nanocrystal solids takes place via a thermally activated hopping mechanism [60]. A determining parameter for the transport in these materials is the inter-nanoparticle distance. The hopping probability depends exponentially on the inter-nanoparticle spacing. High mobility thus mandates for nanocrystal close-packing [61].

A method to reduce inter-nanoparticle spacing of oleate-capped nanocrystals via a solution phase ligand exchange was described in Section 3.1.2. Further reduction of nanocrystal spacing, however, is desirable in order to further increase mobility in these films and therefrom shorten the transit time of majority carriers.

![FTIR spectra of butylamine capped nanocrystals and Neck-then-oxidize nanocrystals](image)

Figure 3.4: FTIR spectra of butylamine capped nanocrystals and Neck-then-oxidize nanocrystals show the significant decrease in absorption of peaks correlated with C-C and N-H bonds suggestive of organic molecule (ligand) removal from the nanocrystal film.
In order to detach any organic ligands from the nanocrystal surface and cause the nanocrystals to sinter, the devices were dipped in a methanol solution. In this thesis, this process is referred to as nanocrystal necking. Methanol is an aggressive non-solvent for the nanoparticles, which, due to the high polarity, removes ligands from their surface. In order to verify the loss of organic ligands from the nanocrystal surface, FTIR spectra were taken before and after nanocrystal necking. Butylamine capped nanocrystal films were deposited on GaAs substrates and measured. Subsequently they were soaked in methanol, dried and measured again. GaAs was used as the substrate to provide transparency in the wavelengths of interest. Figure 3.4 shows the decrease in the peaks related to C-C bonds, as well as the peaks associated with the N-H bonds in butylamine. As it will be shown in section 3.2.1, the loss of ligands is followed by increase of dark and photo-conductivity. This is suggestive of mobility increase due the fact that dark conductivity and photoconductivity are linearly related to majority carrier mobility and majority carrier concentration.

3.2 Photodetector Optimization

For sensitive photodetection, there are two prerequisite features: high photoconductive gain and low noise. Photoconductive gain expresses the number of electrical carriers circulated in the circuit per absorbed photon. This figure of merit determines the detector’s ability to respond to light and is a crucial parameter for high sensitivity at a given noise level. The physical parameters that affect gain in a photoconductor are the minority carrier lifetime and the majority carrier transit time. For a sensitizing center characterized by a given carrier lifetime, therefore, increase in majority carrier mobility leads to higher photoconductive gains. In nanocrystal solids, transport takes place amongst nanocrystals via hopping. High mobility can, thus, be achieved by decrease of the inter-nanoparticle spacing.

Increase in carrier lifetime in a photoconductor, also called photosensitization, can be achieved by introduction of sensitizing centres that trap one type of carriers but not the other. Previous studies in bulk PbS photoconductors have shown that photosensitization
of PbS is followed by oxidation, and in particular formation of lead sulfates (PbSO$_4$) [62 - 65]. These oxide species act as sensitizing centers that prolong the minority (electron) carrier lifetime allowing holes to transverse the device within this carrier lifetime.

Noise in photoconductors is determined by generation-recombination and shot noise. There have been reports, however, of excess noise, observed in polycrystalline photoconductors [66, 67]. This excess noise is introduced by carrier transport along barriers formed at the interfaces of polycrystalline materials. These barriers that are randomly modulated by generation-recombination of thermal or photoexcited carriers cause excess noise superimposed to the shot and G-R noise components.

We sought therefore material processing routes that yield high carrier mobility and long carrier lifetime in order to achieve high photoconductive gain. This, however, must be achieved without compromising the noise performance of the device. We studied therefore the effect of the sequence of the oxidation step on the noise current, in order to minimize the excessive noise. We fabricated and studied, thus, the following four classes of devices:

1. **Butylamine capped**: Devices made of butylamine exchanged nanocrystals.

2. **Neck-then-oxidize**: Devices made of butylamine exchanged nanocrystals followed by necking using methanol treatment.

3. **Neck-then-over-oxidize**: Devices made as neck-then-oxidize followed by further oxidation by annealing the devices in ambient atmosphere at 120$^\circ$C.

4. **Oxidize-then-neck**: Devices made of butylamine exchanged nanocrystals that had been exposed to ambient conditions during the final steps of the ligand exchange so that oxidation takes place at this stage. The devices were then treated with methanol for necking.
Figure 3.5: XPS spectra of (a) S2p peak and (b) Pb4f peak of nanocrystal films along the various material processing stages.
3.2.1 Material analysis studies

The surface chemistry modification of nanocrystals, along the various processing stages, was monitored by X-ray photoelectron spectroscopy (XPS) and FTIR.

XPS is a technique used to analyze the surface chemistry of a material by measuring the binding energy of electrons emitted from the surface upon intense X-ray irradiation [68]. The basic principle of operation of XPS is given in Appendix A. For XPS measurements, nanocrystal films were deposited following the same manufacturing process used for device fabrication. Films were deposited on gold over-coated silicon substrates and transferred to the XPS chamber for measurement. XPS measurements were conducted using a PHI 5500 ESCA system. The XPS spectra were generated by an Al Kα source with photon energy of 1486.6 eV and were recorded at a photoelectron take-off angle of 45° to enhance surface sensitivity. The analysis area was around 0.5 mm² and the depth from the surface of around 6 nm.

Figure 3.5a illustrates the S2p3/2 peak from XPS of the films investigated herein. After background subtraction the binding energy was referenced to the C1s hydrocarbon line at 285.0 eV. The curves were fitted by applying Gaussian-Lorentzian functions and the atomic ratios were obtained by integrating the areas under the signals. The nanocrystals immediately after exchange to butylamine ligands (Butylamine-capped) demonstrate a S²⁻ peak at 160.7 eV corresponding to lead sulfide (PbS) [69, 70], whereas no measurable lead sulfate (PbSO₄) signal could be detected. Nanocrystals that were precipitated in air (oxidize-then-neck) exhibit an SO₄²⁻ at 167.5 eV characteristic of PbSO₄ formation [69, 70]. The ratio of PbS/PbSO₄ for this case was found 3.4:1. XPS of the inert-precipitated nanocrystals after methanol soaking (neck-then-oxidize) exhibits also formation of lead sulfate. The PbS/PbSO₄ ratio in this case was 18.6:1. Further annealing of this film in air at 120°C for 1 hour (neck-then-overoxidize) dramatically increased the amount of sulfate to a ratio of PbS/PbSO₄ of 2.4:1. In Figure 3.5b the Pb4f signal is also presented to corroborate the analysis from S2p signal. The peak at 137.7 eV corresponds to PbS [69, 70] whereas the peak around 138.6 eV is characteristic of PbSO₄ [69, 70]. Figure 3.5b confirms the absence of sulfates in butylamine-capped NCs (nanocrystals), whereas increasing amount of sulfates is found following methanol soaking (neck-then-oxidize)
and further oxidation via annealing (neck-then-oxidize). Pre-oxidized nanocrystals (oxidize-then-neck) also demonstrate sulfate existence in the Pb4f peak analysis.

For FTIR studies films were deposited and treated identically to films used for XPS measurements. The FTIR spectra of exchanged nanocrystals precipitated in inert conditions (butylamine-capped NCs) and precipitated in air-ambient conditions (pre-oxidized NCs) are plotted in Figure 3.6; the inert-precipitated exchanged nanocrystal film after two hours of methanol wash (neck-then-oxidize NCs) is also plotted. The broad feature around 1147 cm\(^{-1}\) is attributed to PbSO\(_4\) [59]. The spectra show that exchanged nanocrystals precipitated in inert do not exhibit this feature; methanol wash introduces some oxidation; Exchanged nanocrystals precipitated under an air ambient show evidence of strong oxidation. These results agree with the XPS data presented.

![FTIR spectra](image)

**Figure 3.6:** FTIR spectra of butylamine capped, neck-then-oxidize and oxidize-then-neck NCs show the growth of PbSO\(_4\) at 1147 cm\(^{-1}\).
3.2.2 Dark and photo conductivity studies

Films made of as-synthesized, capped with oleic acid, nanocrystals were insulating due to the suppression of carrier transport by the long oleate ligand. A ligand exchange was, therefore, performed to increase mobility. After ligand exchange, the film exhibited measurable conductivity and the carrier density reached 0.73 mA/cm$^2$ at 100 V of bias. This is shown in Figure 3.7. Responsivity of this device was also measured 27.7 A/W at 100 V, as shown in Figure 3.8. The experimental methods of dark- and photo-conductivity measurements can be found in Appendix B.

![Figure 3.7: Dark current density as a function of applies bias of photoconductive devices.](image)

Further reduction of inter-nanoparticle spacing was sought by methanol soaking to remove butylamine ligands and cause nanocrystal necking. Figure 3.7 shows that, upon nanocrystal necking, dark current density increased to ~40 mA/cm$^2$ (a fifty-seven-fold increase) followed by an increase in responsivity of two orders of magnitude to 2700
A/W. The combined increase of both dark current density and gain following nanocrystal necking can therefore be attributed to an increase in mobility, since both dark and photo current are linearly related to mobility. Mobility increase, using MeOH and NaOH treatments, in CdSe nanocrystal films has also been reported [71]. The fact that responsivity increased more than the dark current density also suggests that methanol soaking promoted sensitization by formation of oxide species. This is in agreement with the observations from XPS of increasing sulfates after methanol soaking.

Figure 3.8: Responsivity as a function of applied bias of photoconductive devices measured at a wavelength of 975 nm and light intensity of 300 nW/cm$^2$.

To study the effect of the degree of oxidation on responsivity the device was oxidized further by annealing in ambient conditions (neck-then-oxidize). This led to a decrease in both responsivity and dark current density by a factor of ~1.6 which is suggestive of lower mobility. It can be accounted for by the significant formation of sulfates on the nanocrystal surface that effectively act as barriers and also decrease the
content of semiconducting PbS at the cost of the insulating oxide PbSO₄. The linearity of the current voltage characteristics, however, is preserved along the process of oxidation indicating that the hopping phenomenon in both cases is not field activated.

Unlike the aforementioned cases, the dark current voltage characteristic indicates a field-activated transport mechanism when nanocrystals had been exposed to oxygen prior to film formation and necking (oxidize-then-neck). The superlinear behaviour, shown in Figure 3.7, is believed to result from carrier transport limited by potential barriers formed by the oxides. When oxidation takes place prior to film formation and necking, it leads to barriers formed randomly on the nanocrystal surface. Upon necking then, these potential barriers can be found at the points of nanocrystal necking along the carrier transport path (Table 3.1). In the case of neck-then-oxidize NCs, however, oxidation takes place at the exposed nanocrystal surface sites. It should be noted that in the case of oxidize-then-neck NCs, responsivity was as high as $10^3$ A/W, lower by a factor of three compared to the neck-then-oxidize class of devices. The above findings suggest that the sequence of necking and oxidizing does not play a significant role in the responsivity performance of

<table>
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<tr>
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<th>Original NCs (Oleate-capped)</th>
<th>Exchanged NCs (Butylamine-capped)</th>
<th>MeOH washed NCs (Neck-then-oxidize)</th>
<th>Pre-oxidized + MeOH washed NCs (Oxidize-then-neck)</th>
</tr>
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<tbody>
<tr>
<td>R (A/W)</td>
<td>-</td>
<td>40</td>
<td>2700</td>
<td>1200</td>
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<tr>
<td>D* (Jones)</td>
<td>-</td>
<td>$10^{12}$</td>
<td>$10^{13}$</td>
<td>$10^{11}$</td>
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Table 3.1: Nanocrystal ordering and device performance as a function of the sequence of necking and oxidation treatments.
In the following section, we investigate the effect of the sequence of the treatments on the noise current of the device, in order to identify the process that yields the highest sensitivity.

### 3.2.3 Noise current and sensitivity studies

In the previous section, the responsivity before and after necking and oxidizing was presented. Even though a significant increase in responsivity was reported after necking, no dramatic variations in responsivity have been found between devices that were oxidized before and after necking. A photodetector is ultimately characterized by its sensitivity. The noise current of the devices must be known in order to calculate the specific detectivity. The noise current was, thus, measured in order to investigate the effects of oxidation and barrier formation on the noise performance. The sequence of oxidation and necking processes was also considered in the optimization of noise performance. The details of the noise measurement technique are given in Appendix B.

The measured noise current densities of the devices as a function of the dark current, which is the determinant factor of noise in photoconductors, are illustrated in Figure 3.9. This representation allows to cross-compare the devices by their deviation from the lower limit determined by the shot noise. The noise measurement took place at a modulation central frequency of 30 Hz, which is relevant to imaging applications.

By comparing the noise of the three classes of devices of butylamine capped, neck-then-overoxidize and oxidize-then-neck, it is evident that electronic barriers contribute to high noise currents. The potential barriers in the butylamine-capped-nanocrystal case are due to the ligands, whereas in the other two cases, barriers are formed by the surface oxides as confirmed by XPS data. Devices of neck-then-overoxidize nanocrystals, however, showed lower noise levels than the oxidize-then-neck nanocrystal devices, albeit they contained larger amounts of oxides. The oxidation step in the fabrication process is thus of critical importance in the noise performance of the device. The best performing device approached the minimum shot noise limit within 3 dB. The Johnson
The noise limit for the best performed device is also plotted showing no significant contribution to the total measured noise current.

Figure 3.9: Measured noise current as a function of measured dark current. The Johnson noise limit and the shot-noise limit, of the best-performing device (neck-then-oxidize) are also plotted for comparison.

The investigation of noise current dependence on the electrical frequency can provide insights into the modulation lifetimes of the associated barriers that contribute to noise [66]. There have been many reports that associate excess low-frequency noise attributable to trapping and de-trapping of carriers that increase the generation recombination noise [66, 67]. Figure 3.10 illustrates the noise current density as a function of frequency, taken at an applied bias of 40V to ensure dark current uniformity across devices. All devices demonstrated noise components at low frequencies. One noise component demonstrates $1/f$ behaviour, whereas a second component arises with a characteristic onset frequency of ~ 50 Hz. Lifetimes associated with the generation recombination noise can then be assumed to lie in the low frequency regime from few seconds up to tens of ms.
Figure 3.10: Noise current spectrum for three classes of devices: neck-then-oxidize, neck-then-overoxidize and oxidize-then-neck.

In order to present the best performing photoconductive device, responsivity and noise current should be jointly taken into account to yield specific (or normalized) detectivity $D^*$. Normalized detectivity is measured at a modulation frequency of 30 Hz, considering responsivity at wavelength of 975 nm. Figure 3.11 presents $D^*$ of the devices described in the previous sections as a function of applied bias. Detectivity decreases with increasing bias as the noise current increases more dramatically with bias than responsivity. The most sensitive device belongs to the neck-then-oxidize class of materials whereas the less sensitive one is the device that had undergone oxidation prior to necking (oxidize-then-neck). The best performing device demonstrates a $D^*$ on the order of $10^{13}$ Jones, which is roughly an order of magnitude higher than the best epitaxially grown InGaAs photodiodes [41], at modulation frequencies relevant to imaging applications.
3.3 Optoelectronic Characteristics

For most practical applications two important features need to be known: the responsivity and sensitivity of the device at different wavelengths and modulation frequency. The wavelength dependence determines the applicability of the photodetector for an application addressing a particular spectral window, whereas the frequency dependence defines the sampling rate - or frame rate for imaging – that can be achieved.

The photocurrent spectrum was measured for the best performing class of devices. Experimental details of the spectral photocurrent measurements may be found in Appendix B. The responsivity and resultant detectivity, as a function of wavelength, are illustrated in Figure 3.12. The photocurrent spectrum follows the absorption spectrum of nanocrystals covering a broad wavelength range from ~1.5 μm towards the visible. The
The spectral response of the device is suited for night vision and biomedical imaging applications addressing the 800 – 1400 nm spectrum with high sensitivity of $D^*$ greater than $10^{13}$ Jones. The responsivity and detectivity reported in Figure 3.12 are taken with an applied bias of 40 V and modulation frequency of 30 Hz, relevant to imaging applications.

![Figure 3.12: Spectral responsivity and detectivity of the solution processed PbS quantum dot photodetector.](image)

The modulation frequency response is shown in Figure 3.12, where responsivity is plotted as a function of modulation frequency considering a bias of 40 V and wavelength of 1300 nm. The device exhibits an effective 3-dB bandwidth of ~18 Hz. Despite the low 3-dB bandwidth, however, the high responsivity yields $D^*$ greater than $10^{12}$ Jones for modulation frequencies up to 500 Hz.

The temporal response of the device is limited by the minority carrier lifetime [37]. The latter is determined by the lifetime of the electron traps that act as sensitizing centres. Sensitizing centres corresponding to trap states of different energy depths are expected to
reflect into photocurrent decays with different time constants. The effective 3-dB bandwidth indicates an effective time constant of 55 ms. The non-flat response at lower frequencies, however, suggests the existence of photocurrent transient lifetimes in excess of hundreds of ms. Temporal photocurrent response exhibited a multiplicity of time constants associated with the lifetimes of sensitizing centres with a range from multiples of seconds to a few ms.

Figure 3.13: Responsivity and detectivity of the photodetector as a function of modulation frequency.

The devices were measured under ambient conditions. The device performance was not found to change in the course of hours within which the full characterization took place. Dark currents, in particular, increased within 10%, whereas responsivity varied within less than 5%. Storage of the devices in ambient for a period of up to three days led to an increase in responsivity and dark conductivity by ~50%, whereas extensive storage of the
device in ambient conditions led to progressive decrease of dark conductivity and responsivity by a factor of two. Even though significant changes in responsivity after extensive exposure of the device in ambient conditions were not observed, the noise current was found to dramatically increase by an order of magnitude upon storage in ambient for a period of a week. In contrast, no performance variation greater than 10% was observed when the devices were transferred into inert nitrogen atmosphere and stored therein for a period of up to two months.

3.4 Investigation of the Physical Origin of Gain

Photoconductive gain in bulk PbS photodetectors arises from photo-electron trapping in long lived states which effectively increases the hole lifetime. Holes are then allowed to transverse the device a number equal to the ratio of the lifetime over the transit time. Devices with different electrode work functions have been fabricated in order to investigate the validity of this model in the case of PbS quantum dot photodetectors. It was found that when gold and platinum electrodes were used with work functions of ~5 eV and 5.7 eV respectively photoconductive gain was observed. These metals provided ohmic contacts to the valence band of the nanocrystal film, allowing for hole replenishment.

Tungsten was chosen as a low work function metal. The work function is 4.5 eV, which is matched to the conduction band of the PbS nanocrystals. Tungsten electrode devices exhibited responsivities in the order of 0.1 A/W, indicating absence of photoconductive gain. This was a result of the non-ohmic contact for holes required for hole replenishment. The temporal response of the device in this case was not limited by the electron trap lifetimes, fast response with a time constant in the order of ~4 ms was observed. This confirms that having ohmic contacts for the majority carriers is of critical importance in achieving gain.

Time-of-flight measurement was also employed to estimate the transit time of holes across the device. The experimental methodology of the time of flight measurement is presented in Appendix C. The hole mobility was measured in the order of ~10^{-3} cm^2/Vs.
For the applied bias used in the photodetector devices, this value for mobility yields a hole transit time on the order of 5 μs. The ratio of the effective carrier lifetime to the transit time yields a photoconductive gain of 10000. Observed gains in the order of 2700 can then be accounted for considering an absorbance of 0.3.

3.5 Summary

In this chapter we reported the first sensitive solution-processed photodetector. The device operated in the short-wavelength infrared, a spectral regime of interest in night vision and biomedical imaging applications. We presented material processing routes that led to a simultaneous achievement of high photoconductive gain and low noise. Chemical surface modifications essential to increasing the carrier mobility were demonstrated for the first time in nanocrystal photodetectors. The importance of oxidation to the photosensitization of the material was also discussed. The simultaneous achievement of photosensitization and high mobility were the key factors to reporting photoconductive gain in the order of thousands A/W.

The sequence of the material processing was found to be crucial to the optimization of sensitivity. We exploited the solution processibility and surface control offered by colloidal nanocrystals to suppress excessive noise existent in most polycrystalline photodetectors. This study led to the report of D* on the order of $10^{13}$ Jones. This represents an order of magnitude improvement over the best performing single crystalline InGaAs photodiodes [41] and a three-order-of-magnitude improvement over the best previous soft-matter results [46].
Chapter 4

Sensitive Solution-Processed PbS Quantum Dot Photodetectors in the Visible

In Chapter 3, we demonstrated the first sensitive solution-processed photodetector. The device’s performance in the infrared wavelengths relevant to night vision and biomedical imaging applications provided added utility and novelty.

In contrast, sensing in the visible is central to mainstream imaging and video applications. The promising performance reported in Chapter 3 motivated the work of this chapter; herein we exploit the quantum size effect offered by quantum dots to demonstrate a visible solution-processed PbS colloidal quantum dot photoconductive detector.

The behaviour of matter in the nanoscale imposed both opportunities and challenges that invalidated mere extrapolation of the existent material processing routes towards the development of visible-only PbS quantum dot photodetectors. In the present chapter we present these challenges along with the solutions that lead us herein to a sensitive solution-processed PbS quantum dot photodetector. The solution processibility combined with spectral tunability, offered by colloidal quantum dots, is then exploited to demonstrate a multispectral photodetector promising for monolithic integration. Detailed description of the optoelectronic performance of the proposed device is given and particular emphasis is placed upon the effects of the sensitizing centres on dynamic range and frequency response. An investigation of the sensitizing centres and their energy levels responsible for the high photoconductive gain in this material then follows. This allows us to introduce and exploit the concept of trap-state engineering for faster photodetectors.
4.1 Material Processing

4.1.1 Synthesis of PbS nanocrystals to address the visible spectrum

In view of PbS small (0.4 eV) bandgap, a very high degree of quantum confinement is required to make a visible-only photoconductive detector in this material system. The synthetic procedure of previous reports was thus modified in order to synthesize small enough quantum dots so that their absorption onset would be below 800 nm.

A typical synthesis of PbS nanocrystals with an excitonic peak between 700 nm and 800 nm involved injection of 2.0 mmoles of bis(trimethylsilylsulfide) into the reaction flask containing 4.0 mmol of lead oxide (0.9 g), 9.5 mmol of oleic acid (2.67 g), and 18.8 mmol of octadecene (4.73 g) at 80°C. After the injection the reaction was quenched by moving the flask to the ice-water bath. The synthesis was carried out under inert conditions using a Schlenk line. The final PbS oleate-capped nanocrystals were isolated from any remaining starting materials and side products by precipitating with acetone. The precipitate was then redissolved in toluene and precipitated again with acetone. The final nanocrystals were redispersed in toluene for storage and device fabrication. Figure 4.1a illustrates the absorption spectrum of the resultant quantum dots. As seen in Figure 4.1b, the nanoparticles have diameters of 2-3 nm and exhibit faceting.

4.1.2 Solid-state ligand exchange

As synthesized, these nanocrystals were stabilized with oleic acid, a configuration expected and observed to impede carrier transport due to the oleate ligand’s long insulating chain. We had previously found that exchanging to shorter ligands such as butylamine resulted in a dramatic increase in conductivity. In the case of larger (4-6 nm in diameter) nanoparticles, monodispersity and excitonic features were preserved after ligand exchange in solution phase. In the small nanocrystal case, however, the procedure led, instead, to the formation of nanostrings (Figure 4.1c) as previously seen for PbSe.
nanoparticles [72]; and, more problematically, a loss of an abrupt absorption onset (dashed curve, Figure 4.1a) resulting from irreversible aggregation.

Figure 4.1: (a) Absorption Spectra of PbS nanocrystals as-synthesized and after solution phase butylamine ligand exchange, (b) TEM graph of as-synthesized PbS nanocrystals, (c) TEM graph of solution phase butylamine ligand exchanged PbS nanocrystals.
We sought for an approach that would instead preserve a sharp, short-wavelength absorption onset in order to address the selectively the visible part of spectrum. It was hypothesized that ligand exchange in the solid state, performed once thin films had already been formed, would limit the number of nanocrystal reattachment sites and dramatically improve conductivity without dramatically altering quantum-confined energy levels. PbS nanocrystals dispersed in toluene were spincoated onto glass substrates with gold interdigitated electrodes with a 5 μm spacing (as described in chapter 3) to form a solid state film. The optically active area of the detector is determined by the inter-electrode distance (5 μm) and the electrode length (3 mm). The film was then treated in a mixture of butylamine in acetonitrile over two days in an inert nitrogen atmosphere.

Figure 4.2 shows photocurrent spectra of solid-state ligand exchanged devices for different concentrations of butylamine to acetonitrile of 20%, 30% and 40%. Figure 4.2 also illustrates the photocurrent spectrum of a device made from solution phase ligand exchanged nanocrystals. The photocurrent spectra have been normalized to allow for cross-comparison. The photocurrent spectrum of the solution phase ligand exchange nanocrystal devices follows closely the absorption spectrum and extends well into the infrared spectrum. The solid-state ligand exchange nanocrystal devices exhibit progressive expansion of their photocurrent spectrum to the infrared with increasing concentration of butylamine during the ligand exchange. This is suggestive of nanocrystal transformation into nanorods in the presence of high levels of butylamine, even in solid state.

Photoconductivity measurements showed that the solid-state exchange process yielded devices with comparable responsivities, whereas the liquid phase exchange devices yielded typically responsivities higher by a factor of three compared to the solid-state exchange devices. This could be attributed to higher carrier mobility reached in the nanorods compared to quantum dots. Solid-state exchange devices with a concentration of 10% butylamine in acetonitrile were also fabricated and tested to show, however, deteriorated performance with low responsivity and low conductivity, as indication of poor ligand exchange. Untreated samples or samples treated with acetonitrile alone (used as control samples) did not exhibit measurable conductivity.
4.2 Optoelectronic Characteristics

The solid-state ligand exchange device with 20% concentration of butylamine combines high responsivity and sharp absorption onset and was therefore chosen for further investigation of the optoelectronic characteristics. Following this solid-phase ligand exchange, the film exhibited conductivity with dark current density $600 \, \mu\text{A cm}^{-2}$ at applied field of $20 \, \text{V \mu m}^{-1}$, where the current density was calculated by assuming a cross section of film thickness of $360 \, \text{nm} \times 3 \, \text{mm}$. The responsivity reached $\sim 110 \, \text{A/W}$ at 100 V bias at wavelength 400 nm and modulation frequency of 15 Hz.
Figure 4.3: Dark current density and responsivity as a function of applied bias for the 20% solid-state ligand exchange device.

Figure 4.4 exhibits spectral responsivity and normalized detectivity. The photoconductive gain reaches a maximum at wavelength 400 nm of $\sim 113 \text{ A W}^{-1}$ at 15 Hz. The quantum dot photodetector has an increasing responsivity at shorter wavelengths and optimal response in the visible part of spectrum. The electric field, required to achieve this gain, was $20 \text{ V \mu m}^{-1}$, which for the $5 \text{ \mu m}$ inter-electrode gap translates to an applied bias of 100 V. The inset shows the noise equivalent power which is the minimum power than can be detected by the detector with active area of $0.0015 \text{ mm}^2$, corresponding to a signal-to-noise ratio equal to unity.

The responsivity of these devices arises from the product of absorbance with photoconductive gain. The absorbance of this device was measured in the visible to be 0.2. Photoconductive gain arises from sensitization of PbS quantum dots with electron trap states that prolong the hole carrier lifetime, as discussed in detail in Chapter 3. According to Figure 4.5a, the 3-dB bandwidth of the device is 8 Hz which corresponds to an effective lifetime of 125 ms. A measured value of gain on the order of hundreds is consistent with a transit time in the hundreds of microseconds, in turn consistent with a mobility of order $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.
Figure 4.4: Spectral responsivity and normalized detectivity. The inset shows the spectral noise equivalent power.

Figure 4.5a illustrates the noise current spectrum. At low frequencies noise current density follows closely the responsivity curve, suggesting that the carrier traps responsible for high-gain also contribute to noise. Noise current approaches a white-noise figure at higher frequencies. The Johnson noise of the detector is estimated by $(4kTb/R)^{1/2}$ to be $\sim 0.9$ fA Hz$^{1/2}$ whereas the shot noise limit $(2qIdB)^{1/2}$ is found 0.04 pA Hz$^{1/2}$ where $k$ is Boltzmann’s constant, $T$ the temperature, $R$ the resistance of the detector in dark, $B$ the noise bandwidth, $q$ the electron charge and $Id$ the dark current. Our detector approaches the shot noise limit to within 3-dB at 80 Hz.

The resultant D* is plotted as a function of frequency in Figure 4.5b (the inset also illustrates the dependence of noise equivalent power to modulation frequency). At low frequencies ($< 5$ Hz), the detector exhibits D$* \sim 10^{13}$ Jones. This photoconductive device, though it exhibits higher dark current than sensitive photodiodes, achieves excellent sensitivity by virtue of its low noise current. The bandwidth is limited by long-lived sensitizing electron traps that provide gain.
Figure 4.5: Optoelectronic characteristics as a function of modulation frequency taken at 400 nm and 100 V bias. (a) Responsivity and noise current density demonstrate similar dependence on modulation frequency. (b) D* versus modulation frequency plot exhibits high sensitivity for frame rates relevant to imaging; Inset shows the NEP as a function of frequency.
4.3 The Effects of Sensitizing Centers on Optoelectronic Performance

The gain observed in sensitized photoconductors is due to sensitizing centres that prolong the carrier lifetime, which, in turn, determines the temporal response. This principle of operation influences the magnitude and temporal behavior of photoresponse with variation in the illumination level. The proportion of photo-activated sensitizing centers determines the effective responsivity and temporal response at a given optical intensity. Each sensitizing center has a specific energy depth that determines the lifetime and therefrom the gain. The number of occupied sensitizing centers affects therefore the total responsivity and temporal response of the detector. The deeper trap states dominate the photoresponse at low optical intensities, resulting in slower temporal response and higher gain. Increasing illumination causes saturation of the deeper trap states followed by population of shallower centers. This reflects as an effective decrease of responsivity and acceleration of photocurrent decay with increasing illumination.

Figure 4.6: Modulation frequency response of the detector at different impinging optical power levels at illumination wavelength of 630 nm.
Further investigation of the effect of the trap states, in quantum dot photodetectors, on the optoelectronic characteristics of the device, was sought. In particular frequency response and responsivity, two features of practical interest, are measured at various optical intensities. The experimental setup used to investigate the effect of illumination intensity on the frequency response and responsivity is described in Appendix B.

Figure 4.6 illustrates responsivity as a function of modulation frequency for a number of different optical power levels incident on the device. The decrease of responsivity with increasing optical power originates from filling of the lowest-lying, longest-lived trap states that provide the highest photoconductive gain at low intensities. As intensity increases the effective responsivity drops as a result of increasing contribution in photocurrent from the shorter-lifetime shallower sensitizing centers. The 3-dB bandwidth increases from ~8 Hz at 5 nW/cm² to ~17 Hz at 60 nW/cm² and beyond 300 Hz at 6 mW/cm². The 3-dB bandwidth increase is followed by a two-order-of-magnitude decrease in responsivity. This phenomenon can provide detector the ability of self-limiting gain mechanism to avoid electronic saturation at high optical power.

A significant figure of merit in photodetectors is dynamic range that expresses the intensity range within which the detector can distinguish among different optical intensities. Dynamic range is given as $20\log(P_{\text{max}}/P_{\text{min}})$, where $P_{\text{max}}$ is the maximum impinging power before saturation – a condition where photocurrent ceases to increase with increasing optical power; $P_{\text{min}}$ is the minimum detectable optical power – or NEP.

In order to characterize the impact of high-gain trap state filling on the dynamic range of the detector, we measured the dependence of photocurrent on optical intensity at a modulation frequency of 30 Hz. We observed a monotonic, though at high intensities sublinear, dependence of photocurrent on intensity over more than 7.5 orders of magnitude in incident intensity corresponding to over 150 dB of intensity dynamic range (Figure 4.7). The linear part of the curve extends for over 3 orders of magnitude corresponding to 60 dB of intensity linear dynamic range, which is what typically required for most imaging applications. At higher optical intensities, however, the detector exhibits an inherent sub-linear transformation of the optical signal to electrical output desired for increased intra-scene dynamic range [73]. The inset of Figure 4.7
shows the onset of responsivity decrease, which is due to the filling of the high gain trap states at higher intensities.

Figure 4.7: The photocurrent plot versus optical illumination reveals a dynamic range of 7.5 orders of magnitude (conventionally expressed as 150 dB). The inset shows the responsivity as a function of optical intensity.

4.4 Multispectral Photodetection

In Chapter 3, a sensitive solution-processed PbS quantum dot photodetector was developed to address the short wavelength and near infrared part of spectrum, preserving however its sensitivity also in the visible. In the current chapter a solution-processed PbS quantum dot photodetector was presented the absorption of which was tailored to address the visible part of spectrum.
The superiority of solution processibility is demonstrated in this section by combining the two classes of photodetectors to compose a dual-spectral photodetector that can sense light from 1500 nm to 400 nm in a broadband or selective mode of operation. This was achieved based on the same material of PbS quantum dots. The inset of Figure 4.8 shows the photodetector architecture that demonstrated dual-spectral detection. The device consists of two stacked PbS quantum dot photodetectors of different nanocrystal size. The top detector is fabricated by small PbS quantum dots that detect effectively in the visible part of spectrum. The buried photodetector consists of larger PbS quantum dots to detect light in the SWIR and NIR. This layer however is prone to detecting light in the visible. The top layer then serves not only as a photosensitive layer of the visible but also as a filter to prevent visible photons from reaching the second layer. The sensitivity of the buried photodetector is thus suppressed in the visible part of spectrum.

The structure shown in the inset consists of gold electrodes with length 3 mm, width 5 μm and height 100 nm. The spacing between the electrodes is 20 μm and the applied bias was 100V. The thickness of the large quantum dot photodetector is ~750 nm, whereas that of the small quantum dot photodetector is ~500 nm. The resultant responsivity spectra of the photodetectors are shown in Figure 4.8. The responsivities of the large quantum dot device in both cases have been normalized to their exciton peak value at 1230 nm. The large photodetector in the stacked structure preserves responsivity at wavelengths longer than 900 nm whereas demonstrates significant decrease in responsivity at shorter wavelengths following the absorption onset of the small quantum dot photodetector. The spectral responsivity of the small-bandgap detector prior to stacking is also shown to demonstrate the achieved suppression of responsivity in the visible by over 20-dB at 500 nm and beyond. Further optimization can be anticipated by increasing the thickness of the small quantum dot photodetector in order to absorb, ideally, all visible impinging photons. The large quantum dot photodetector can then sense exclusively in the SWIR.
Figure 4.8: Spectral responsivity of the stacked device shown in the inset for dual-spectral detection. The small quantum dot (QD) layer detects effectively the short wavelength light, whereas the longer wavelengths are detected from the large quantum dot (QD) layer. The responsivity of the large-quantum dot device before the stacking is also shown for comparison.

4.5 Investigation of the Sensitizing Centres’ Energy Depths

Since extended trap state lifetime lowers the speed of response – if excessive, it can lead to unacceptably long lag in imaging applications – control over the trap states present in a quantum dot solid is of high importance. There exists a considerable body of evidence pointing to the existence of a multiplicity of trapping centres in colloidal quantum dot solids. As shown in section 4.3, the frequency-dependent response varied systematically with the level of illumination: longer-lived, deeper-lying traps were presumably filled first, providing gain but slow response at low light, and lower gain but
faster response under higher levels of illumination. The shape of the responsivity dependence on frequency also indicates the existence of multiple poles suggestive of multiple sensitizing centers – each one with a characteristic lifetime – that contribute to photoconductive gain. For these reasons, a detailed elucidation of the physical picture of the trap states that exist in PbS colloidal quantum dot films, is necessitated. Bulk PbS has been widely-studied [62, 63]; However, conventional polycrystalline PbS and colloidal quantum dot PbS differ substantially – in their characteristic dimensions (50-150 nm vs. 1-10 nm), their surface passivation (oxides and sulfates vs. organic ligands plus oxides and sulfates), and the absence or presence of quantum confinement.

Temperature spectroscopy is a powerful tool to identify trap states and calculate their energy depths from the band edge. Photocurrent temperature spectroscopy is employed in the present work due to its applicability in photoconductive photodetectors and the ability to extract information about traps related to photoconductivity [39]. This technique originates from the deep level transient spectroscopy (DLTS) [74], which is based on the formation of Schottky barriers or p-n junctions and yields information about deep traps. Two approaches are followed to extract the energy depths of sensitizing centers, independently, for cross-comparison reasons:

- Photocurrent quenching spectroscopy
- Transient photocurrent spectroscopy

For these studies, photoconductive photodetectors were fabricated following the methodology described in section 4.1. All optoelectronic studies were performed under vacuum inside a liquid nitrogen cryostat. For photocurrent measurements, samples were illuminated using a 642 nm LED modulated using a square wave (rise and fall times less than 1 μs) at a frequency of 100 mHz, to allow for complete relaxation of photocurrent. Temperature dependencies were explored in 10 K increments with an increase rate of 1K/min; samples were also left to equilibrate 10 min at each temperature level. Samples were measured at room temperature before and after the full temperature and measurement cycle; before-and-after hysteresis of less than 5% was observed.
4.5.1 Photocurrent quenching spectroscopy

Photocurrent in photoconductive photodetectors is proportional to the product of mobility with the number of photoexcited carriers. In sensitized photoconductors, increase of temperature results in responsivity decrease due to thermal depopulation of electrons from the sensitizing centers [37]. The rate of responsivity decrease with temperature provides information about the energy depths of the sensitizing centers [39].

The logarithm of responsivity as a function of temperature is presented in Figure 4.9a. At low temperatures (below 250 K), photocurrent increases with a single activation energy of 0.16 eV. Dark current measurements of the devices, as shown in Figure 4.9b, demonstrate an activation energy of ~0.15 eV identical to the photocurrent activation energy, within experimental uncertainty over this same temperature range. Since photocurrent and dark current are both linearly proportional with mobility, the growth in photocurrent with temperature up to 250 K can be attributed to improved transport and the 0.16 eV activation energy is associated with mobility. Thermally-activated hopping transport has previously been observed in colloidal quantum dot solids [60].

At temperatures above 250 K, photocurrent shows a dramatic saturation followed by quenching with increasing temperatures, whereas dark current continues to grow at or above the 0.16 eV rate. In this higher-temperature regime, thermal energy is presumed to become sufficient to accelerate the emptying of the electron traps whose long lifetimes are responsible for photosensitivity. In this temperature regime there are two competing mechanisms that affect responsivity. Increasing hole mobility with temperature leads to responsivity increase, which however is compensated by the thermal activation of sensitizing centers that causes de-sensitization of the material. A deconvolution between the two competing mechanisms is required to allow extraction of the sensitizing centers’ energy depths.
Figure 4.9: (a) Photocurrent as a function of temperature at two illumination levels. The activation energy of the photocurrent is determined by the mobility activation energy. At higher temperatures photocurrent quenching is observed. (b) Dark current dependence on temperature reveals thermal activation energy of 0.15 eV attributed to mobility activation.
Responsivity $R$ is proportional to mobility and the number of sensitizing photoexcited carriers [36]:

$$R \propto \mu_o \exp(-E_a / kT) \cdot \frac{N_s}{N_c} \exp(\Delta E / kT)$$  \hspace{1cm} (4.1)

Where $\mu_o$ is the temperature invariant mobility factor, $E_a$ is the mobility activation energy $\sim 0.15$ eV, $N_c$ is the density of states in the conduction band, $N_s$ is the sensitizing center density, and $\Delta E$ is the energy depth from the conduction band.

Figure 4.10: Photocurrent quenching taken as the photocurrent at higher temperatures with the mobility contribution component subtracted. The slope of the quenching provides the depth of the sensitizing centers from the conduction band.

Responsivity quenching is defined as the ratio of responsivity divided by mobility to yield a normalized parameter proportional to the number of trapped photoelectrons in the sensitizing centers that contribute to photoconductive gain. The activation energy of quenching is thus determined by the thermal activation of the desensitization. The
photocurrent quenching as a function of temperature is plotted in Figure 4.10. The quenching activation energies that are revealed as a result enable a first estimation of the energy depth of the sensitizing centers measured relative to the conduction band edge. Figure 1b indicates two levels, ~0.1 eV and ~0.3 eV. The smooth transition between the two is suggestive of the existence of more sensitizing centers lying energetically between these two levels.

### 4.5.2 Transient photocurrent spectroscopy

An alternative approach to estimate the energy depths of the sensitizing centers is via information extracted by the dependence of the time constant, associated with the sensitizing center, on temperature. The emission rate of a trap state into the conduction band is given by [37]:

\[
\tau^{-1} = \sigma_n N_c \nu_{th} \exp(-\Delta E / kT)
\]  

Where \( \tau \) is the time constant, \( \sigma_n \) is the capture cross section of the trap, \( N_c \) is the density of states in conduction band, \( \nu_{th} \) is the thermal velocity of the carriers, and \( \Delta E \) is the energy depth of the trap measured relative to the conduction band edge. The transient decays of photocurrent revealed three main components, each having its own temperature-dependent time constant. Figure 4.11a shows the three temporal components that at room temperature exhibit characteristic time constants of ~60 ms, 300 ms and 2 s.

Figure 4.11b illustrates the natural logarithm of the product \( \tau T^{1/2} \) (plotted to account for the dependence of thermal velocity on temperature and thus simplify the extraction of the exponential activation process). These components exhibit characteristic activation energies 0.09 eV, 0.22 eV, 0.34 eV, the deeper center accounting for the slower component of temporal response. These values agree well with the activation energies extracted from the photocurrent quenching analysis above, whereas photocurrent temperature spectroscopy revealed also another sensitizing center at 0.22 eV, the existence of which, photocurrent quenching spectroscopy implied. The temperatures at
which desensitization onset observed are also in good agreement with photocurrent quenching technique: 260 K for the 0.1 eV center and 310 K for the 0.3 eV center.

Figure 4.11: (a) Transient photocurrent measurements as function of temperature exhibit 3 exponential decay components with time constants at room temperature of 60 ms, 300 ms and 2 s at 300 K. (b) The plot shows the dependence of the time constants as function of temperature and provides additional information on the sensitizing centers’ depths.
By comparison of these findings with those observed in polycrystalline PbS photodetectors, there are some distinct differences on the nature of the sensitizing centers. Sensitizing centers attributable to oxidation sites on PbS have been found to lie 0.16 eV and 0.32 eV below the conduction band of bulk PbS [39] and vary with the growth mechanism and deposition conditions. If the sensitizing centers in PbS nanocrystals were due purely to highly localized states at the nanoparticle surface, and were uninfluenced by quantum-confined electron states within the nanoparticles, one would expect to see at least one much-deeper electron trap in the quantum dot case compared to the bulk. Since this is not observed experimentally, it appears that the combination of dot surface passivation and quantum confinement together determine the trap state energy.

4.6 Summary

Herein we demonstrated the first solution-processed quantum dot photodetector to exceed silicon photodiodes’ sensitivity in the visible. The proposed technology is compatible with CMOS process and flexible organic electronics circuitry for future thin flexible imagers.

The need to reconsider the ligand exchange process developed in Chapter 3 arose from the need to preserve sharp absorption onset so that the visible part of spectrum is addressed exclusively. A new ligand exchange process, this one occurring in solid state, was thus developed to increase mobility without sacrificing the visible absorption onset. This resulted in a recorded detectivity D* of $\sim 10^{12}$ Jones, representing a two-order-of-magnitude improvement over previously-reported, visible, solution-processed quantum dot photodetectors [75]. The resultant photodetector exhibits also a dynamic range of 150 dB with linear dynamic range of 60 dB suitable for most high contrast imaging applications [11].

This chapter also reported the first exploration of the applicability of solution-processibility and quantum confinement size tunability to generate a multispectral solution-processed photodetector. The proposed technology lays the groundwork for
fabrication of monolithically-integrated low-cost and high-pixel-count multispectral imagers.

The role of sensitizing centres in the optoelectronic performance of the detector was also investigated in the present chapter. The dependence of responsivity on modulation frequency and optical illumination were found to be in good agreement with a model, developed in this chapter, of how multiple sensitizing centres contribute to photoconductive gain. Our use of temperature spectroscopy allowed us to determine the energy depths of the sensitizing electron traps measured relative to the conduction band edge. The resultant findings provide physical insight into the operation of sensitive high-gain PbS colloidal quantum dot photodetectors. The energy levels of the sensitizing centres responsible for high gain were determined to lie ~0.1 eV, ~0.2 eV and ~0.3 eV below the conduction band edge. These findings are directly relevant to device optimization, pointing as they do towards trap state engineering aimed at improving further the temporal response of photoconductive devices for low-lag imaging applications.
Chapter 5

Engineering the Temporal Response of Photoconductive Photodetectors

In the previous chapters, we demonstrated the first achievement of highly sensitive photodetection in each of the visible and the infrared based on solution-processed materials. This was achieved by sensitizing colloidal quantum dots using surface trap states such as to prolong the carrier lifetime. Photoconductive gain, responsible for high sensitivity, is given by \( \tau_c/\tau_t \), where \( \tau_t \) is the time for the flowing carrier to transit the extent of the device, and \( \tau_c \) is the carrier lifetime [36]. From a sensitivity point of view alone, this argues for longer trap state lifetimes.

Also important in photodetection is the temporal response. If the response of a photodetector to an optical transient exceeds the frame period, then lag, or ghosting, will be perceptible in the image. Conventional imaging applications typically require frame rates in the range of 10, 15, 30, or 60 frames per second. Temporal responses having time constants in the range of tens of milliseconds are thus required.

The temporal response is directly determined by the carrier lifetime. The challenge of practical photoconductive photodetector design is thus to establish a suitable balance between gain and temporal response; and to control material composition with care to implement the resultant design.

The energy levels associated with trap states in PbS colloidal quantum dot photodetectors that exhibit gains of order hundred A/W were investigated in chapter 4. Three sensitizing centers at 0.1, 0.2 and 0.34 eV from the conduction band resulted in carrier lifetimes of \(~60\) ms, \(300\) ms and \(2000\) ms. Although the shortest lifetime of \(30\) ms is suited for many imaging applications, the longer ones, which dominate at lower optical intensities in view of their lower energies, introduce unacceptable lag.
In the present chapter we identify oxide species existent on the quantum dot surface and associate the resultant sensitizing centres with measured time constants and their related trap state energies. We then propose a novel material processing methodology that facilitates suppression of the longest lived trap states. In so do, we preserve sensitization only via the shortest (temporally), thus the shallowest (energetically), trap state. As a result we report the first solution-processed photoconductive photodetector to combine application-relevant temporal response with superb sensitivity.

5.1 Material Processing

Photoconductive devices were fabricated by spin-coating oleic acid-capped nanocrystals onto pre-patterned interdigitated gold electrodes. The quantum dots’ first excitonic peak lay at 790 nm. The thickness of the devices was kept constant around 250 nm. The active area of the device is circumscribed by the 5 µm separation of the electrodes and their 3 mm length. For illumination, a 642 nm light-emitting diode, producing 3.1 µW/cm² of optical intensity at the sample, was used, unless otherwise stated. The bias applied to the devices studied herein was 10 V, corresponding to an electric field of 2 V/µm. All photoconductive measurements were performed with devices loaded in a cryostat under vacuum conditions so that oxygen and moisture physisorption effects are eliminated.

For the purpose of this work, photoconductive devices made of nanocrystals with ligands of various head functional groups attaching to nanocrystal surface are fabricated. Three types of ligands with different functional groups employed as follows:

- Butylamine treated nanocrystals: Devices were fabricated following the route described in Chapter 4, section 4.1.
- Formic acid treated nanocrystals: Devices were fabricated by dipping devices of oleate-capped nanocrystal films in a mixture of 30% by volume of formic acid in acetonitrile, for ~5 minutes. The devices were then removed from the solution, rinsed with acetonitrile and dried.
• Ethanethiol treated nanocrystals: Devices were fabricated by dipping devices of oleate-capped nanocrystal films in a mixture of 40% by volume of formic acid in acetonitrile, for ~5 minutes. The devices were then removed from the solution, rinsed with acetonitrile and dried.

5.2 Correlation between Surface Species and Temporal Photocurrent Response

The correlation study between nanocrystal surface species and temporal response begins with butylamine treated nanocrystal devices, as described in chapter 4. These devices demonstrate multiple photocurrent decay time constants of ~60 ms, 300 ms and 2000 ms, at room temperature (Figure 5.1). X-ray photoelectron spectroscopy (XPS) is employed to monitor the material variations on the nanocrystal surface.

![Figure 5.1: Temporal response of photocurrent in butylamine, formic acid and ethanethiol treated nanocrystal films.](image)

Figure 5.1: Temporal response of photocurrent in butylamine, formic acid and ethanethiol treated nanocrystal films.
XPS analysis of nanocrystal treated using butylamine revealed the presence of lead sulfate (PbSO₄), lead sulfite (PbSO₃), and lead carboxylate attributable to oleic acid ligands attached to the nanoparticles’ surfaces. Pb4f peak signal analysis revealed oxidized states assigned to PbSO₄ and PbSO₃ at 138.5 eV and a highly oxidized state of Pb found at 139.1 eV associated with Pb-carboxylate (Figure 5.2a). To verify this last finding, XPS measurement was performed on Pb-oleate (the same used for PbS nanocrystal synthesis), revealing a single peak of Pb at 139.1 eV (see Appendix D for detailed analysis of XPS results). XPS analysis of the S2p signal corroborates the findings by demonstrating a peak at 165.5 eV attributable to PbSO₃ and a peak 167.8 eV resulting from PbSO₄ (Figure 5.2b). The number of the species found on the nanocrystal surface (PbSO₄, PbSO₃ and Pb-carboxylate) is equal to the number of the photocurrent decay time constants; this is suggestive that each of the identified species be responsible for a single time constant, associated with the energy depth of the trap.

The correlation between the lead carboxylate peak (due to the oleic acid-Pb bond) and a corresponding sensitizing trap state, having a specific temporal response, is initially addressed. Nanocrystal films were treated with formic acid to exchange the long oleic acid ligand with a shorter one, preserving the carboxylic functionality to prevent sulfate formation. In so doing, the inter-nanoparticle spacing was reduced while preserving the carboxylate moiety bound to Pb atoms on the nanocrystal surface. In this way, insulating devices were transformed into photoconductive detectors. Temporal measurements of photocurrent response revealed a main time constant of ~ 420 ms (Figure 5.1) and also a faster component with time constant ~33 ms. XPS revealed an oxidized component to the Pb4f signal at 139.1 eV characteristic of the Pb-carboxylate group, as illustrated in Figure 5.2a as well as a signal at 138.5 eV arising from the existence of PbSO₃ as verified by the S2p signal (Figure 5.2b). This evidence suggests that either Pb-carboxylate or PbSO₃ serves as a sensitizing species having an (undesirably long-lived) ~420 ms time constant.

Complete removal of the oleate ligands was sought, in order to unmask which among the carboxylate/sulfite species is responsible for the ~420 ms time constant. A ligand, short enough to promote transport and lacking carboxylate functionality, is needed. To make the replacement of the carboxylate-terminated ligand thermodynamically favourable, a functional head-group that would bind to the Pb more strongly than Pb-
carboxylate, was also required. Ethanethiol was chosen for its short length and its thiol moiety, expected to bind strongly with Pb. Photoconductive devices were thus fabricated from thiol-treated nanocrystals.

Figure 5.2: XPS spectra of Pb4f (a) and S2p (b) signal from butylamine, formic acid and ethanethiol treated nanocrystal films used as photodetectors. The lines show the energy levels associated with the reported species.
The absence of Pb4f peak at around 139.1 eV (Figure 5.2a) suggests that oleate ligands were indeed entirely removed from the nanocrystal surface. Thiol treatment also removed poly-sulfites and lead sulfate from the nanocrystal surface leaving PbSO$_3$ as the sole oxidized species (Figure 5.2b). Transient photocurrent measurements showed that ET treated nanocrystal films exhibited a single transient component having a ~27 ms time constant at room temperature (Figure 5.1).

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Oxides</th>
<th>Time constants</th>
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<tr>
<td>As-synthesized</td>
<td>PbSO$_3$, Pb-carboxylate, PbSO$_4$</td>
<td>-</td>
</tr>
<tr>
<td>Butylamine</td>
<td>PbSO$_3$, Pb-carboxylate, PbSO$_4$</td>
<td>~60 ms, ~300 ms, ~2 s</td>
</tr>
<tr>
<td>Ethanethiol</td>
<td>PbSO$_3$</td>
<td>~27 ms</td>
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<td>ET + aging in ambient</td>
<td>PbSO$_3$, PbSO$_4$</td>
<td>~38 ms, ~3 s</td>
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<tr>
<td>Formic acid</td>
<td>PbSO$_3$, Pb-carboxylate</td>
<td>~33 ms, ~420 ms</td>
</tr>
</tbody>
</table>

Table 5.1: Summary of the correlation studies between oxide species and photocurrent time constants observed in variously treated PbS nanocrystal films.

Table 5.1 summarizes the correlations between species and temporal components. PbS nanocrystal films having lead sulfate (PbSO$_4$), lead sulfite (PbSO$_3$), and lead carboxylate manifested photocurrent decays having time constants ~2 s, 300 ms and ~60 ms. PbS nanocrystals possessing lead carboxylate and PbSO$_3$ exhibited a photocurrent decay with time constants ~420 ms and ~33 ms. Thiol treated nanocrystals on which only lead sulfite
was present exhibited a single photocurrent relaxation time constant of \(~27\) ms. The association between the sulfate and the two-second time constant was also confirmed by ageing a thiol-treated device in ambient for several hours: a slow component emerged having the several-second time constant, followed by significant growth of lead sulfate, as shown by XPS analysis (Appendix D).

5.3 Determination of the Sensitizing Centre’s Energy Depth

Photocurrent temperature spectroscopy was employed to investigate in greater detail the energy level associated with the desired 25 millisecond trap state. The method of experimental investigation and analysis is the one used in the butylamine treated nanocrystal devices and is described in detail in Chapter 4.

Figure 5.3a shows the photocurrent as a function of temperature. At low temperatures, where the sensitizing centers are not thermally quenched, and therefore the devices are fully sensitized, responsivity increases with temperature following the mobility thermal activation of 0.14 eV similarly reported for such materials [76]. At elevated temperatures, photocurrent quenching takes place as a result of thermal deactivation of the sensitizing center [39]. The slope of the quenching rate with temperature (inset of Figure 5.3a) yields an activation energy of 0.16 eV.

The same activation energy has been ascertained using an independent method, investigating the dependence of the photocurrent transient on temperature. Using this method, the sensitizing center’s energy was found to be 0.12 eV below the conduction band, in reasonable agreement with the responsivity quenching results (Figure 5.3b).
Figure 5.3: Photocurrent temperature spectroscopy results. (a) Photocurrent vs temperature and photocurrent quenching vs temperature (shown in inset) reveal a single sensitization centre 0.16 eV below the conduction band. (b) Photocurrent temporal response as a function of temperature reveals an activation energy of the sensitizing centre of 0.12 eV below the conduction band.
5.4 Optoelectronic Performance of the Fast Photodetector

We conclude with the results of full characterization of the thiol-treated device, focusing on its applicability to imaging applications requiring the combination of sensitivity and acceptable temporal response. Experimental details of the measurement methodologies are described in Appendix B. The spectral responsivity is reported in Figure 3a. Responsivity was measured at intensity levels of ~300 nW/cm² using a 642 nm LED. The device was biased to 10 V. The noise current in the device was measured and the resultant normalized the detectivity, D*, plotted in Figure 3a. Sensitivity is retained without compromise: D* \( \sim 10^{12} \) Jones is obtained across the visible spectrum. Figure 3b also illustrates the device responsivity and detectivity as function of modulation frequency. The absence of long lived trap states is evident from the flat response of responsivity at frequencies below 5 Hz where the sensitizing centres associated with the \( \sim 400 \) ms and \( \sim 2 \) s time constants would determine the responsivity roll-off.

5.5 Summary

Prior to this work, we had demonstrated solution-processed photoconductive detectors that exhibited high sensitivity but which suffered from temporal response unsuited to imaging video-rate applications. Their practical value was therefore limited, raising the question: Could a high-sensitivity photoconductive photodetector be achieved that had acceptable temporal response?

In this chapter, we demonstrated that macroscopically-observed device performance can be fine-tuned via careful manipulation of the chemical species present on semiconductor nanoparticle surfaces. Specifically, an unacceptably slow photoconductive photodetector was transformed into one that is sufficiently fast to be suitable in imaging applications. By simultaneously reducing inter-nanoparticle spacing, this improvement was achieved without losing the advantage of photoconductive gain. More broadly, the
work demonstrates the applied power of careful compositional control on the nanometer scale.

Figure 5.4: (a) Spectral responsivity and detectivity of the ethanethiol treated device considered a modulation frequency of 10 Hz. (b) Responsivity and specific detectivity as function of modulation frequency at wavelength of 450 nm.
Chapter 6

Conclusions

The advent of solution-processed optoelectronic materials such as colloidal quantum dots has, for many decades now, been known to offer the potential of a revolution in optoelectronics. Their solution processibility offers unprecedented reduction in manufacturing cost and ease of large-area fabrication. Control over material definition on the nanoscale also enables for device functionalities impossible to achieve with conventionally-grown semiconductors. Device physics and performance in colloidal nanocrystal devices, unlike bulk semiconductors, are determined by the nanocrystal surface and size. These two factors can readily be tuned via wet chemistry to tailor the material properties: the absorption and emission spectra can be tailored by choice of the nanocrystal size; the photoluminescence quantum efficiency can be increased by careful passivation of the nanocrystal surface; mobility may be controlled through the length of the capping ligands and nanocrystal size, shape and ordering; carrier doping can be transformed between n-type and p-type by surface modification; carrier lifetime, determined by surface traps, can be tuned via selective passivation of the nanocrystal surface trap states.

This thesis therefore showcases the high degree of control offered by nanoscale materials engineering. It proves this power in the form of solution-processed photoconductive photodetectors suited to imaging applications – devices exhibiting performance never before seen in soft materials.

In this concluding chapter, the contributions of this work are briefly summarized. The broader potential impact for the work on the field of solution-processed optoelectronic devices is then portrayed. The prospects of further research that build on the findings of this thesis are then expounded.
6.1 Thesis Findings

Colloidal quantum dots are characterized by electron-hole pair quantum-length scale localization and a large surface-to-volume ratio. Each of these features militates against carrier mobility.

This set of properties mandated the search for a class of optoelectronic devices whose physical basis of operation would benefit from, rather being curtailed by these material properties. Photoconductive photodetectors represent an important class of devices that were seen to offer this potential.

Sensitive photoconductors exploit trap states that prolong carrier lifetime; provided they possess sufficient carrier mobility, they offer the possibility of photoconductive gain. There nevertheless existed, prior to the present work, significant challenges that would have to be addressed in order to achieve sensitive photoconductors based on colloidal quantum dots:

- Colloidal quantum dots are passivated by organic molecules that inhibit transport. A method to remove these moieties from the nanocrystal surface to improve transport would be required. Whether the highly desired feature of quantum size-effect tuning could then be retained was not a priori obvious.
- The large ratio of interfacial area to volume in a nanocrystal solid introduces an abundance of surface states that lead to excessive noise. A careful manipulation of the surface would be required to suppress noise in photoconductive photodetectors based on such materials.
- Carrier lifetime determines the temporal response of a photoconductor. The abundance of trap states on the nanocrystal surface and their associated carrier lifetimes would require careful attention in order to preserve the trap states that yield temporal response acceptable for imaging applications.

Addressing, within the present work, the preceding challenges led to the following findings:
• **Mobility increase via novel ligand exchange process and nanocrystal sintering:** A ligand exchange was developed to replace the long oleate ligand from the surface of as-synthesized nanocrystals with shorter ligands. Mobility was further improved to $\sim 10^{-3}$ cm$^2$/Vs by removing the organic ligands from the nanocrystals, causing the particles to become electrically interconnected.

• **Carrier lifetime prolongation via introduction of surface trap states:** A method to photosensitize the material was discovered. Surface oxidization led to the formation of trap states that prolong the electron carrier lifetime. This in conjunction with high mobilities led to the first demonstration of photoconductive gain in solution-processed photodetectors.

• **Noise minimization via controlled oxidation of surface:** The effect of the oxidation/sensitization process on the noise performance was studied for the first time. A material process route was discovered that led to minimization of the noise current in colloidal quantum dot photoconductors, preserving at the same time high photoconductive gain.

• **Engineering the temporal response via selective introduction of surface states:** It was shown for the first time that the temporal response of a quantum dot photoconductor can be tailored by careful control over surface chemistry. Materials species were identified as responsible for particular photocurrent temporal components. We were able to exploit these findings to isolate and remove surface species responsible for undesirably long time constants.

### 6.2 Contributions

The above findings led to following contributions:

• The first solution-processed infrared quantum dot photodetector was reported with photoconductive gain on the order of $10^3$ and normalized detectivity $\sim 10^{13}$ Jones [77]. Its performance exceeds that of the best performing single-crystalline photodiodes.
The first solution-processed visible quantum dot photodetector was reported. The device exhibited photoconductive gain in the order of $10^2$ and normalized detectivity $\sim 10^{12}$ Jones, comparable to widely-used silicon photodiodes [78]. Taken together, the combination of visible and infrared solution-processed photodetectors shows for the first time the feasibility of a monolithic, sensitive, solution-processed, multi-spectral photodetector.

Investigation of the energy levels of the sensitizing centers, responsible for the high photoconductive gain, and their association to specific material species, found on the nanocrystal surface [79] led to the first report of solution-processed quantum dot photodetector with gain in the order of 10, at electric-bias conditions suitable for CMOS integration, sensitivity $\sim 10^{12}$ Jones and temporal response suitable for imaging applications [80].

In sum, this work demonstrated the development of sensitive photodetectors, based on colloidal quantum dots that exhibit all the required characteristics demanded for most imaging applications. In addition to this, significant advantages arise from the solution processibility leading to low cost, high resolution, sensitive, infrared imaging systems, visible imaging systems with high fill factors and therefrom improved sensitivity, low cost multispectral imaging systems; all of the above being integrable not only on rigid CMOS platforms but also on flexible organic electronic platforms.

Prior to this work, there existed no reports of solution-processed photodetectors showing promise for successful competition with the established bulk-semiconductor technology and consequently possible commercialization. The current work opens up a new and promising research field of colloidal quantum dot optoelectronics giving rise to new research initiatives in the fields of photodetectors [81-83] as well as fundamental studies of physics in such devices [84-86].
6.3 Future Work

The integration of the sensor technology devised herein with existing CMOS technology will be greatly improved if dark current can be further decreased. At the moment, the present technology exhibits dark current densities as low as \( \sim 50 \, \mu\text{A/cm}^2 \), which is approximately three orders of magnitude higher than the physical limit imposed by the intrinsic carrier density. Read-out using conventional CMOS image sensor circuits would require either the use of large capacitors for charge storage or current subtracting circuits that require extra complexity. The devices reported in this thesis were found to be p-doped. Preliminary evidence suggest that the p-type dopant in PbS nanocrystals is the PbO found on their surface, similar to bulk PbS. Processing techniques that would retain the favorable oxides but would eliminate the undesired lead oxide (PbO) are thus of great interest. Alternatively, doping compensation could be employed.

The electric fields required to achieve high photoconductive gain in the reported devices are imposed by the low hole mobility. Carrier mobility in nanocrystal solids is limited by the hopping nature of transport among nanocrystals. Significant mobility increase can be expected by replacing colloidal quantum dots by nanorods. Quantum confinement benefits can then be retained in the two dimensions, whereas the third non-confined dimension of the nanorod can be exploited for carrier transport. Such an achievement could lead to higher photoconductive gain or equivalently lower bias for the same gain.

The present work focused on material development and reported single-pixel photodetectors. Integration with CMOS read-out integrated circuit arrays to generate image sensors would further advance the demonstrated relevance of the present work.

PbS nanocrystals, employed in this work, contain the heavy metal of lead. Similarly, the vast majority of reports on optoelectronic devices (light emitting diodes, photodetectors, photovoltaics) based on colloidal nanocrystals rely on the heavy metal Cd (CdS, CdSe). There is much work to be done in this field to synthesize high-performance semiconducting colloidal quantum dots based on ‘green’ materials.
6.4 Final Remarks

Prior to the present work, the following question could well have been posed: Could size-tunable, conveniently-processed materials offer compelling performance – at best, even greater than those of their traditional grown-crystal counterparts – in an important optoelectronic device context?

The answer to this question was, at the beginning of this work, unknown. More discouragingly, the broadly-based assumption within the scientific and engineering community was ‘no.’ Colloidal quantum dots have traps; a significant organic component; likely issues in purity; a propensity to oxidation – all seemingly insurmountable obstacles to achieving the control needed to refine devices to the degree afforded in conventional semiconductor technology.

The surprise of this work is that the answer to the above questions is the counterintuitive one: soft matter, solution-processed semiconductors can, and now regularly do, yield devices that can even outperform traditional crystalline semiconductor optoelectronic devices.
Appendix A

Spectroscopic Techniques

The present appendix introduces the basic principles of operation of the spectroscopic techniques used in the present work.

A.1 Fourier-Transform Infrared Spectroscopy

Infrared spectroscopy identifies the vibration characteristics of chemical functional groups in a sample, by measuring the molecular absorption in the infrared. Matter interacts with infrared radiation by absorbing energy which is then consumed in stretching, contracting and bending of chemical bonds. A chemical functional group absorbs infrared radiation of specific energy (or wavenumber, as expressed in FTIR spectroscopy) regardless of the structure of the rest of the molecule. The technique thus identifies specific chemical structures rather than chemical substances. A combination however of data acquired by a scan provides a set of functional groups present in a chemical substance than can yield to identification of the material. It is also possible to extract information on the structure of the material by observation of the perturbation of the characteristic energies of each functional group. When many functional groups interact in a molecular system the characteristic energies of each one of them are shifted shedding light to the structure of the molecule.

FTIR is implemented using a Michelson interferometer. The incoming infrared beam is split into two beams. One beam is reflected by a fixed-position mirror, whereas the other beam is reflected by a mirror moving typically a few millimeters away from the beamsplitter. The two beams are then combined in the beamsplitter creating interference. The resultant signal, called interferogram, is the result of interference in the time domain,
as defined by the spatial displacement of the moving mirror at a given speed. When the interferogram signal is transmitted through the sample, the specific frequencies of energy that correspond to characteristic vibration, stretching or contracting energy of the functional groups of the molecules are absorbed. The final interferogram is then guided to a broadband detector. A Fourier transformation is applied to the signal in order to extract the power spectrum of the signal and yield the absorbance of the material as a function of the wavenumber.

A.2 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is an analytic tool that provides insights on the chemical structure and composition of materials. It does so by bombarding the material with high energy monochromatic X-rays. The core (inner-shell) electrons are ionized in the presence of the high energy radiation and their number and kinetic energy is measured. High vacuum conditions are required to prevent collisions of emitted electrons with atoms that would distort their kinetic energy. The kinetic energy of the electrons yields information on the binding energy of the electrons in the material by subtracting the energy of the excitation from the measured kinetic energy of the electron. The resultant spectrum yields the number of extracted electrons as a function of binding energy. The binding energy of the electron is determined by the electronic structure of the material. XPS can thus provide information on the chemical composition of the material as well as the elemental composition in atomic percentages.
Appendix B

Experimental Setups

The experimental setups used in characterization of the optoelectronic performance of the quantum dot photodetectors are described in the current appendix.

B.1 Responsivity Measurement

The responsivity was measured by two different methods:

1. A 2 mm radius beam from a 975 nm laser was incident, first through a series of optical attenuators of known transmittance, and through the glass substrate, onto the device from the backside. On the top surface, infrared-opaque interdigitated gold electrodes were separated by 5 μm over a 3 mm path length. The optical power incident on the device was obtained by integrating the intensity profile of the laser over the unobstructed area of the device. Current-voltage characteristics were acquired using an Agilent 4155 semiconductor parameter analyzer. The responsivity at different frequencies was measured by electrical modulation of the laser. The 975 nm laser source was employed for the characterization of the SWIR photodetectors described in Chapter 3; The 975 nm laser source was replaced with a red light emitting diode at 642 nm, for the characterization of visible quantum dot photodetectors presented in Chapters 4 and 5.

2. A bias was applied to the sample connected in series with a 2 MΩ load resistor. Illumination was provided by a white light source (ScienceTech Inc. TH-2) dispersed by a Triax 320 monochromator and mechanically chopped at the frequency of interest. Optical filters were used to prevent grating overtones from illuminating the sample. The voltage across the load resistor was measured using a Stanford Research Systems SR830 lock-in amplifier. The intensity transmitted through the monochromator at each
wavelength was measured separately using calibrated Ophir PD-300 Si and Ge photodetectors to cover the range from 400 – 1600 nm. The optical power impinging on the active area of the detector was taken by dividing the active area of the device by the collimated beam area and multiplied by the total power measured with the calibrated detectors. The photocurrent at each wavelength was subsequently scaled according to this system calibration. The results of the two aforementioned techniques agreed to within less than 10%.

The aforementioned setup (illustrated in Fig. B.1) allowed measurement of spectral responsivity by using a variable attenuator programmed to fix the optical power at each wavelength at ~500 nW/cm$^2$. The recorded photocurrent vs wavelength yielded the spectral responsivity.

![Experimental setup for responsivity measurement.](image_url)
B.2 Dynamic Range Measurement

The setup shown in Figure A.1 was also used for measuring the dynamic range of the photodetector. The wavelength was fixed at 830 nm and the variable attenuator combined with neutral density filters was used to vary the light intensity up to ~10 μW. For higher intensities, a semiconductor laser at 830 nm was employed to provide optical powers up to 10 mW.

B.3 Noise Current Measurement

The photoconductive device was placed inside an electrically shielded and optically sealed probe station placed on an optical table to minimize environmental mechanical vibrations (Figure B.2). The device was connected in series with a low-noise resistor load of 4 MOhms. Batteries were used to bias the circuit for the measurement of the noise current to minimize noise components from the bias source. A lock-in amplifier was connected in parallel to the load resistor to measure the noise voltage across the resistor. Differential cabling was used to minimize ambient interference noise. Through the choice of integration time, sensitivity and central electrical frequency, lock-in amplifier reported a noise current in A/Hz$^{1/2}$. The noise current divided by the responsivity under the same experimental conditions (applied bias and electronic bandwidth) yielded the noise equivalent power (NEP). The normalized detectivity D* was obtained as a function of wavelength, applied bias, and modulation frequency by dividing the square root of the optically active area of the device by the NEP.

To validate the NEP obtained using this technique, the identical procedure was carried out using a commercial Si detector with known NEP. The system described above reported NEP values of the same order of magnitude, but typically larger than (i.e. inferior to) the specified NEPs. The NEP and D* determination procedure used herein thus provides a conservative estimate of these figures of merit. In addition to this, low-
noise resistors were also connected in the circuit in order to measure their Johnson noise. The lock-in measured the Johnson noise with a 20% experimental accuracy.

Figure B.2: Experimental setup for noise current measurement.
Appendix C

Time-of-flight Measurement

Time of flight measurement was employed to estimate the hole mobility in the quantum dot photodetector material developed in this thesis. The time-of-flight measurement setup and results are discussed in the present appendix. This technique is based on optical excitation of carriers in the vicinity of one of the metal contacts (anode) followed by monitoring the time required for the carriers (holes) to reach the other contact (cathode) producing a transient photocurrent.

The broad absorption profile of PbS nanocrystals imposed a challenge in localizing the optically excited zone. A double layer structure was therefore used, consisted of different size PbS nanocrystals. The nanocrystal films were treated identically as the PbS quantum dot photodetectors described in Chapter 3. The large-nanocrystal medium consisted of nanocrystals the first excitonic peak of which is found at 1670 nm. The first layer was spin-coated on an indium-tin-oxide covered glass substrate to form a film with thickness ~80 nm. Indium tin oxide was used as the transparent cathode that allowed optical penetration into nanocrystal film. The small nanocrystal medium consisted of nanocrystals with exciton peak at 1200 nm, which was spin-coated atop the large-nanocrystal film. The thickness of this layer was measured ~1.1 μm. Au was then sputtered to form the anode of the device with surface area ~7 mm².

The experimental setup is illustrated in Figure C.1. An optical pulse of sub-μJ energy was generated by a topaz optical parametric amplifier, pumped by a Titan Ti:Saph laser. The pulse impinged on the device through ITO surface with duration of 1 ps and repetition rate of 1 kHz. The wavelength was chosen 1570 nm so that light was absorbed in the large nanocrystal layer. The absorbing medium absorbed approximately 0.01% of the impinged light. Electron-hole pairs were therefore created within a zone of ~80 nm equal to the thickness of the large nanocrystal medium. The holes then drifted across the
device under the imposed electric field from the external bias. Electrons were extracted from the device through the ITO contact. The thickness of the small nanocrystal medium was chosen an order of magnitude larger than the absorbing medium so that the mobility is extracted from the carrier transport in the non-absorbing medium. Optical illumination effects on mobility could therefore be neglected. The physical conditions then, under which mobility is considered, are relevant to these of the photodetectors, which were tested under low optical illumination.

Figure C.1: Experimental setup of time-of-flight measurements for mobility extraction.
Figure C.2: Transient photocurrent in log-log plot for mobility estimation. The inset shows the photocurrent in linear scale.

The transient photocurrent was recorded using a fast Tektronix oscilloscope that measured the voltage across a 50 Ohm resistor. In disordered materials, such as nanocrystal solids, the carrier transport is dominated by dispersion [87]. In the inset of Figure C.2 the resultant photocurrent is shown, plotted in a log-log scale to allow for the extraction of the transit time [88]. The extraction of mobility requires the plot of photocurrent as a function of time in a log-log scale; the transit time $\tau_t$ is defined as the time required for the peak of the charge packet to reach the back electrode. $\tau_t$ is then determined by the time when the slopes of photocurrent change as shown in Figure C.2. The hole mobility can then be estimated by assuming that all the electric field, responsible for hole drift, drops across the transport medium. From Figure C.2 the transit time is found $\sim$700 ns, yielding hole mobility in the order of $5 \times 10^{-3}$ cm$^2$/Vs. This is in agreement with other reports of mobility in similarly treated nanocrystal films [71, 89].
Appendix D

XPS Analysis of Treated PbS Nanocrystal Films

XPS analysis of PbS nanocrystal films as described in Chapter 5 is provided herein. The Pb4f and S2p peaks are illustrated with the corresponding fittings as extracted by the Multipak Software. The Pb4f peak of Pb-oleate is also shown. The S2p peak of the ambient-aged ethanethiol treated nanocrystal film is illustrated as well.

As-synthesized oleic acid capped nanocrystals

Figure D.1: Pb4f signal of oleate-capped PbS nanocrystals. Three components can be distinguished: PbS (~137.7 eV), PbSO₄ and PbSO₃ (~138.4 eV) and Pb-carboxylate (~139.1 eV).
Figure D.2: S2p signal of oleate-capped PbS nanocrystals. The s2p signal exhibits a PbS peak (160.8 eV) a poly-sulfide peak (163.9 eV), a PbSO₃ peak (165.6 eV) and a PbSO₄ peak (167.9 eV).
Pb-oleate

Figure D.3: Pb4f signal of Pb-oleate. There is a single peak at 139.1 eV attributable to Pb-carboxylate bond of Pb-oleate.
Butylamine treated nanocrystals

Figure D.4: Pb4f peak of butylamine treated nanocrystals. The identified species are: PbS (137.7 eV), PbSO$_3$ and PbSO$_4$ (~138.4 eV) and Pb-carboxylate (~139.1 eV).
Figure D.5: S2p signal of butylamine treated nanocrystals: The identified species are: PbS (160.9 eV), PbSO$_3$ (~165.6 eV) and PbSO$_4$ (167.8 eV).
Formic Acid treated nanocrystals

Figure D.6: Pb4f signal of PbS nanocrystals treated with formic acid. 3 species are identified: PbS (137.7 eV), PbSO$_3$ (138.5 eV) and Pb-carboxylate (139.2 eV).
Figure D.7: S2p signal of PbS nanocrystals treated with formic acid. Two species are found: PbS (160.9 eV) and PbSO\(_3\) (165.6 eV).
Ethanethiol treated nanocrystals

Figure D.8: Pb4f signal of ethanethiol treated nanocrystals. Two species are found: PbS (137.7 eV) and PbSO\textsubscript{3} (∼138.6 eV).
Figure D.9: S2p peak of ethanethiol treated nanocrystals. The 3 existent species can be identified as: PbS (160.8 eV), PbSO$_3$ (165.8 eV) and thiol signature of S-C bond (161.9 eV).
Ethanethiol treated nanocrystals aged in ambient

Figure D.10: S2p signal of ethanethiol treated nanocrystals followed by ageing in ambient conditions. There exist 4 species: PbS (160.9 eV), PbSO$_3$ (165.8 eV), PbSO$_4$ (167.8 eV) and the thiol signature from the S-C bond (162 eV).


[70] [http://srdata.nist.gov/xps/Elm_comp.asp](http://srdata.nist.gov/xps/Elm_comp.asp)


